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SEPIOLITE–PALYGORSKITE: A CONTINUOUS POLYSOMATIC SERIES

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Abstract—A compositional gap between sepiolite and palygorskite has long been accepted even though they have similar structures, but recent studies found that such a gap does not exist and that the compositional series is continuous between them. If this is true, intergrowths between these two minerals should exist. The purpose of the present study was to demonstrate the existence of sepiolite-palygorskite intergrowths in all possible proportions, in order to establish the compositional links between ideal sepiolite and ideal palygorskite and to define the compositional limits of these two minerals. Sepiolite and palygorskite have similar structures but different chemical compositions: sepiolite is the most trioctahedral and magnesic extreme, while palygorskite is dioctahedral with Al and Mg in its octahedral sheet. The existence of all intermediate compositions between these two pure extremes has led to the definition of the intermediate minerals, Al-sepiolite and Mg-palygorskite, which can have similar chemical composition. The structural relations between the different minerals of the palygorskite–sepiolite series were studied here by powder X-ray diffraction (XRD), and continuous variation in the chemical composition is explained by the existence of intergrowths of sepiolite and palygorskite polysomes forming a continuous polysomatic series. The existence of intergrowths by mixtures of polysomes in modulated structures can be considered in the same way that the mixed-layer minerals in layered structures are considered. The continuous polysomatic series of sepiolite–palygorskite can be expressed by the general formula: $[Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4]_y \cdot [Si_8O_{20}(Mg_2Fe_2)_x(Mg_2Al_2)_{(1-x)}(OH)_2(OH_2)_4]_{(1-y)} \cdot nH_2O$, where sepiolite and palygorskite are the end-members. The y and x values can be calculated using a ternary plot with the oxide contents of the main octahedral cations (Al_2O_3, Fe_2O_3, and MgO). The proposed model, which is based on the intergrowth of sepiolite and palygorskite polysomes, explains both the variability in the chemical composition and the compositional limit for the identification of these minerals by X-ray diffraction.

Key Words—Continuous Polysomatic Series, Diffraction Domains, Intergrowths, Palygorskite, Polysomatic Model, Polysome, Sepiolite.

INTRODUCTION

The structure and chemical composition of sepiolite and palygorskite have been known since the first half of the 20th century (Bradley, 1940; Brauner and Preisinger, 1956). More recent studies (Guggenheim and Eggleton, 1987; Guggenheim *et al*., 2006; Guggenheim and Krekeler, 2011) have shown that both are modulated phyllosilicates, where the modulated components are octahedral sheets. Both minerals can be described as 2:1 type ribbons, or polysomes, running parallel to the *c* axis. Polysomes are connected by oxygen atoms. The oxygen planes are continuous but periodic inversion of the apical oxygen (every two tetrahedral chains in palygorskite and every three in sepiolite) limits the lateral dimensions of the octahedral sheet (Figure 1). Ideal palygorskite has a dioctahedral character (80% of the octahedral positions are occupied) and sepiolite is a pure trioctahedral mineral.

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The ideal structural formula for sepiolite, according to the model of Brauner and Preisinger (1956) is $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4(H_2O)_8$, where Mg can be substituted by Al, Fe(III), Fe(II), Ti, and occasionally Cr(III) and Ni, and the number of octahedral cations is between 6.95 and 8.11. The ideal structural formula for palygorskite, based on the model of Bradley (1940), is $Si_8O_{20}(Mg_2Al_2)(OH)_2(OH_2)_4(H_2O)_4$. Palygorskite has three different octahedral positions (Figure 1e) where *M*1 is vacant in a pure dioctahedral palygorskite. The *M*3 position (Figure 1) is always occupied by Mg (Güven *et al*., 1992; Suárez and García-Romero, 2006a), while *M*2 is mainly occupied by Al or Fe(III).

In a comparative study on the composition of sepiolite and palygorskite, individual particles from palygorskite-smectite and sepiolite-smectite assemblages were analyzed by Paquet *et al*. (1987) who concluded that the octahedral composition fields of the smectites and the fibrous clays overlap partially. The sepiolite field is clearly in the trioctahedral domain, whereas the palygorskite field is in the dioctahedral domain and between the trioctahedral and dioctahedral domains. In a later study, Galán and Carretero (1999) suggested that palygorskite is intermediate between di-

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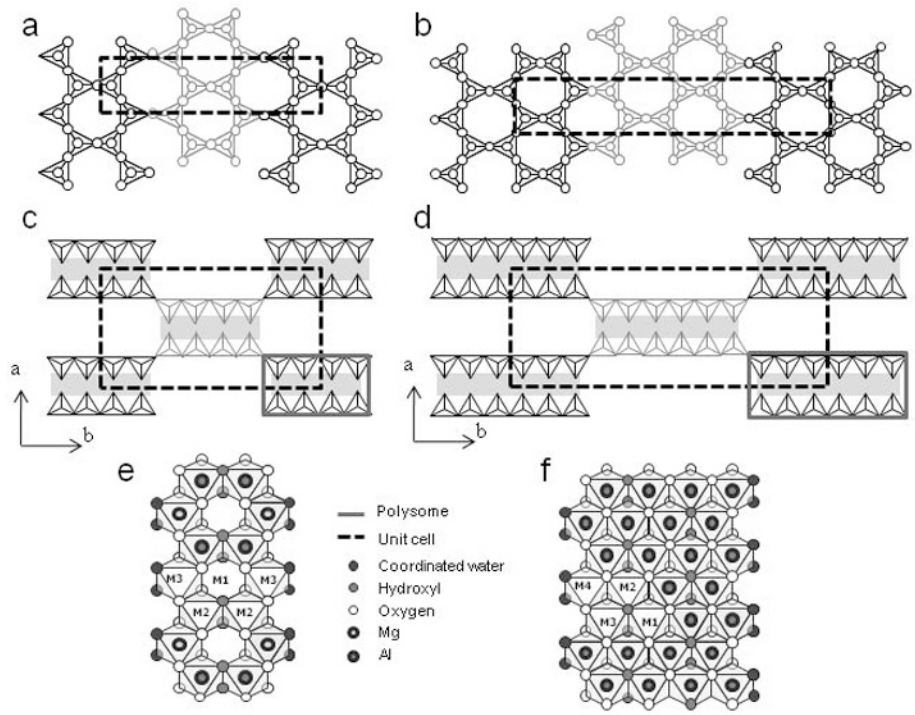


Figure 1. Structural schemes of palygorskite and sepiolite. (a,b) Tetrahedral sheets of palygorskite and sepiolite projected on (001). Black and gray indicate tetrahedra with apical oxygens pointing in opposite directions. (c,d) Tetrahedral sheets of palygorskite and sepiolite projected on (100). The gray shading indicates the octahedral sheet. (e,f) Octahedral sheet of palygorskite and sepiolite projected on (001) (adapted from Suárez and García-Romero, 2011).

and trioctahedral phyllosilicates and that the octahedral sheet contains mainly Mg, Al, and Fe with an *M(II)*/*M(III)* ratio close to 1, and four of the five octahedral sites are occupied. The compositional limits of sepiolite and palygorskite were evaluated by Galán and Carretero (1999) who concluded that sepiolite is a true trioctahedral mineral with negligible structural substitutions and eight octahedral positions filled with Mg. A compositional gap between sepiolite and palygorskite was, therefore, widely accepted (Martín-Vivaldi and Cano Ruiz, 1956; Paquet *et al*., 1987; Galán and Carretero, 1999).

In the most recent studies of the chemical composition of sepiolite and palygorskite, however, the existence of Al-sepiolite and Mg-palygorskite was confirmed (García-Romero and Suárez, 2010; Suárez and García-Romero, 2011). Palygorskite and sepiolite can be so rich in Mg and Al, respectively, that the compositions of the two groups of minerals overlap significantly. The minerals that have a composition between those of sepiolite and palygorskite are referred to as intermediate minerals. A continuous series exists, therefore, with no compositional gap between sepiolite and palygorskite.

Mg-palygorskite was defined by Suárez *et al*. (2007) when they proposed a classification of palygorskites into three types that can be easily differentiated by X-ray diffraction (XRD):

Type I – ideal palygorskite, which has an octahedral composition near that of ideal palygorskite, with similar Al and Mg contents and negligible substitutions.

Type II – common palygorskite, which has an octahedral Al content less than that of the ideal formula and, as a consequence, the Mg content is greater, but the number of octahedral cations per half unit cell is close to 4 (vacant octahedral positions = 1). Although Al may be partially substituted by Fe(III) and/or Mg, this type of palygorskite has a dioctahedral character.

Type III – Mg-palygorskite which is the most trioctahedral extreme. The number of octahedral cations is >4 (vacant octahedral positions <1).

Type IV – Al-palygorskite, a new type of palygorskite mineral that has Al/Mg>1, proposed by García-Romero and Suárez (2010), is defined by a total number of octahedral cations per half unit cell <4, with Mg <2, and consequently (Al+Fe(III)) >Mg.

Two types of sepiolite can also be described considering the variability of its chemical composition: sepiolite and Al-sepiolite. A limit between these two types can be established from the octahedral occupancy based on the work of Suárez and García-Romero (2011). Al-sepiolites are those that have >10% of the octahedral positions vacant and >0.5 ^{VI}Al atoms per half unit cell.

Mg-palygorskite diffracts as palygorskite and exhibits extreme trioctahedral character. When the chemical

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composition of a pure and Mg-rich palygorskite (from XRD) is fitted, >4 occupied octahedral positions are obtained. In fact, Mg-palygorskite has ~4.5 occupied octahedral positions, with a ratio of $M(II)/M(III) \approx 3.5$. Using near-infrared (NIR) spectroscopy, Stathopoulou *et al*. (2011) demonstrated that the trioctahedral entities in palygorskite are not pure trioctahedral palygorskite, but rather sepiolite polysomes intergrown with palygorskite. The Mg-rich palygorskites are described, therefore, by the formula $y Mg_8Si_{12}O_{30}(OH)_4 \cdot (1-y)[x Mg_2Fe_2 (1-x)Mg_2Al_2]Si_8O_{20}(OH)_2$, where y indicates the sepiolite polysome content and x indicates the Fe(III) content ($0<x<0.7$ and $0<y<0.33$).

The aims of the present study were, therefore, to: (1) demonstrate the existence of sepiolite-palygorskite intergrowths in all possible proportions, thus justifying the continuous compositional variation between ideal sepiolite and ideal palygorskite; and (2) define the compositional limit of both minerals as identified by XRD.

MATERIALS AND METHODS

The data recorded during the present study resulted from analysis of a large and representative collection of sepiolite and palygorskite samples using a number of techniques. Some aspects related to the characterization and crystallochemistry of sepiolite and palygorskite have been published. Previous studies by the present authors and others contain the original data on which the present study is based (García-Romero *et al*., 2004, 2006, 2007; Sánchez del Río *et al*., 2005, 2006, 2009a, 2011a, 2011b; Suárez and García-Romero, 2006a, 2006b, 2011, 2012; Gionis *et al*. 2006, 2007; Suárez *et al*., 2007; Chryssikos *et al*., 2009; Tauler *et al*., 2009; García-Romero and Suárez, 2010; Stathopoulou *et al*., 2011; Mondelli *et al*., 2012). More than 50 samples of sepiolite and palygorskite have been studied using the following techniques: conventional XRD, high-resolution microdiffraction using synchrotron radiation, infrared (IR) spectroscopy, near-infrared (NIR) spectroscopy, Mg-X-ray absorption near-edge spectroscopy (XANES) with synchrotron radiation, Raman spectroscopy with synchrotron radiation, adsorption of N_2, thermal analysis (ATD and TG), inelastic neutron scattering, transmission electron microscopy (TEM), electron diffraction, analytical electron microscopy (AEM), and scanning electron microscopy (SEM).

The proposed new structure shown here is based on the following sources: (1) the data recorded in the aforementioned studies; and (2) chemical data from the 145 references recorded by Suárez and García Romero (2011).

RESULTS AND DISCUSSION

The intermediate minerals

Al-sepiolite and Mg-palygorskite exist between two pure extremes, sepiolite and palygorskite, and while sepiolite can contain only a small proportion of octahedral substitutions, palygorskite can have a very wide range of substitutions. The intermediate forms, Al-sepiolite and Mg-palygorskite, can have similar chemical compositions; therefore, a certain degree of polymorphism must be considered to explain these intermediate minerals. References in the literature to the two minerals appearing together are scarce (*e.g.* Galán and Pozo, 2011), as expected, because the two minerals have close, but different, stability fields. On the other hand, sepiolite and palygorskite grow together in some cases, or at least appear to grow together, *e.g.* in the Allou-Kagne deposit (García-Romero *et al*., 2007).

Intermediate minerals have been referred to occasionally in the literature. Al-sepiolites have been reported by Argast (1989), Cetisli and Gedikbey (1960), García-Romero *et al*. (2007), McLean *et al*.(1972), Rogers *et al*. (1956), and Zaaboub *et al*. (2005), and Mg-palygorskites have been referenced by Chryssikos *et al*. (2009), Drits and Aleksandrova (1966), Garcia-Romero *et al*. (2004), Garcia-Romero *et al*. (2007), Gibbs *et al*. (1993), Post and Crawford (2007), Suárez and García-Romero (2006a, 2006b), Suárez *et al*. (2007), and Zheng (1997). Chemical data corresponding to intermediate compositions are more common, and in several studies the chemical compositions of the sepiolite or palygorskite in question are clearly intermediate (Figure 2), though this was not mentioned when the materials were described (*e.g.* Aqrawi, 1993; Arranz *et al*., 2008; Chahi *et al*., 1997; Chen *et al*., 2004; Corma *et al*., 1987; Huertas *et al*., 1971; Imai and Otsuka, 1984; Post and Crawford, 2007; Starkey and Blackmon, 1984; Torres-Ruiz *et al*., 1994; Teodorovich, 1961; Weaver and Polland, 1973). The area of the plot (Figure 4) in which both minerals are projected together corresponds to the intermediate minerals. The same area of sepiolite-palygorskite overlap is observed when comparing data from spot analyses by AEM of a wide range of representative samples (the samples studied by García-Romero and Suárez, (2010), represented in Figure 2b). The composition interval in which sepiolite content is possibly as much as palygorskite ranges approximately between 3.5 and 5 for the SiO_2/MgO ratio, and between 0.2 and 1 for the $(Al_2O_3+Fe_2O_3)$/MgO ratio (Suárez and García-Romero, 2011).

Sepiolite and palygorskite can exist with very similar chemical compositions as demonstrated unequivocally using both raw analyses and spot analyses, and Mg-palygorskite occurs much more frequently than Al-sepiolite. Two possible explanations are: (1) the analyses correspond to a mixture of individual crystals of sepiolite and palygorskite; or (2) these analyses correspond to individual crystals with mixtures of polysomes of sepiolite and palygorskite. These possibilities are discussed below.

Are the intermediate minerals the result of a mixture of sepiolite and palygorskite crystals? To answer this question, the samples corresponding to intermediate

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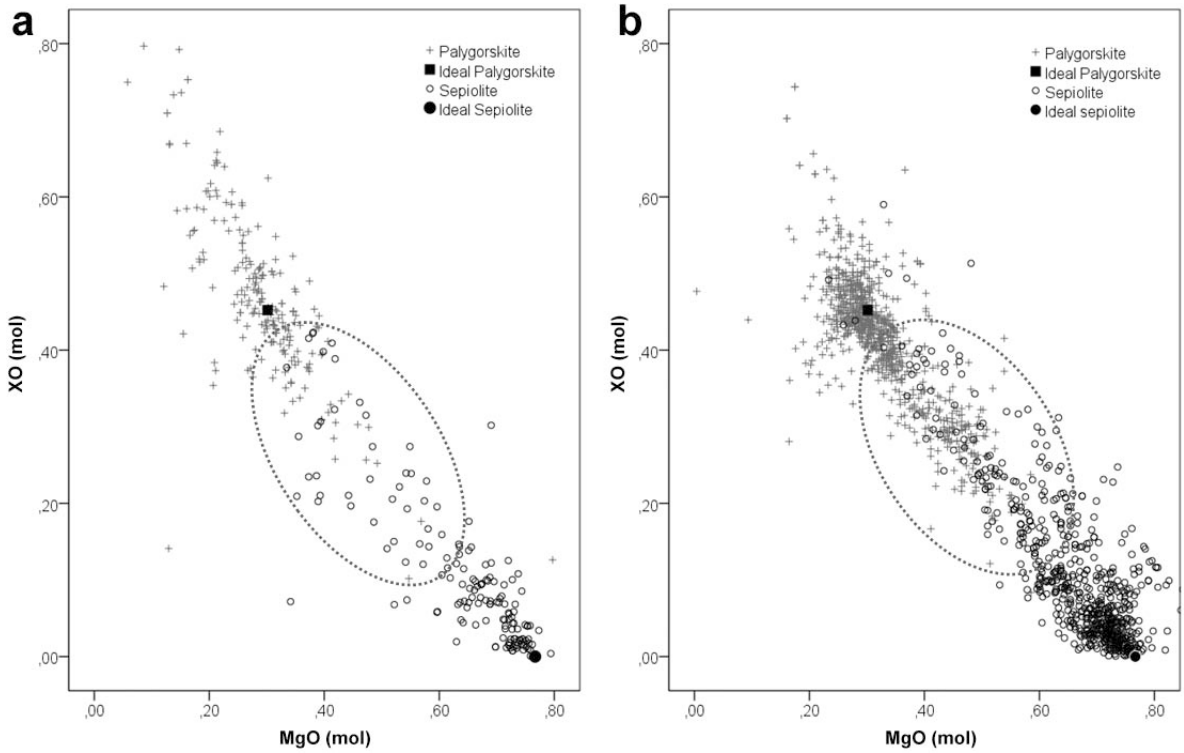


Figure 2. Moles of MgO *vs*. moles of XO for sepiolites and palygorskites from (a) data from references compiled by Suárez and García-Romero (2011) and (b) data from AEM analysis (García-Romero and Suárez, 2010).

minerals must be studied in depth. The analyses of Mg-palygorskite could result from sepiolite impurities in palygorskite analyzed together and, in the same way, Al-sepiolite could be the result of palygorskite impurities in sepiolite. In the case of sepiolite and palygorskite with low crystallinity and wide diffraction peaks, the main peaks of the minor mineral would not be seen in the diffraction patterns. Moreover, peaks of impurities are not even seen by high-resolution (HR) XRD using synchrotron radiation (Suárez *et al.*, 2007; Sánchez del Río *et al.*, 2011), confirming that the intermediate compositions are not derived from small amounts of impurities. The amount of sepiolite impurities in palygorskite necessary to obtain a raw chemical composition equivalent to the Mg-palygorskite by mixture of the two minerals is very large, >40% in the case of the richest Mg-palygorskites, *e.g.* E10 sample, without showing sepiolite reflections in its XRD pattern (Figure 3).

Chemical analysis values from raw samples corresponding to an intermediate mineral may result from a mixture of the two minerals in which the amount and crystallinity of the minor component was too small to diffract. In that case, however, results corresponding to pure sepiolite and pure palygorskite should be obtained for the spot analyses of individual crystals or fibers of an intermediate sample. Nevertheless, in all of the intermediate samples, all of the spot analyses show intermediate composition with a certain degree of variability in the mean structural formula. The variability in the octahedral content of the different types of sepiolites and palygorskites can be observed when the contents of the main octahedral oxides are represented according to the classification of the sample based on the structural formula determined from the XRD results (Figure 4). A continuous trend appears (Figure 4)

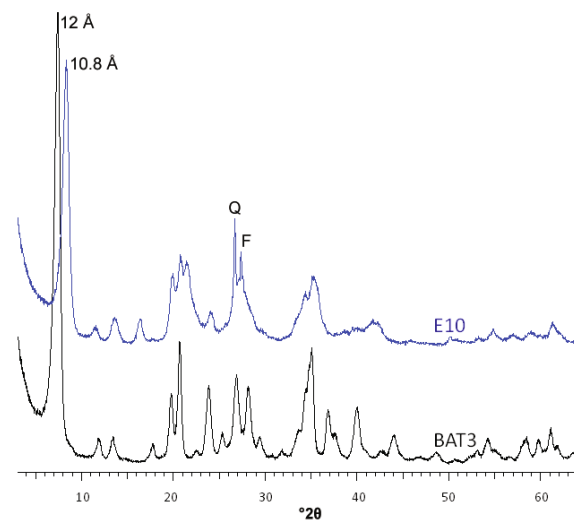


Figure 3. XRD patterns of a Mg-palygorkite (sample E10) and an Al-sepiolite (BAT3 sample).

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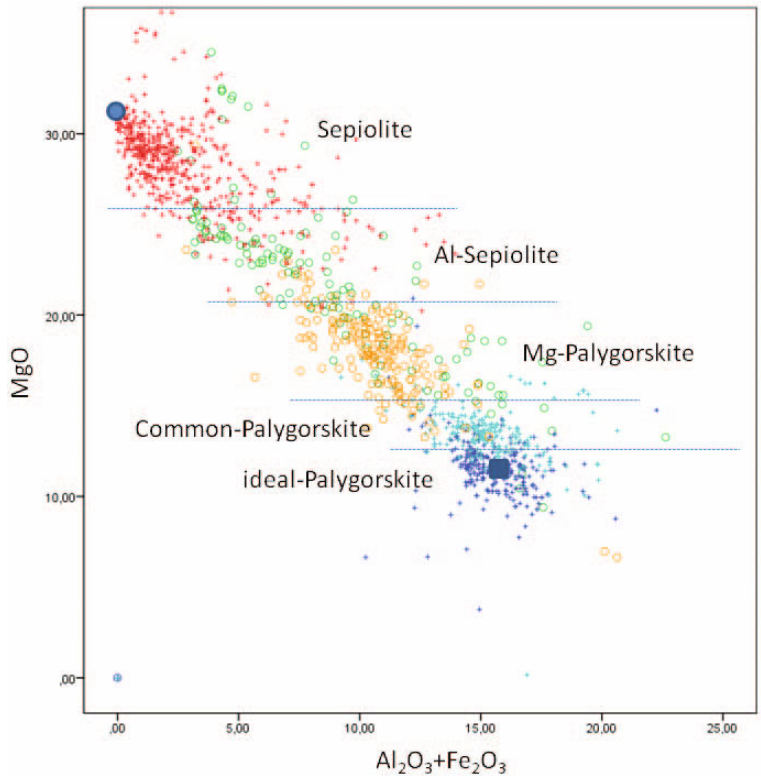


Figure 4. Variability in the octahedral cation content of the different types of sepiolites and palygorskites.

according to García-Romero and Suárez (2010), and all spot analyses which correspond to intermediate compositions, both Al-sepiolite and Mg-palygorskite, are projected in the same area. The continuous trend continues from sepiolite to Al-sepiolite, to Mg-palygorskite, to common palygorskite, and finally to ideal palygorskite.

Are the intermediate minerals the result of intergrowths of sepiolite and palygorskite polysomes? If the previous possibility does not explain the data, the existence of individual particles or crystals composed of polysomes of both minerals must be considered. Individual particles like these would be similar to the mixed-layer minerals in layered structures (Millot, 1964; Moore and Reynolds, 1989; Meunier, 2005), which are well known in clay mineralogy. The mixed-layer minerals like rectorite or random I-S are interstratified and have, for example, alternating 2:1 layers of illite and smectite (the structural units). For mixed-layer sepiolite-palygorskite minerals, the intergrowth is also defined by two alternating structural units: the polysomes of sepiolite and palygorskite and these two types of polysomes can be mixed in all possible proportions (Figure 5).

As a first possibility, when a crystal of palygorskite contains ~25% sepiolite polysomes (Figure 5b), a large amount of Mg is introduced into the chemical composition of the particle. This portion of sepiolite does not have a complete unit cell in the *b*-axis direction, however, and is unable to diffract and so could be observed as a defect in the *b* direction.

The existence of polysome mixtures in different proportions explains the variability in the chemical composition of a sample from the AEM analyses because each crystal can have different proportions of the two polysomes. In this type of intergrowth, the Al-sepiolite is determined to have a proportion of palygorskite polysomes. Mg-palygorskite and common palygorskite (types III and II, according to the classification of Suárez *et al*. (2007)) have sepiolite polysomes but in different proportions (Figure 5), as proposed by Suárez and García-Romero (2011). According to this model, the mixture of sepiolite and palygorskite can be produced in all proportions.

The mixture of polysomes with different widths was demonstrated by Krekeler *et al*. (2005) and Guggenheim and Krekeler (2011) who used HR-TEM to show the intergrowths of polysomes with different widths in the transformation of palygorskite to smectite. The polysomes can correspond not only to two and three tetrahedral chains, *i.e.* to palygorskite and sepiolite, respectively, but also to four and even more tetrahedral chains. The existence of intergrowths in modulated structures by mixtures of polysomes has to be considered in the same way that they are considered in the layered structures. The same phenomenon occurs in layered clay

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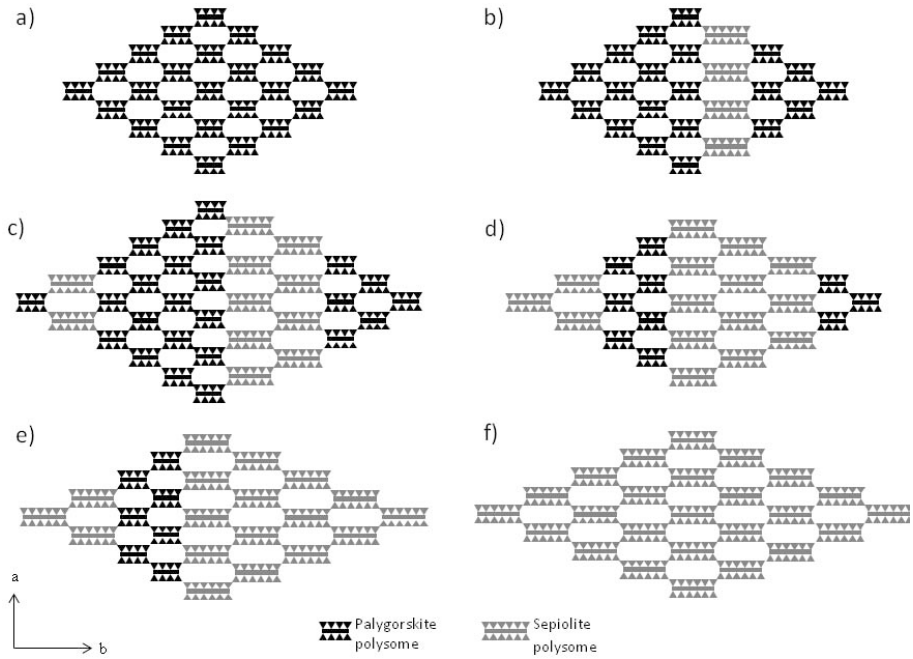


Figure 5. Structural scheme for the sepiolite–palygorskite polysomatic continuous series: (a) palygorskite; (b) palygorskite with a small proportion of sepiolite polysomes; (c) palygorskite with sepiolite polysomes; (d) sepiolite with palygorskite polysomes; (e) sepiolite with a small proportion of palygorskite polysomes; and (f) sepiolite.

minerals where the existence of all types of intergrowths is accepted. In addition, the existence of these intergrowths also explains the large variability found in the physical and chemical properties of these materials (Álvarez *et al*., 2011; Nishimura *et al*., 1972; Suárez and García-Romero, 2012) as indicated by Krekeler *et al*. (2005).

From detailed study of samples with intermediate composition, the existence of intergrowths in most sepiolites and palygorskites is consistent with the experimental data. Sepiolite and palygorskite are the end-member of a continuous polysomatic series that can be expressed, according to the general formula for polysomatic series, as $M_mM'_{m'}$ (Ferraris *et al*., 2008). The structural formula proposed by Stathopoulou *et al*. (2010) for Mg-palygorskite is, therefore, valid for this continuous polysomatic series, sepiolite–palygorskite. The structure can be expressed by the general formula $[Si_{12}O_{30}Mg_8(OH)_4(OH_2)_2]_y\cdot[Si_8O_{20}(Mg_2Fe_2)_x(Mg_2Al_2)_{(1-x)}(OH)_2\cdot(OH_2)_2]_{(1-y)}\cdot nH_2O$.

The presence of intergrowths influences the XRD pattern because the positions of the main reflections, 110 and 020, can vary depending on the mineral crystal chemistry (Suárez *et al*., 2007; Stathopoulou *et al*., 2010; Sánchez del Río *et al*., 2011). In palygorskite, the *d* spacing of these reflections increases as the Mg content increases; while in sepiolite, the 110 reflection appears at smaller values at larger Al contents. As an example, the presence of sepiolite polysomes in palygorskite moves the 110 reflection to 10.8 Å (Figure 3), for the palygorskites richest in Mg (Suárez *et al*., 2007). Below, structural models which allow justification of the absence of sepiolite reflections in Mg-palygorskite and the absence of palygorskite reflections in Al-sepiolite are discussed in order to find the limit of detection of sepiolite and palygorskite.

The compositional limit of sepiolite-palygorskite

In a fibrous Al-Mg phyllosilicate consisting of different amounts of two types of polysomes, or structural units, with the formulae $Si_8O_{20}Al_2Mg_2(OH)_2(OH_2)_2$ (half unit cell of palygorskite) and $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_2$ (half unit cell of sepiolite), how does one know when one is dealing with a palygorskite or with a sepiolite? The answer is found in the XRD patterns and is as simple as it is well known: if the 110 reflection appears at ~10.4 Å, then the sample is palygorskite, and if this reflection appears at 12 Å, then the sample is sepiolite. In the case of intergrowths of the two minerals (Figure 5), both can diffract only if coherent domains of diffraction exist for them, *i.e.* if the number of contiguous identical unit cells is large enough or if they are repeated on a regular basis. In the well known case of random mixed-layer illite-smectite, if illite is present with a small proportion of random smectite layers, the observable effect in the resulting powder XRD pattern is a broad (10 Å) peak that is displaced at lower angles. The compositional limit to diffraction is not as simple as 50% of each chemical formula, however. To determine the compositional limit,

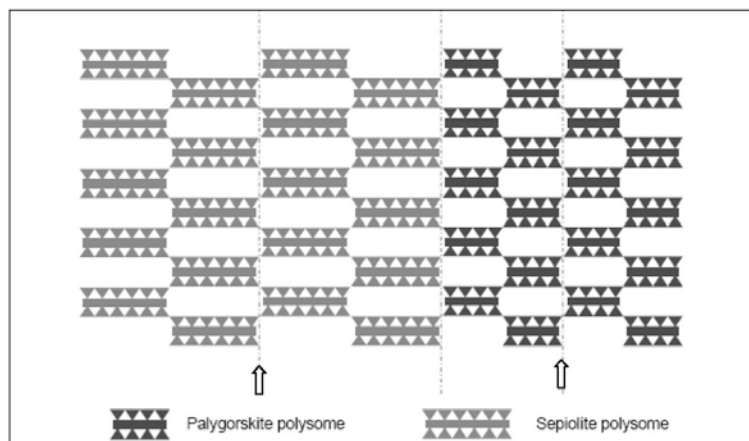
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two factors must be taken into account: (1) the sepiolite unit cell is larger than the palygorskite unit cell; and (2) sepiolite has Mg only as the octahedral cation, whereas palygorskite has both Mg and Al.

The influence of these two factors is easy to understand when a simplified structural scheme is considered (Figure 5). Firstly, small proportions of a type of polysome in the structure of 'another' mineral are represented (Figure 5b,e). The influence of the polysomes on the chemical composition of the raw sample, and the presence of palygorskite polysomes in the sepiolite (Figure 5e), imply a very small amount of Al in the global data (because each palygorskite polysome in the sepiolite adds two atoms of Al and also Mg, as in the sepiolite). In the case of sepiolite polysomes in palygorskites, however (Figure 5b), each sepiolite polysome adds eight atoms of Mg. Therefore, although these two schemes (Figure 5b,e) represent the same type of intergrowth from a structural point of view, their influence on the chemical analyses will be different. When the chemical analysis of the first structure (Figure 5b) is fitted as a palygorskite, a Mg-rich palygorskite will be obtained. However, when the chemical analysis of the structure of sepiolite with intergrowths of palygorskite polysomes (Figure 5e) is fitted as a sepiolite, small amounts of Al-like octahedral cations will be obtained. In addition, because the palygorskite is richer in SiO_2 than is the sepiolite, a crystal of palygorskite but with intergrowths of sepiolite polysomes (Figure 5b) fitted as a pure palygorskite will lead to a lack of Si, and a proportion of Al will be interpreted as a tetrahedral cation. On the contrary, a crystal of sepiolite with intergrowths of palygorskite (Figure 5e) fitted as a sepiolite, will lead to an excess of Si. The most extreme situations in the case of the palygorskite (Figure 5c) would be interpreted as a palygorskite very rich in Mg, whereas in the case of sepiolite (Figure 5d) it would be a sepiolite rich in Al.

To find the compositional limit of the two minerals, the ratio between the number of polysomes and the formula weight of each type of polysome must be considered. Fifty percent of the formula weight and 50% of the type of polysome are not equivalent. In the first case, 50% of each mineral polysome throughout the [010] direction is not the same as 50% of the weight (Figure 6). The sepiolite contributes 61% of the total weight in a crystal that consists of half sepiolite polysomes and half palygorskite polysomes.

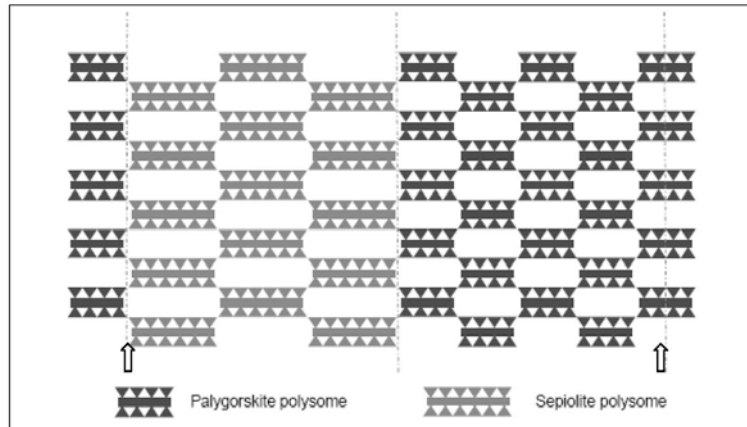
In the second case, a similar volume of palygorskite and sepiolite polysomes (~50 wt.%) is considered (Figure 7). In principle, the two minerals must diffract; no periodicity for sepiolite exists in this case, however. Consequently, the sepiolite does not diffract because only 1.5 sepiolite unit cells exist in the [010] direction. In this example, sepiolite does not diffract even though the sepiolite polysomes make up 40% of the structure; the sepiolite does contribute a large amount of Mg. When material like this is studied: (1) a peak corresponding to palygorskite at 10.4 Å in the diffraction pattern appears, but no evidence of sepiolite is seen; and (2) a large MgO content is noted, as determined by chemical analysis. When the mineral that diffracts as palygorskite is fitted as palygorskite, the structural formula obtained will be very rich in Mg and will have a deficit of Si.



	Polysomes	Wt.%	Unit cells	XRD	Chemical analysis
Palygorskite	1	~40	1	Palygorskite	Palygorskite
Sepiolite	1	~60	1	+sepiolite	+sepiolite

Figure 6. Structural scheme showing a portion of a crystal with the same number of palygorskite and sepiolite polysomes. As the periodicity is the same, the two minerals diffract the same.

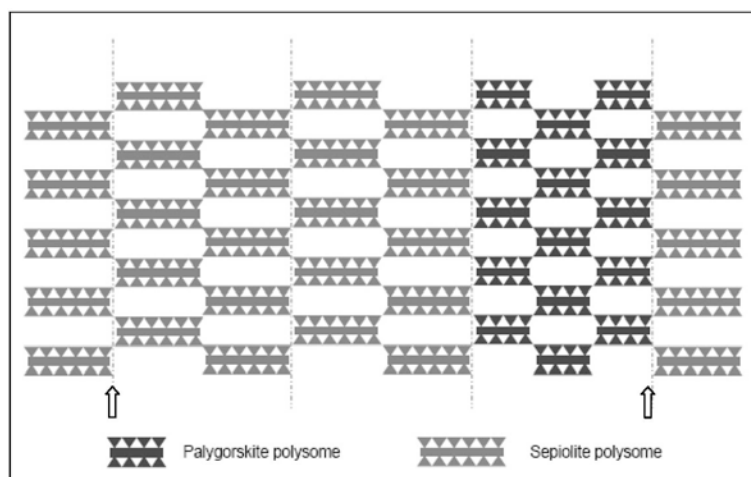
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	Polysomes	Wt.%	Unit cells	XRD	Chemical analysis
Palygorskite	4.5	~50	2.2	Palygorskite	Mg-palygorskite
Sepiolite	3	~50	1.5		
Structural Formula	$Si_{7.8}Al_{0.2}O_{20}$ Al_1 $Mg_{3.5}(OH)_2$ $(OH_2)_2$ nH_2O (fitted as palygorskite)				

Figure 7. Structural scheme showing a portion of a crystal with aproximately the same polysome weights of palygorskite and sepiolite, and with a ratio of unit cells of 2.2P/1.5S (between the lines). Sepiolite has no periodicity, so it does not diffract.

In the last example, about two palygorskite unit cells and 1.5 unit cells of sepiolite over [010] were considered. What would happen in the opposite case? If the same ratio of units cells was used, *i.e.* 2:1.5 (2 of sepiolite and 1.5 of palygorskite), without palygorskite periodicity (Figure 8), then the palygorskite makes up



	Polysomes	Wt.%	Unit cells	XRD	Chemical Analysis
Palygorskite	3	~33	1.5	Sepiolite	Al-sepiolite
Sepiolite	4	~66	2		
Structural Formula	$Si_{12.1}O_{30}$ Al_1 $Mg_{6.5}(OH)_4$ $(OH_2)_2$ nH_2O (fitted as sepiolite)				

Figure 8. Structural scheme showing a portion of a crystal containing palygorskite and sepiolite polysomes with a ratio of unit cells of 1.5P/2S. Palygorskite has no periodicity, so it does not diffract.

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only ~33% of the crystal. When such material is studied by XRD, sepiolite is the only mineral that diffracts. In the chemical analysis, a small amount of Al_2O_3 is observed, and the MgO content is only slightly smaller than in the theoretical sepiolite. This is because the palygorskite also contributes Mg. These data will be interpreted as a sepiolite with a small amount of Al substituting for Mg and with a very small excess of Si.

The chemical composition of a palygorskite that has 33% sepiolite polysomes without periodicity changes with respect to the ideal and has smaller SiO_2 and Al_2O_3 contents and a larger MgO content. In this scenario, 78% of the octahedral cations would be Mg and only 22% would be Al. The structural formula obtained by fitting these data for 21 negative charges gives a Mg-rich palygorskite with ~1 octahedral position occupied by Al and ~0.5 vacant sites per half unit cell. Similar formulae have been obtained by several authors (*e.g.* Zheng, 1997; Chahi *et al*., 2002; García-Romero *et al*., 2004; Post and Crawford, 2007). At the other extreme, a sepiolite rich in palygorskite polysomes (Figures 5d, 7) and containing 33% palygorskite polysomes has only 10% of the total octahedral positions occupied by Al. Thus, the chemical analysis found only a small amount of Al_2O_3. When the chemical analysis of this mineral is fitted as a sepiolite, one octahedral position occupied by Al is observed. Similar Al-rich sepiolites were found by Rogers *et al*. (1956), Zaaboub *et al*. (2005), and García-Romero and Suárez (2010).

Based on this model, although all the various proportions of the two types of polysomes are possible, the palygorskite type is more commonly detected by XRD because the palygorskite unit cell is smaller than the sepiolite unit cell, and the existence of the coherent domains of diffraction is easier to detect. Therefore, although intermediate compounds Al-sepiolite and Mg-palygorskite may be found equally in nature, their analysis is biased by the limit of detection by XRD, which is better at detecting palygorskite (smaller cell) than sepiolite. More evidence of Mg-palygorskite than of Al-sepiolite is, therefore, found in the literature.

Approximation of the polysomatic content of an intermediate mineral

The existence of polysome intergrowths of different widths, *i.e.* the inversion of the silica tetrahedra with different periodicity, explains the large variability found in the chemical composition of sepiolite and palygorskite. As shown above, this can occur without significant evidence from the XRD patterns. The question is how does one determine the polysomatic content? Using XRD, the type (I, II, or III) of palygorskite can be determined (Suárez *et al*., 2007), *i.e.* pure palygorskite, palygorskite with small amounts of sepiolite polysomes (Figure 5b), or palygorskite with a large proportion of sepiolite polysomes. The problem is that XRD and chemical analyses do not reveal the values of y and x in the general formula. To be able to fit the chemical analysis to a structural formula, the number of negative charges or one element must be fixed. In the case of this polysomatic series, this is impossible because both the proportion of polysomes (y) and the number of negative charges are unknown, and no element can be fixed. Nevertheless, the chemical composition of the raw sample expressed as oxides can be made known and the main octahedral-element content can be proposed from its plotted position on the triangular graph (Figure 9). The values of y and x can then be determined when the chemical composition of a problem sample is projected. Using this graph, an approximation to the structural formula can be obtained by determining: (1) the proportion of sepiolite and palygorskite polysomes, *i.e.* the y value; and (2) the Fe content in palygorskite polysomes, *i.e.* the x value. Two samples from Figure 3 are plotted in Figure 9: (1) Mg-palygorskite from Esquivias (García-Romero *et al*., 2004; García-Romero and Suárez, 2010) with 7.52% of Al_2O_3, 19.82% of MgO, and 1.64% of Fe_2O_3; and (2) Al-sepiolite from Cerro Batallones (Sánchez del Río *et al*., 2011) with 24.61% of Al_2O_3, 4.11% of MgO, and 1.13% of Fe_2O_3. The projection of these contents in the plot indicates a structural formula of $[Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4]_{0.32}[Si_8O_{20}(Mg_2Fe_2)_{0.12}(Mg_2Al_2)_{0.88}(OH)_2(OH_2)_4]_{0.68}$ or $Sep_{0.32}$–$Pal_{0.68}$ for the sample from Esquivias and $[Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4]_{0.58}[Si_8O_{20}(Mg_2Fe_2)_{0.13}(Mg_2Al_2)_{0.87}(OH)_2(OH_2)_4]_{0.42}$ or $Sep_{0.58}$–$Pal_{0.42}$ for the sample from Batallones.

As stated above, this is an approximation to the polysomatic content in sepiolite and palygorskite and this triangle is useful if all Fe cations are considered to be in the octahedral sheets in the polysome palygorskite;

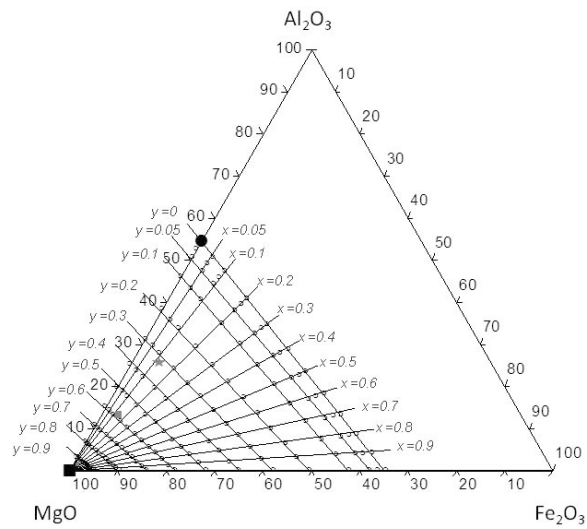


Figure 9. Ternary graph which allows the calculation of the x and y values for the sepiolite-palygorskite polysomatic series from the Al_2O_3, Fe_2O_3, and MgO contents. (square = BAT3 sample; star = E10 sample).

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the presence of Fe in sepiolite cannot be ruled out, however.

CONCLUSIONS AND UNANSWERED QUESTIONS

The model proposed here, based on the intergrowth of sepiolite and palygorskite polysomes, explains the variability in the chemical composition of these minerals. Although the compositional gap between the two minerals has been disproved, a compositional limit, or limit of detection, for the identification of these minerals with XRD is proposed. Sepiolite and palygorskite can be expressed by the general formula $[Si_{12}O_{30}Mg_8(OH)_4(OH_2)_2]_y[Si_8O_{20}(Mg_2Fe_2)_x(Mg_2Al_2)_{(1-x)}(OH)_2 \cdot (OH_2)_2]_{(1-y)} \cdot nH_2O$, and the values of y and x can be determined from raw chemical analysis using the graph proposed (Figure 9).

Intermediate forms of the sepiolite–palygorskite polysomatic series with a composition rich in palygorskite polysomes diffract as palygorskite up to ~50 wt.% of palygorskite and sepiolite (y = 0.4). A composition with >66 wt.% sepiolite (y = 0.57) is required to observe sepiolite by XRD, and the composition between these limits can diffract like palygorskite + sepiolite or as one of them only depending on the ordering of polysomes. Regarding the chemical composition, these proportions can be expressed by the theoretical SiO_2/MgO and MgO/(Al_2O_3+Fe_2O_3) ratios. Fe-rich minerals cannot be considered for this limit, however, because Fe-rich sepiolites can have a SiO_2/MgO ratio as large as that observed in the palygorskite. In the present model, Fe is considered to be an octahedral cation in palygorskite polysomes but it can also be an octahedral cation in sepiolite polysome taking into account that Fe-sepiolite occurs.

The model proposed here is an idealized model to try to explain something that is imperfect because sepiolite and palygorskite, like clay minerals, are characterized by large numbers of crystalline defects. Nevertheless, the model allows us to approach the structure of these minerals and to interpret the chemical data and the differences found in their XRD patterns. The intergrowths of polysomes with different widths can probably exist as "polysome width disorder," as proposed by Guggenheim and Krekeler (2011), and this could help to answer some of the unanswered questions that remain regarding the chemical composition of these minerals: (1) How does the presence of Fe influence these structures? (2) Is the present model useful for explaining Al-rich palygorskite? Al-rich palygorskite (or Type IV palygorskite) is common in nature (Suárez *et al*., 2009; García Romero and Suárez, 2010) and could be explained by the intergrowth of pure dioctahedral polysomes in palygorskite. These new types of polysomes could be formed by units of four or more tetrahedral chains, as shown by Krekeler *et al*. (2005), in transition toward laminar minerals. The chemical analysis of a palygorskite with dioctahedral 4-chain polysomes would be richer in Al_2O_3 and poorer in SiO_2 relative to the palygorskite.

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