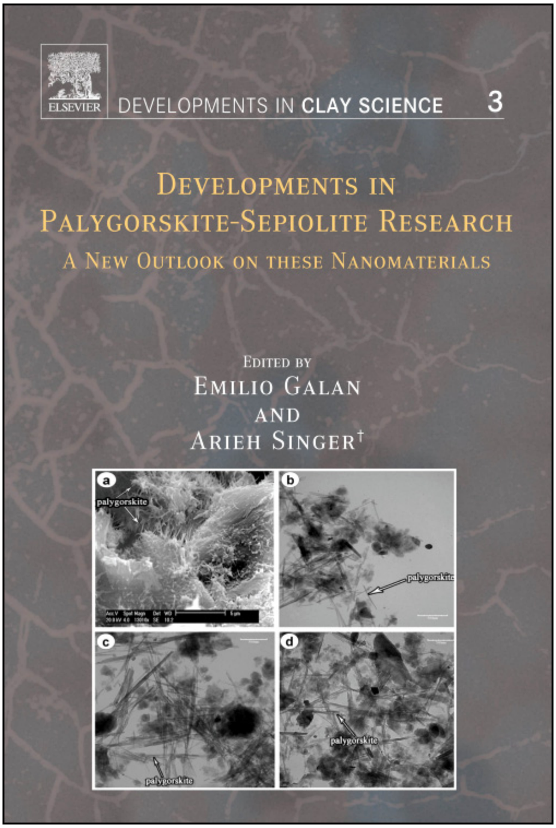

DEVELOPMENTS IN CLAY SCIENCE 3

DEVELOPMENTS IN
PALYGORSKITE-SEPIOLITE RESEARCH
A NEW OUTLOOK ON THESE NANOMATERIALS

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Chapter 2

Advances in the Crystal Chemistry of Sepiolite and Palygorskite

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1. INTRODUCTION

The structure and chemical composition of sepiolite and palygorskite are known from the first half of the twentieth century based on work by Caillère (1936, 1951), Bradley (1940), Nagy and Bradley (1955), Brauner and Pressinger (1956), Martin Vivaldi and Cano Ruíz (1953, 1955, 1956a,b), Drits and Aleksandrova (1966), and others. Later, studies on the structure and chemical composition of both minerals have found many different aspects, and logically, as more cases are studied more differences are found. Recently Mg-rich palygorskites, Fe-rich palygorskites and Al-rich sepiolites have been reported and it seems that the compositional limits accepted until now could be too narrow. The aim of this chapter is define the limit of chemical composition of both minerals, if it exists, using the data from the literature available today.

Sepiolite and palygorskite are modulated phyllosilicates. The modulated components are the octahedral sheets (Guggenheim et al., 2006). Both minerals can be described as 2:1 type ribbons running parallel to the *c*-axis. Ribbons are connected by oxygen atoms. There are continuous oxygen planes, but the periodical inversion of the apical oxygen (each two tetrahedral chains in palygorskite and each three in sepiolite) limits the lateral dimensions of the octahedral chain (Figure 1). Ideal palygorskite has a dioctahedral character (80% of octahedral position occupied) and sepiolite is a pure trioctahedral mineral.

A great number of sepiolite and palygorskite references (159 sepiolites and 216 palygorskite analyses) were compared and studied to obtain this general

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review of their composition. The number of articles offering chemical data on the fibrous clay minerals is more numerous than those used in this report, since the number of studies made on the genesis, properties and application is very abundant and is increasing yearly. However, we only consider analyses coming from pure or almost pure samples in this chapter.[1] In general, sepiolite and palygorskite, as do most clay minerals, appear in natural occurrences as mixtures with other clay minerals and with impurities like carbonates, feldspar and quartz. The presence of small amounts of other clay minerals on the final data of composition could change significantly the results of analyses. As an example, palygorskite frequently has illite and montmorillonite impurities containing ~30 wt% of Al_2O_3, that is, approximately twice of the fibrous mineral and, consequently, lower amounts of silica. If the whole sample analysis is considered, and the structural formula is fitted from it, the formula of palygorskite obtained could have more tetrahedral substitutions than it really does.

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[1] Akbulut and Kadir (2003), Aqrawi (1993), Pérez et al. (1989), Argast (1989), Arranz et al. (2008), Artioli and Galli (1994), Artioli et al. (1994), Bonatti and Joenssu (1968), Bonatti et al. (1983), Botha and Hughes (1992), Boules et al. (1971), Bradley (1940), Brauner and Pressinger (1956), Caillère (1936, 1951), Caillère and Henin (1957, 1961, 1972), Caillére and Rouaix (1958), Cetisli and Gedikbey (1960), Chahi et al. (1993, 1997, 2002), Chen et al. (2004, 2008), Corma et al. (1987), Dahab and Jarjarah (1989), Drits and Aleksandrova (1966), Dromashko (1953), Ece (1989), Fahey et al. (1960), Fersmann (1913), Fleischer (1972), Frank-Kamenetskiy et al. (1969), Fukushima and Okamoto (1987), Galán (1987), Galán et al. (1975), Galán and Carretero (1999), Galán and Castillo (1984), Galán and Ferrero (1982), Galopim De Carvalho et al. (1970), García-Romero and Suárez (2010), García-Romero et al. (2004, 2006), Gibbs et al. (1993), Gionis et al. (2006), Giusteto et al. (2006), Gonzalez et al. (1993), Güven (1992) Güven and Carney (1979), Haji-Vassiliou and Puffer (1975), Hathaway and Sachs (1965), Hay and Stoessell (1984), He et al. (1996), Heystek and Smidh (1953), Hoe and Hayashi (1975), Huertas et al. (1971), Huggins et al. (1962), Imai and Otsuka (1984), Imai et al. (1966, 1969), Inukai et al. (1994), Jamoussi et al. (2003), Kadir et al. (2002), Kamineni et al. (1993), Kauffman (1943), Komarneni et al. (1986), Krekeler et al. (2004, 2005), Krekeler and Kearns (2008), Kulbicki (1959), Leguey et al. (2010), Li et al. (2007), Linqvist and Laitakari (1981), Lapparent De (1935, 1936), Long et al. (1997), López Aguayo and González López (1995), López-Galindo (1987), López-Galindo et al. (1996, 2008), López-Galindo and Sánchez Navas (1989), Magalhaes et al. (2009), Maksimovic and Radukic (1961), Martín Pozas et al. (1983), Martin Vivaldi and Cano Ruíz (1953), Mayayo et al. (1996), McLean et al. (1972), Midgele (1964), Millot et al. (1977), Minato et al. (1969), Muchi et al. (1965), Muraoka et al. (1958), Nagata and Sakae (1975), Nagy and Bradley (1955), Neaman and Singer (2000), Otsuka et al. (1966), Paquet (1983), Post and Heaney (2008), Post (1978), Post and Crawford (2007), Post and Janke (1984), Pozo and Casas (1999), Preisinger (1957), Rautoureau et al. (1972, 1979), Robertson and Stot (1974), Robertson (1961), Rogers et al. (1954, 1956), Santaren et al. (1990), Shannon (1929), Serna (1973), Shimosaka et al. (1976, 1980), Siddiki (1984), Singer (1976, 1981), Singer and Norrish (1974), Singer et al. (1998), Smith and Norem (1986), Starkey and Blackmon (1984), Stoessell and Hay (1978), Stphen (1954), Suárez et al. (1991, 1994, 1995), Suárez and García-Romero (2006a, 2006b), Tauler et al. (2009), Takahashi (1956), Tien (1973), Torres-Ruíz et al. (1994), Verrecchia and Le Coustumer (1996), Vicente Rodriguez et al. (1994), Watts (1976), Weaver (1984), Weaver and Polland (1973), Wiesma (1970), Yalçin and Bozkaya (1995, 2004), Yeniyol (1986), Zaaboub et al. (2005), Zheng (1991, 1997).

The chemical composition of the two pure dehydrated minerals calculated from the theoretical formulae is very simple: 69.1 wt% SiO_2 and 30.9 wt% MgO for sepiolite; 72.47 wt% SiO_2, 15.37 wt% Al_2O_3 and 12.5 wt% MgO for palygorskite. The deviations from these values are due to three different possibilities: (1) isomorphic tetrahedral and octahedral substitutions; (2) contamination by impurities of other minerals in the sample analysed mainly other clay minerals like illite, smectites and quartz or zeolite; and (3)

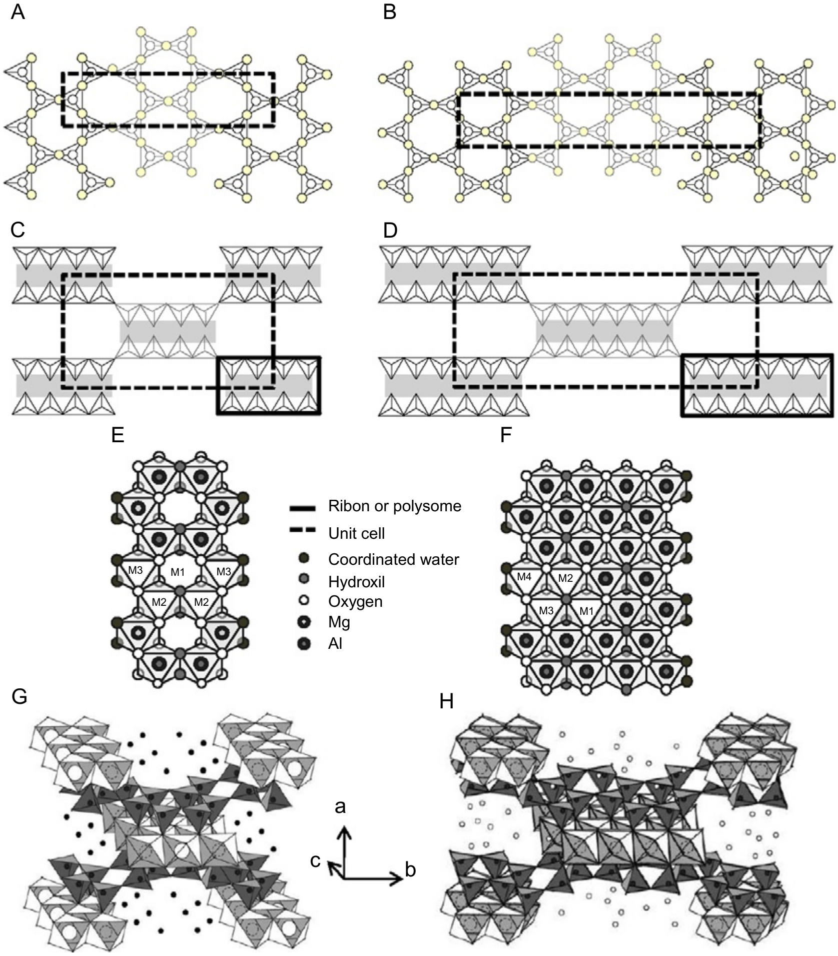

FIGURE 1 Structural schemes of palygorskite and sepiolite. (A and B) Tetrahedral sheet of palygorskite and sepiolite, respectively, projected on (001), black and grey mean tetrahedrons with apical oxygens pointing in opposite directions. (C and D) Tetrahedral sheet of palygorskite and sepiolite, respectively, projected on (100), grey shadow corresponds to the octahedral sheet. (E and F) Octahedral sheet of palygorskite and sepiolite, respectively, projected on (001). (G and H) Schematic view (from Sánchez del Rio et al., 2005) of a 1 × 1 × 2 supercell of palygorskite and sepiolite, respectively.

instrumental errors. In the past decades, the use of transmission electron microscopy to obtain analyses (AEM) of very small particles makes it possible to obtain more accurate data from the individual particles and to avoid the influence of impurities. Bound or structural water is used in many different ways in the literature; so in this chapter, most of the reported chemical data have been recalculated on an anhydrous basis to compare them.

The objective of this chapter is to establish the variations in the chemical composition of natural sepiolites and palygorskites from the ideal composition which correspond to pure and "perfect" minerals of sepiolite and palygorskite without any type of isomorphic substitutions. The range and type of isomorphic compositions in the two fibrous minerals can be obtained by analysing already published data of pure or almost pure sepiolites and palygorskites. Therefore, it is possible to look for the compositional limits between the two minerals, taking into account the existence of recently reported Al-sepiolite and Mg-palygorskite.

2. CHEMICAL COMPOSITION OF SEPIOLITE

Ideal sepiolite, $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4(H_2O)_8$, is a pure trioctahedral mineral, and the four possible octahedral positions (Figure 1) are occupied by Mg. The earliest experimental references about chemical composition of sepiolite or palygorskite are from the early decades of the twentieth century (Fersmann, 1913; Kauffman, 1943; Lapparent De, 1935; Shannon, 1929). However, the most outstanding works are those of Caillère (1936, 1951), Bradley (1940), Nagy and Bradley (1955) and Brauner and Pressinger (1956) or the review of chemical analyses for both sepiolite and palygorskite done by Caillère and Henin (1961). We must not forget, in this review, a special mention to the pioneer works of Martín Vivaldi and collaborators. In 1953, Martín Vivaldi and Cano Ruíz reported a chemical characterization of five different Spanish sepiolites. They compared the analyses with others from the bibliography and defined the SiO_2/MgO ratio for an ideal, wholly magnesian sepiolite. In 1956 (Martín Vivaldi and Cano Ruíz, 1956c), the same authors did a detailed study of the dehydration of sepiolite. In addition in Martín Vivaldi and Cano Ruíz (1956b), they suggested that the minerals of the palygorskite–sepiolite group occupy the region of discontinuity between dioctahedral and trioctahedral minerals. They affirm that there is a series of minerals. Martín Vivaldi and Linares found fibrous clays with intermediate properties between sepiolite and palygorskite in the Cabo de Gata (Almería, Spain) in 1962. They interpreted that this structure could be a random intergrowth. Later, Martín Vivaldi and Fenol Hach-Ali (1970) and Martín Vivaldi and Robertson (1971) made an excellent revision about both fibrous fillosilicates.

The first comparative study on the composition of sepiolite and palygorskite by scanning electron micrsocopy (SEM) was done by Paquet et al. (1987)

studying 145 individual particles from palygorskite–smectite and sepiolite–smectite assemblages. They conclude that the octahedral composition fields of the smectites and fibrous clays partly overlap. The sepiolite field is clearly in the trioctahedral domain, whereas the palygorskite field is both in the dioctahedral and between the trioctahedral and dioctahedral domains.

Nowadays, the ideal structural formula for sepiolite based on the model of Brauner and Pressinger (1956) is $(\mathrm{Mg}_{8\text{-}y\text{-}z}\mathrm{R}_y^{3+}\square_z)(\mathrm{Si}_{12-x}\mathrm{R}_x^{3+})\mathrm{O}_{30}(\mathrm{OH})_4(\mathrm{OH}_2)_4\mathrm{R}^{2+}_{(x-y+2z)/2}\cdot(\mathrm{H_2O})_8$, where the number of octahedral cations lies between 6.95 and 8.11. The cations are mainly Mg with some Al, Fe^{3+}, Fe^{2+}, Ti and occasional Cr^{3+} and Ni. Mg varies between 4.96 and 8.1.

According to the review by Newman and Brown (1987), tetrahedral occupancy ranges from $(\mathrm{Si}_{11.96}\mathrm{Al}_{0.05})$ to $(\mathrm{Si}_{11.23}\mathrm{Fe}_{0.53}^{3+}\mathrm{Al}_{0.24})$ and the total number of octahedral cations ranges from 7.01 to 8.01 (Table 1). Afterwards, Jones and Galan (1991) affirm that the theoretical $\mathrm{SiO_2/MgO}$ ratio of sepiolite is 2.23 with $\mathrm{SiO_2} = 55.6$ wt%; $\mathrm{MgO} = 24.99$ wt%. But usually, $\mathrm{SiO_2}$ falls in the range of 53.9 ± 1.9 wt%, and MgO between 21 and 25 wt%. Galán and Carretero (1999) evaluated compositional limits for sepiolite and palygorskite and concluded that sepiolite is a true trioctahedral mineral, with negligible structural substitutions and eight octahedral positions filled with magnesium (Table 1).

The most recent study about chemical composition of sepiolite was made by García-Romero and Suárez (2010), from a study of more than a thousand AEM analyses. They concluded that "some octahedral substitutions of Mg by Al and/or Fe are possible, which produces an increase in the number of octahedral vacancies. Sepiolite can contain large proportions of Al and be considered as Al-rich sepiolite". They affirm that the mean MgO content in sepiolite varies greatly between 30.57% and 18.58%, and the largest proportion of $\mathrm{Al_2O_3}$ that they found was 8.35 wt%. The content of other oxides like

TABLE 1 Compositional Ranges Found for Sepiolite by Different Authors.

	Tetrahedral Positions	Octahedral Positions	
	Si	*Number of Cations*	*Mg*
Brauner and Pressinger (1956)		6.95–8.11	4.96–8.1
Newman and Brown (1987)	11.96–11.23	7.01–8.01	
Galán and Carretero (1999)		≈8	≈8
García-Romero and Suárez (2010)	11.50–12	6.87–7.96	4.88–7.92
This study	11.16–12.05	6.7–8.03	4.28–8

TiO_2, K_2O and Na_2O is generally very low or zero. Exceptionally, there are mean contents somewhat greater (~1 wt% TiO_2 or 0.94 wt% Na_2O), but in these cases, the standard deviation is similar to the mean value which indicates the high variability of these oxides in the spot analyses.

From the published literature, SiO_2 and MgO are the only essential oxides in sepiolite (Figure 2), and the other oxides could appear in different amounts or be absent. Sepiolite from Eskisehir (Turkey) is one of the purest sepiolite taking into account the isomorphic substitutions. It has been studied by different authors and they all agree that this is the ideal chemical composition (Cetisli and Gedikbey, 1960; Ece, 1989; García-Romero and Suárez, 2010; Yalçin and Bozkaya, 2004 among others).

In general, SiO_2 in sepiolite ranges from 57.96 to 74.67 wt%, but most of the data show less dispersion. In fact, 66 wt% of the references reported sepiolites with SiO_2 between 68 and 71 wt% (±2% over the theoretical content; Figure 3). The mean value is 67.59 wt%, very close to the theoretical amount of SiO_2 for sepiolite. For AEM data, SiO_2 ranges between narrower extremes due to the presence of impurities in the other raw samples.

MgO, the most important oxide with SiO_2, ranges from 13.48 to 32 wt%, but most of the data are grouped within narrower limits, 17% of the analyses have less than 20 wt% of MgO (Figure 3). The mean value is 25.57 wt%. The sepiolites with lower amounts of Mg are richer in Al_2O_3 and Fe_2O_3.

Al_2O_3 is present in most sepiolites. Only a few references report sepiolite with no Al (Arranz et al., 2008; Imai and Otsuka, 1984; Mayayo et al., 1996; Muraoka et al., 1958). This oxide could reach as much as 8.9 wt% (Rogers

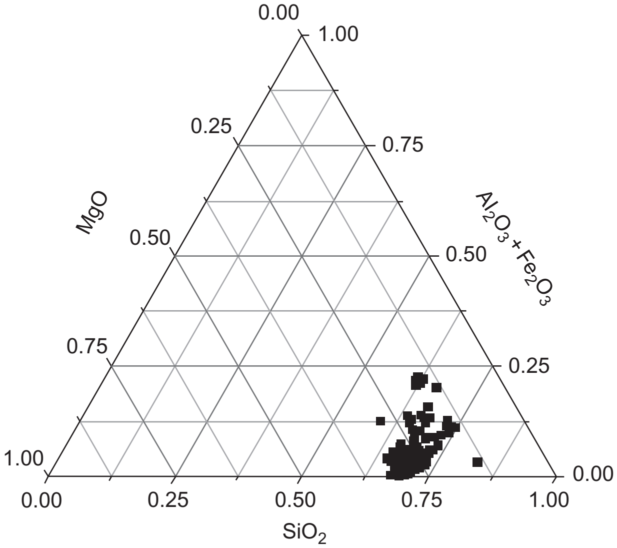

FIGURE 2 Proportions of the main oxides in sepiolite from the references.[1]

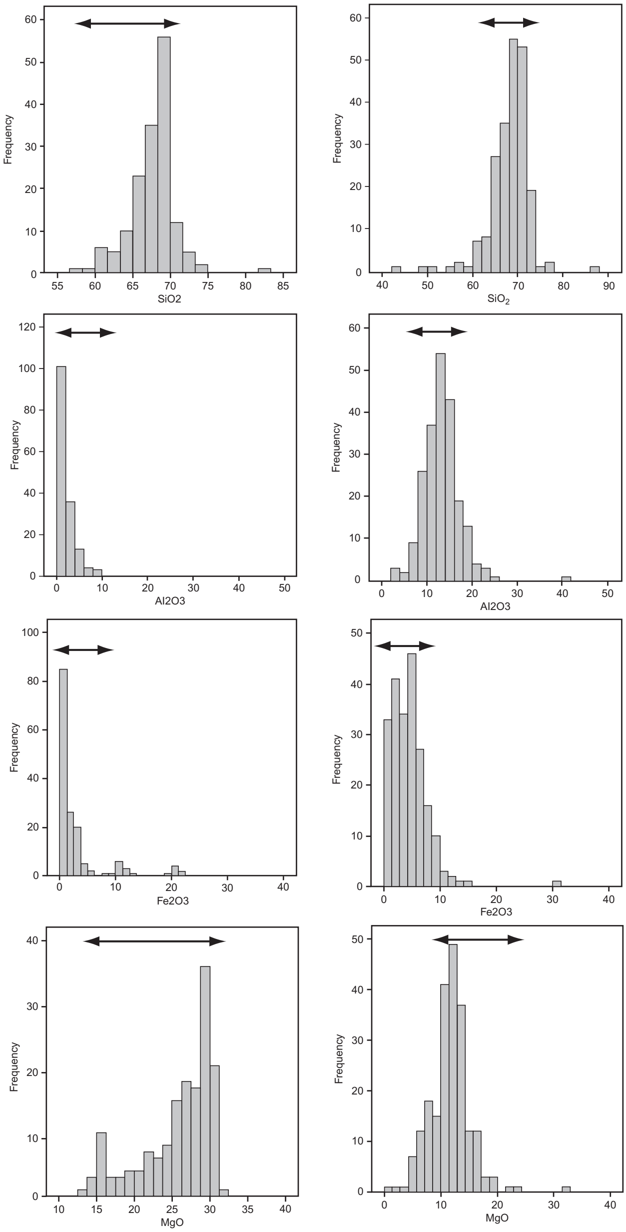

FIGURE 3 Variations of the main oxides in sepiolites (left column) and palygorskites (right column) from the references,[1] the double arrows show the compositional range founded by AEM of individual particles by García-Romero and Suárez (2010).

et al., 1956). However, 88% of bibliographic data have less than 4 wt% of Al_2O_3, and 40% of analyses have less than 1 wt% (Figure 3). Among the Al-rich ($Al_2O_3 > 7$ wt%) are those in the Ninetyeast Ridge, Indian Ocean (Argast, 1989) and those in Polatti, Turkey (García-Romero and Suárez, 2010). The richest Al-sepiolite occurs (Mclean et al., 1972) in a lacustrine deposit of the Southern High Plains. This sepiolite has an Al_2O_3/MgO ratio ~0.5, but it might have a minor amount of illite as impurities.

After Al, Fe is the main element substituting for Mg in the octahedral sheet, and it can appear in different proportions. As can be seen in Figure 4, there are certain sepiolites that have no Al and are plotted on the MgO–Fe_2O_3 axis. There are eight locations where sepiolite has been cited with more than 10 wt% of Fe_2O_3 and a ratio of Fe_2O_3/MgO is greater than 0.5. Several of them are from Japan and they appear in dolomitic rocks. The most Fe-rich sepiolites are from Middle Atlas of Morocco (Arranz et al., 2008) and from Tyrol (Brauner and Pressinger, 1956; Preisinger, 1957). In both locations, the Fe_2O_3/MgO ratio is greater than 1 and the Fe_2O_3 content is ~20 wt%. This high amount of Fe_2O_3 means that more than two octahedral positions are occupied by Fe. The name xylolite had been used for Fe-rich sepiolite (Brauner and Pressinger, 1956), and also for Fe-rich minerals for the serpentine group (Caillère, 1936) however; nowadays, it is not accepted by the IMA (International Mineralogical Association). In García-Romero and Suárez (2010), the Fe_2O_3 ranges between 3.22 and 0.07 wt%, although 70% of the samples have less than 2 wt% of this oxide. That is in agreement with the references used here.

Although Al and Fe are the main cations substituting for Mg, other elements can appear in the octahedral sheet of the sepiolite. Ni-rich sepiolite can exist, varying from Ni-sepiolite to falcondoite (nickel analogue with $Ni > Mg$; Springer, 1976). Falcondoite is a rare mineral species that has been found in the Dominican Republic in Ni laterite deposits (Lewis et al., 2006; Proenza et al., 2007). The chemical compositions of Central Dominican Republic cover a large interval of falcondoite–sepiolite solid solution (Fal3 and Fal70). These compositions suggest a complete miscibility along the sepiolite–falcondoite join. The maximum NiO content is 30.42 wt% and the (Ni + Mg)/Si ratio varies from 0.6 to 0.73 (Tauler et al., 2009). In addition, Ni-sepiolites are common constituents of garnierite mineralization in hydrous silicate-type lateritic nickel deposits (Brand et al., 1998; Freyssinet et al., 2005). Ni-sepiolite has been described in the weathering profile of the Cerro Matoso silicate Ni laterite deposit in northwest Colombia with ~10.6 wt% NiO (Gleeson et al., 2004), and in garnierites from Poro Mine nickel ore deposit in New Caledonia with 12.8 wt% NiO (Manceau et al., 1985). Sepiolite with up to 1.5wt% Ni occurs in millimetre-thick veins and has a thin coating on the slickensided surface of fractures in the lateritic deposits at Nickel Mountain, Oregon (Hotz, 1964). Sepiolite can have other elements like Ti or Mn. Very small amounts of TiO_2 have been reported for around half of

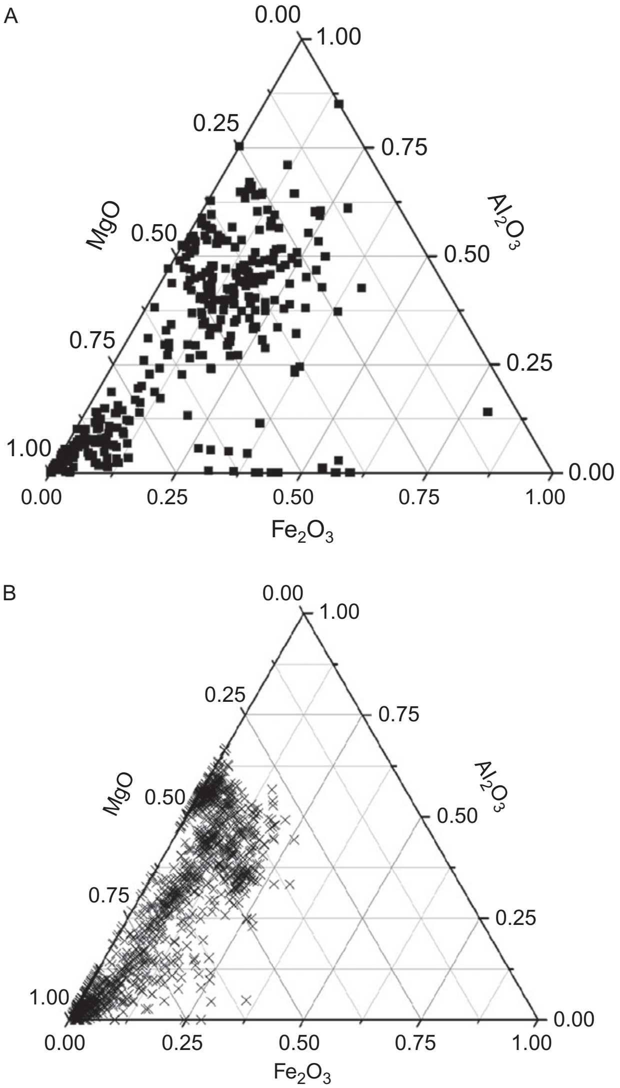

FIGURE 4 Proportions of the oxides of the three main octahedral elements in sepiolite and palygorskite from the data: (A) from the references,[1] (B) from AEM analysis (García-Romero and Suárez (2010).

the data considered herein, but most of them have less than 0.5 wt%. Only three sepiolites, all of them Al-rich sepiolites and studied by AEM, those from Polatty, Turkey, and Batallones, Spain (García-Romero and Suárez, 2010) and from Oum El Kaheb, Tunisia (Zaaboub et al., 2005), contain between 1 and 2.2 wt% TiO_2. MnO is rarer, appearing in the chemical analyses of only a few sepiolites. It reaches a maximum of 3.7 wt% in the sepiolite from Akatani, Japan (Imai and Otsuka, 1984).

Sepiolite usually has small amounts of Ca, K and/or Na, but they are always scarce, the first is frequently related to small amounts of calcite impurities. The sum of these atoms rarely reaches 0.5 atoms per half unit cell. As suggested by Newman and Brown (1987), "it is possible that part of the Ca, K and Na reported in some analyses may be enclosed within the channel frameworks and cannot be readily exchangeable".

There is a Na analogue named louglhinite which has four atoms of Na p.h.u.c. (Fahey and Axelrod, 1948; Fahey et al., 1960; Kadir et al., 2002). These references describe a fibrous mineral, similar to sepiolite, with the main X-ray powder diffraction (XRD) reflection at 12.9 Å and ~8 wt% of Na_2O which means the Na/Mg ratio = 2/3. However, they do not explain whether Na could be both in octahedral positions and inside the channels or only in the latter position. Preisinger (1963) proposes that loughlinite has two Na substituting for two Mg at the edges of the ribbons, with two Na in the channels.

Regarding the sepiolite structural formulae, the number of Si atoms referred to in the literature ranges from 11.16 to 12.05 (Table 1), a little wider than the range from 11.50 to 12 found by García-Romero and Suárez (2010). This study, as said before, was made by AEM on a score of samples, and the results are not influenced by impurities. They conclude that only a few samples of sepiolite have very few atoms (<0.04) of tetrahedral Fe(III). The number of total octahedral cations ranges from 6.87 to 7.96. These values correspond to 0.5–14% octahedral vacancies. Clearly, Mg is the main octahedral cation in sepiolite (4.88–7.92 p.h.u.c.), but most have more than seven atoms of Mg p.h.u.c. The new data indicate that sepiolite contains only minor amounts of Al (0.01–1.24 atoms p.h.u.c.) and Fe(III) (0.01–0.43 atoms p.h.u.c.) and very small amounts of Ti. These elements can occupy M1, M2 and M3 positions in sepiolite (Figure 1). Ca is always present as exchangeable cation, and Na and K appear in most samples.

In general, all studies have found that the structural formulae of sepiolites can be affected by the presence of small amounts of impurities or by the accuracy of the method employed, and as a consequence, the dispersion of the data is higher than in AEM analyses. The number of octahedral cations reported in former studies ranges from 6.7 to 8.03 with a mean value of 7.63 (Table 1). The main octahedral cation is the Mg, which ranges from 4.28 to 8 atoms per half unit cell, with a mean value of 7.11. Sixty-six percent of the formulae have seven or more Mg atoms. The rest of the octahedral positions are filled by Al and even by Fe^{3+} in some occasions (<15% of samples). These samples have the same distribution of Fe contents. The octahedral Al can reach 1.49 atoms per half unit cell although there are numerous samples that do not have that quantity (~30% of samples). Half of the data considered here have more than 0.5 atoms per half cell. The mean content of octahedral Al is 0.22. There are only four sepiolites that have more than one Al atoms per half cell. They come from China (Lieyang), Turkey (Polattli and Eskisehir) and South Australia (Tintinara) (Cetisli and Gedikbey, 1960; García-Romero and Suárez, 2010; Rogers et al., 1956). This last study demonstrates the existence of sepiolite so rich in Al that several of them could be fitted as palygorskite obtaining very acceptable results of the occupancy of the positions and the balance of the charges. The composition of Al-rich sepiolites is so similar to the Mg-rich palygorskite that it points to the possibility of a certain degree of polymorphism.

Al-rich sepiolite had been referred to several times, first by Rogers et al. (1956), as we said before. Zaaboub et al. (2005) studied by AEM the sepiolites from Selja and Oum El Kcheb (Tunisia) which have 0.91 and 0.73 octahedral positions occupied by Al and only ~75% of the octahedral positions occupied by Mg. García-Romero et al. (2007) found a very Al-rich sepiolite in the Allou Kagne deposit (Senegal) related to a Mg-rich palygorskite. García-Romero and Suárez (2010) affirm that the most Al-rich sepiolites have only between 85% and 61% of the octahedral position occupied by Mg, and they concluded that sepiolite can be classified into two types: sepiolite and Al-sepiolite. A limit for these two types can be established from the octahedral occupancy, and Al-sepiolites are those that have more than 10% of octahedral positions vacant and more than 0.5 ^{VI}Al atoms. The data obtained in this review support the data of previous reviews made by other authors. The little differences are due to more data taken into account; different analytical techniques and some of the samples may not have been very pure.

There are very few references (Bonatti et al., 1983; Torres-Ruíz et al., 1994; YalÇin and Bozkaya, 2004; Zaaboub et al., 2005) regarding trace elements and/or rare earths. Usually, the variations between them are high and related to the procedence of the mineral (detritical, formed in the depositional basins, or formed by transformation processes).

A few researchers (Cuevas et al., 2003; Santaren et al., 1990; Torres-Ruíz et al., 1994) have studied F in sepiolite. The Vallecas-Vicalvaro samples contain higher values of this element than any other Spanish sepiolites (Torres-Ruíz et al., 1994). Santaren et al. (1990) studied sepiolites of the same locality by nuclear magnetic resonance (NMR) spectroscopy and found that this sepiolite contains 1.3 wt% of fluorine, and that this element is located in the interior of the sepiolite structure, probably substituting for OH^- groups bound to Mg.

Sepiolite contains different types of water in its structure (Figure 1): zeolitic, coordinated (or bound) and structural water (OH groups). These have been described dating back to the first studies on this mineral. The number of OH^- groups, structural water and coordinated water is well constrained in the procedure for the calculation of the structural formula, but the amount of zeolitic water is not constant, and probably it is not the same for all sepiolites. From the first sepiolite studies (Preisinger, 1963), eight molecules of zeolitic water (p.h.u.c.) have been considered. However, the most recent data based on thermal studies and synchrotron XRD (Frost and Ding 2003; Post et al., 2007 among others) show that the amount of zeolitic water is lower than this value.

3. CHEMICAL COMPOSITION OF PALYGORSKITE

The most widely accepted model for palygorskite is the one proposed by Drits and Aleksandrova (1966), which is based on the model by Bradley (1940). After this, ideal palygorskite $Si_8O_{20}(Al_2Mg_2)(OH)_2(OH_2)_4{\cdot}H_2O)_4$ has dioctahedral character. Al atoms occupy the M2 positions, Mg the most external M3 and M1 is vacant (Figure 1). Isomorphic substitutions can occur and the approximate structural formula is $(Mg_{5\text{-}y\text{-}z}R_y{}^{3+}\square_z)(Si_{8\text{-}x}R_x{}^{3+})O_{20}(OH)_2(OH_2)_4{\cdot}R^{2+}{}_{(x-y+2z)/2}{\cdot}(H_2O)_4$. Weaver and Polland (1973) reported that tetrahedral occupancy for Al ranges from $(Si_{7.99}Al_{0.01})$ to $(Si_{7.31}Al_{0.69})$ (Table 2), and after Newman and Brown (1987), tetrahedral occupancy ranges from $(Si_{7.88}Al_{012})$ to $(Si_{7.34}Al_{0.66})$. They also report two cases in which the occupancies are 8.06 and 8.09, more than the eight available sites. However, they confirm that this could be possible within normal limits of accuracy. Galán and Carretero (1999) suggest that palygorskite is intermediate between di- and trioctahedral phyllosilicates and that the octahedral sheet mainly contains Mg, Al and Fe with an R2/R3 ratio close to 1, and four of the five octahedral sites were occupied. The M3 position (Figure 1) is always occupied by Mg (Güven et al., 1992; Suárez and García-Romero, 2006a), and M2 can be occupied by Al or Fe^{3+}, mainly. In a pure dioctahedral palygorskite M1 is vacant. The sum of octahedral cations lies between 3.74 and 4.64 with a mean value of 4.00, indicating that the minerals should be classified as dioctahedral. Octahedral cations range from about 2.5, trivalent plus 1.5 divalent for samples with much Al, to 4.5 for the highly magnesian samples.

TABLE 2 Compositional Ranges Found for Palygorskite by Different Authors.

	Tetrahedral Positions	Octahedral Positions		
	Si	*Number of Cations*	*Mg*	*Al*
Weaver and Polland (1973)	7.31–7.99			
Newman and Brown (1987)	7.34–7.88	3.74–4.64		
Galán and Carretero (1999)	∼8	∼4	1.72–2.10	∼2
García-Romero and Suárez (2010)	7.88–8.06	3.35–4.40	1.79–3.34	0.92–1.99
This study	7.20–8.13	2.86–4.66	0–3.91	0.12–2.35

From published data,[1] we can summarize that SiO_2 ranges between 42.1 and 76.3 wt%, although 95% of values are between 60 and 75 wt% SiO_2 (Figure 3), with a mean value of 75 wt%. Al_2O_3 ranges between 2.41 and 24.4 wt%, with a mean value of 13.17 wt%. MgO is between 2.33 and 22.9 wt% and its mean is 11.65 wt%. Logically, these two oxides vary inversely. The amount of Al_2O_3 and MgO in palygorskite depends on the type of palygorskite (García-Romero and Suárez, 2010). According to these authors, the limits are narrower with SiO_2 ranging between 72.93 and 68.90 wt%, the oxides of the main octahedral cations. Al_2O_3 ranges between 15.88 and 7.52 wt% and between 19.82 and 10.75 wt% for MgO.

The whole sample data support the idea that most palygorskites have Mg in excess of the theoretical composition as can be seen in Figures 3, 5 and 7. For more than 200 chemical analyses of palygorskite from different localities, ~75% have $MgO/(Al_2O_3+Fe_2O_3) > 0.5$. That is to say, the majority are a few richer in Mg than the ideal palygorskite. In addition, Mg-palygorskite has been described. Magnesic palygorskites are those from Spain, in Esquivias and Los Trancos (García-Romero and Suárez, 2010; Garcia-Romero et al., 2004), Russia (Drits and Aleksandrova, 1966), Eastern China (Zheng, 1997), Pacific Ocean (Gibbs et al., 1993) and Silver Bell Mine (Post and Crawford, 2007). All of them have large amounts of Mg and are similar in composition to the Al-rich sepiolites. García-Romero et al. (2007) found samples very rich in Mg-palygorskite together with Al-rich sepiolite in the Allou-Kagne deposit.

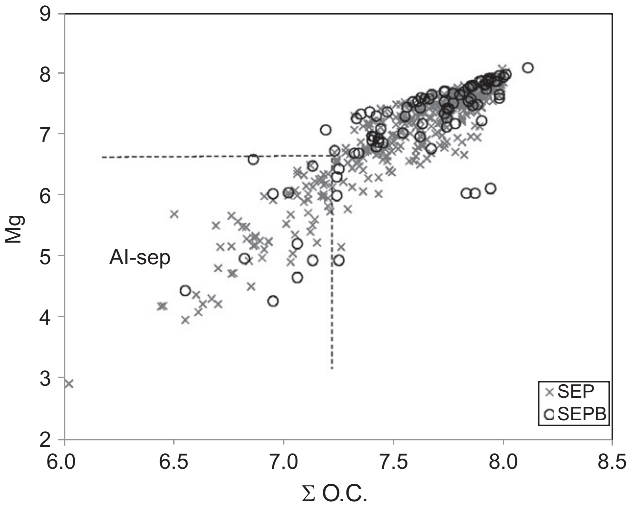

FIGURE 5 From García-Romero and Suárez (2010). Mg content (p.h.u.c.) versus total octahedral content in sepiolite, for data from the literature (○) and from AEM data (×). The two kinds of data are projected in the same region of the plot.

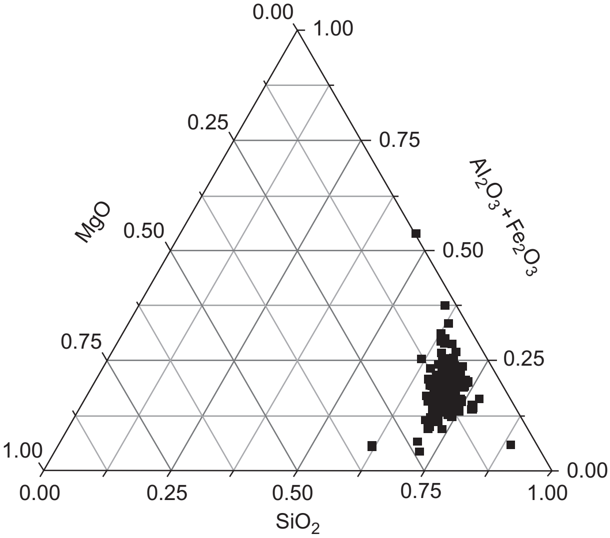

FIGURE 6 Proportions of the main oxides in palygorskite from references.[1]

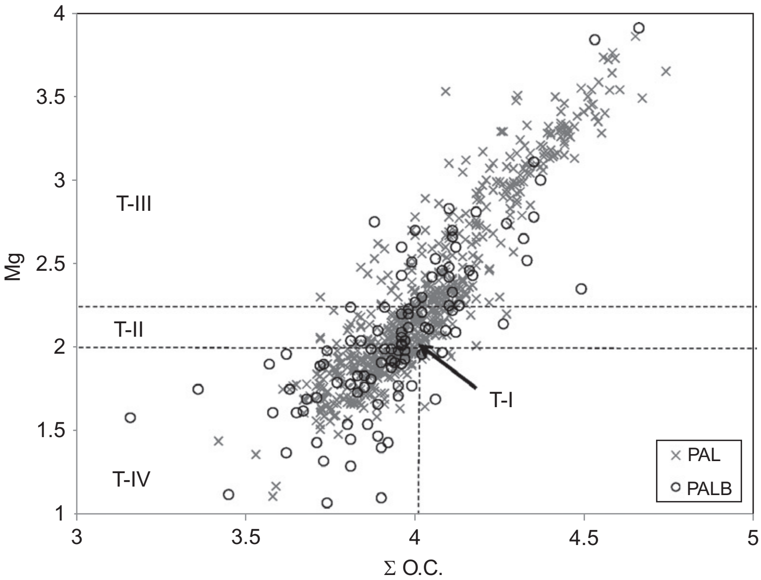

FIGURE 7 From García-Romero and Suárez (2010). Mg content (p.h.u.c.) versus total octahedral content in palygorskite, for data from literature (○) and from AEM data (×). The two kinds of data are projected in the same region of the plot. T-I, ideal palygorskite; T-II, common palygorskite; T-III, magnesic–palygorskite; and T-IV, aluminic-palygorskite.

Fe substituting for Al in M2 position (Figure 1) is common in palygorskite. We found only three references to analyses where Fe_2O_3 was not present (Drits and Aleksandrova, 1966; Fersmann, 1913; Haji-Vassiliou and Puffer, 1975). As can be seen in Figure 4, almost all points are separated from the Al_2O_3–MgO axis indicating the presence of Fe. The Fe_2O_3 content can reach 14.8 wt%, with a mean value of 4.35 wt% in the references considered, but only seven samples had over 10 wt% (Figure 3). Fe_2O_3 can also appear as impurities of oxides or other clay minerals, but the presence as octahedral cation in most palygorskites is unquestionable based on the results of AEM analyses and IR spectroscopy (Chryssikos et al., 2009; Frost et al., 1998, 2001; Gionis et al., 2007; Suárez and García-Romero, 2006a). Although Fe is almost always present in palygorskite, Fe-rich palygorskites are scarce. The term Fe-rich palygorskite is used when $Fe > Al$. This type has been reported by different authors (Chryssikos et al., 2009; Gionis et al., 2006, 2007; Imai and Otsuka, 1984; Stathopoulou et al., 2011). García-Romero and Suárez (2010) found that all samples studied by AEM contain Fe_2O_3 and it can reach 5.54 wt%, with a standard deviation equal to ± 0.51. Fe is almost always considered to be ferric, and there are a few studies in which FeO was analysed. Taking into account that palygorskite is a supergenic mineral formed in oxidizing conditions ferrous Fe cannot be abundant, although Botha and Hughes (1992) and Drits and Aleksandrova (1966) have reported it to be a major oxide in palygorskite.

Almost half of the references to palygorskite contain a small proportion of TiO_2. This element could be related to impurities, but it could also be an octahedral cation in palygorskite because it was found by AEM analyses of isolated fibres (Krekeler et al., 2004; Suárez and García-Romero, 2006b). The richest TiO_2 palygorskite found is the one studied by Krekeler et al. (2004) in the sediments from the Hawthorne Formation which contains 3.5 wt%. MnO is even scarcer than TiO_2 but appears in palygorskite from Georgia (Krekeler et al., 2004) and from Atlantic Ocean (Boules et al., 1971). A manganoan variety has been called yofortierite (Perrault et al., 1975) and is a fully trioctahedral mineral with four positions occupied by Mn(II).

Na_2O, K_2O and CaO appear, as in sepiolite, as minor components; the latter, in all samples studied, is clearly related to carbonate impurities. In certain analyses of palygorskite (Weaver and Polland, 1973), K_2O can be over 3 wt% due to small amounts of illite and smectite. Influence of these impurities in the analyses of palygorskite is greater than in sepiolite because they are more frequently found in the rock and cause the dispersion of the data in the central region of Figure 4B.

The dependence of cell parameters in palygorskite on the octahedral composition was studied by Suárez et al. (2007) using high-resolution X-ray diffraction (HRXRD) with synchrotron radiation. They propose a very simple way to produce a good approximation of the palygorskite structural formula (octahedral sheet) that depends on the *d*-spacing of the 200 reflection: $Al_{(VI)} = 49.1617 - 7.4401 * d_{200}$ and octahedral vacancy $= 24.0047 - 3.6065 * d_{200}$. In their work, a classification of the palygorskites into three types is proposed: (Type I) *Ideal palygorskite* with an octahedral composition near to the ideal palygorskite, similar contents of Al and Mg and negligible substitutions. (Type II) *Common palygorskite* where ^{VI}Al content is less than in the ideal formula and as a consequence the Mg content is higher, but the number of octahedral cations 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 dioctahedral character. (Type III) *Magnesic palygorskite* is the most trioctahedral extreme. The number of octahedral cations is greater than 4 (vacant octahedral positions < 1), and M1 position (Figure 1) is partially occupied. Recently, García-Romero and Suárez (2010) from a study of more than a thousand AEM analyses of 22 very pure palygorskites from different localities corroborated the validity of this classification and showed that the most abundant are Type II varieties with an excess of Mg related to the theoretical content (Figure 7). In the same work, a new type of palygorskite was proposed for the minerals which have Al/Mg > 1. Thus Type IV or *Aluminic-palygorskite* is defined by a total number of octahedral cations (p.h.u.c.) < 4, with Mg < 2 and consequently $(Al + Fe^3) > Mg$.

Gionis et al. (2007) and Chryssikos et al. (2009) proposed a more complex structural formula for palygorskite taking into account that most palygorskites have, as a result of the substitution of Al in M2 position by Mg, an excess of Mg which produces trioctahedral domains in the mineral. The structural formula has two parts, the trioctahedral fraction is represented by the coefficient *y*, and the content in Fe occupying M2 position in the dioctahedral component is indicated by *x*. The formula is $y Mg_5Si_8O_{20}(OH)_2 \cdot (1-y) [x Mg_2Fe_2 \cdot (1-x) Mg_2Al_2]\ Si_8O_{20}(OH)_2$. Later, this same group (Stathopoulou et al., 2009) demonstrated from near infrared spectroscopy that the trioctahedral entities in palygorskite are not pure trioctahedral palygorskite but sepiolite polysomes intergrown with palygorskite. Therefore, the Mg-rich palygorskites are described by the formula $y Mg_8Si_{12}O_{30}(OH)_4 \cdot (1-y) [x Mg_2Fe_2 \cdot (1-x) Mg_2Al_2]\ Si_8O_{20}(OH)_2$, where *y* indicates the content in sepiolite polysomes ($0 < x < 0.7$ and $0 < y < 0.33$).

There are few palygorskites with structural formulae close to the ideal, that is to say, corresponding to Type I (García-Romero and Suárez, 2010). One of them is from Palygorskaya (Russia), the type locality of the mineral. In general, both tetrahedral and octahedral substitutions can be found in the structural formulae. The number of Si atoms ranges from 7.20 to 8.13 atoms for half unit cell (Table 2), but the mean value is close to 8 (7.91). Eighty percent has values between 7.5 and 8 atoms per half unit cell. The number of octahedral cations ranges from 2.86 to 4.66 atoms per half unit cell, but most of them have values close to 4, thus the mean value is 3.96 p.h.u.c. The main octahedral cations are Al (0.12–2.35 p.h.u.c.) and Mg (0.00–3.91 p.h.u.c.). In the theoretical formula, both atoms have the same values (close to 2) although analyses in the older literature show slightly higher values of Mg. The mean value of Mg atoms per half unit cell is 2.1 and 1.47 the Al mean. Palygorskite has minor proportions of octahedral Fe(III). It could be as high as 1.31 atoms per half unit cell, with a mean value of 0.36. About 75% of them have less than 0.5 Fe(III) atoms per half unit cell. Only some samples have high Fe content. The most Fe-rich samples come from Maderuelo, Spain (1.31 and 1.16 atoms of Fe(III)) (Torres-Ruíz et al., 1994), from Western Macedonia, Greece (1.12 Fe(III)) (Gionis et al., 2006), from Serinhisar-Acipayam Basin, Denizli, SW, Turkey (1.05 Fe(III)) (Akbulut and Kadir, 2003) and from Mayaosan, Eastern China (0.04) (Li et al., 2007). As with sepiolite, the AEM analyses of palygorskite found narrower limits (García-Romero and Suárez, 2010; Garcia-Romero et al., 2004; Krekeler et al., 2004; Zheng, 1997, among others). Si ranges from 7.88 to 8.06 and the total octahedral cation content ranges from 3.35 to 4.40 atoms for palygorskite. These values correspond to between 12% and 23.6% octahedral vacancies for palygorskite. Palygorskite shows greater octahedral variability than sepiolite: Mg (1.79–3.34), Al (0.92–1.99), Fe(III) (0.02–0.47). There are also very small amounts of Ti, never exceeding 0.17 atoms. Ca, Na and K appear in most samples as exchangeable cation.

As with sepiolite, references about trace elements and/or rare earths in palygorskite are scarce (Jamoussi et al., 2003; Kamineni et al., 1993; López-Galindo et al., 1996; Torres-Ruíz et al., 1994; Zaaboub et al., 2005), and the variations are a consequence of the origin of the mineral. Sánchez del Río et al. (2009) found that the contents in rare earths present in palygorskite from the Yucatan Peninsula vary according to the deposition environment.

Just like sepiolite, palygorskite also contains zeolitic, coordinated and structural water. As the palygorskite channel width is lower than that in sepiolite (Figure 1), the number of zeolitic water molecules is also lower and generally four molecules of zeolitc water (p.h.u.c.) are considered. However, the most recent studies based on thermal analyses and synchrotron XRD (Frost and Ding, 2003; Post et al., 2007 among others) show that the amount of zeolitic water is lower than this value. Attention was placed on the dehydration, folding and rehydration processes of palygorskites (Frost and Ding, 2003; Giustetto et al., 2005; Kuang et al., 2004; Van Scoyoc et al., 1979). However, the number of zeolitic water molecules is not considered. Only a few studies, as Hirsiger et al. (1975), quantify this type of water. They find minor amounts of zeolitic water (3.9 molecules p.h.u.c.) than in the theoretical formula studying palygorskite from Bürgenstock (Switzerland).

4. IS THERE A COMPOSITIONAL GAP BETWEEN SEPIOLITE AND PALYGORSKITE?

The existence of Al-sepiolite and Mg-palygorskite is unquestionable, taking into account the data presented here. As a consequence, two questions can be proposed: first, is there a compositional gap between the two minerals, as suggested in the earliest studies on the composition of sepiolite and palygorskite (Martin Vivaldi and Cano Ruíz, 1956a,b,c) and second, what is the compositional limit for both minerals?

If the content in the oxides of the three main octahedral cations (Mg, Al and Fe) is taken into account (see Figure 4), there is no compositional gap and all possible compositions between the two ideal minerals exist. As stated before, small amounts of impurities can exist and influence the chemical analysis. However, the raw data confirmed which obtained by García-Romero and Suárez (2010) from more than 1300 AEM analysis. Both mineral data groups coming from different deposits with different origins exhibit the same trends, and it is possible to find all the intermediate compositions between the two extremes corresponding to the two pure minerals. Palygorskite can be so rich in Mg and sepiolite so rich in Al that the projections of the compositions of the two groups of minerals overlap, and a continuous trend is obtained when all samples are considered. Due to the presence of iron in most samples, the points in Figure 4 are separated from the axis MgO–Al_2O_3. Only the iron-rich sepiolites separate of this trend and they project on the Fe_2O_3–MgO axis. If we project all data considered here[1] into the plot used by Martin Vivaldi and Cano Ruíz (1956b) in which moles of MgO are plotted, versus XO moles ($Al_2O_3 + Fe_2O_3$ expressed as MgO moles), the continuity of the plotted points can be observed (Figure 8) and no compositional gap can be observed.

Al-rich sepiolites and Mg-rich palygorskites are not very frequent. In earlier papers, only two references to Mg-palygorskites and Al-sepiolites could be found (Rogers et al., 1954, 1956). The more samples studied, the more variability observed. If whole rock data and AEM analyses are taken into account, the existence of minerals with an intermediate composition is unquestionable. García-Romero and Suárez (2010) show the overlap of the composition of intermediate palygorskites and sepiolites (Figures 9 and 10). They establish that a range of compositions between the two structures is possible. If the bibliographic data (SiO_2/MgO and $Al_2O_3 + Fe_2O_3$/MgO ratios) are plotted in the same way that those AEM analyses, the same kinds of curve are obtained. In both cases, sepiolite and palygorskite overlap in a very wide range of compositions. Although bibliographic data are influenced by the presence of impurities, the intervals of composition in which sepiolite and palygorskite are possible are similar to that obtained from AEM analyses of particles. Both sepiolite and palygorskite are possible for SiO_2/MgO between $\sim$3.5 and 5 and $Al_2O_3 + Fe_2O_3$/MgO between $\sim$ 0.2 and 1. In consequence, there are sepiolites so rich in Al, that they could be almost fitted as palygorskites, and Mg-palygorskites that overlap sepiolite. These authors call these minerals, which have a composition between the two ideal sepiolite and palygorskite, *intermediate*. Intermediate mineral could be interpreted as both Al-sepiolite and Mg-palygorskite but only if chemical data are taking into account. Horizontal lines in Figures 9 and 10 define the compositional ranges for intermediate minerals. XRD data indicate that intermediate composition samples are either sepiolite or palygorskite.

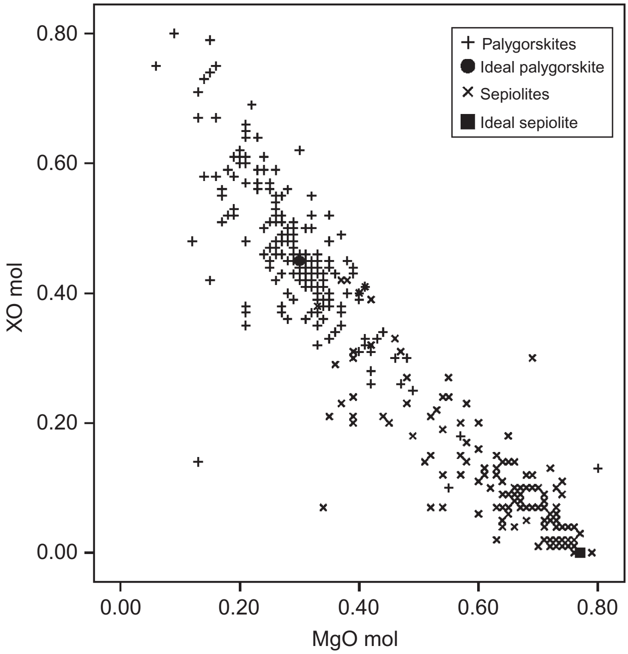

FIGURE 8 Moles of MgO versus moles of XO for sepiolites and palygorskitesfrom references and ideal values.

The existence of a large amount of samples, with all possible intermediate compositions between sepiolite and palygorskite (Figures 4 and 8–10), shows that not only is there no compositional gap, but on the contrary, a continuous series exists.

5. POSSIBLE STRUCTURAL ARRANGEMENTS OF THE *INTERMEDIATE MINERALS*

Mumpton and Roy (1958) pointed out that "in nature there does not seem to be any evidence of a continuous solid solution series between the two, although this might be expected from the postulated similarity of their structures". Half a century later, with numerous studies performed, and the possibility of studying the chemical composition of individual particles, allows us to affirm that a continuous composition series exists. As can be seen in Figure 8, sepiolite and palygorskite overlap, and there are compositions for which both minerals are possible (Figures 10 and 11).

First of all, one must make sure that the data are not influenced by impurities. When data come from a reference, it is not possible to be sure about sample purity. However, by using AEM, the composition of individual crystals is obtained. Suárez et al. (2007) studied several palygorskites, some

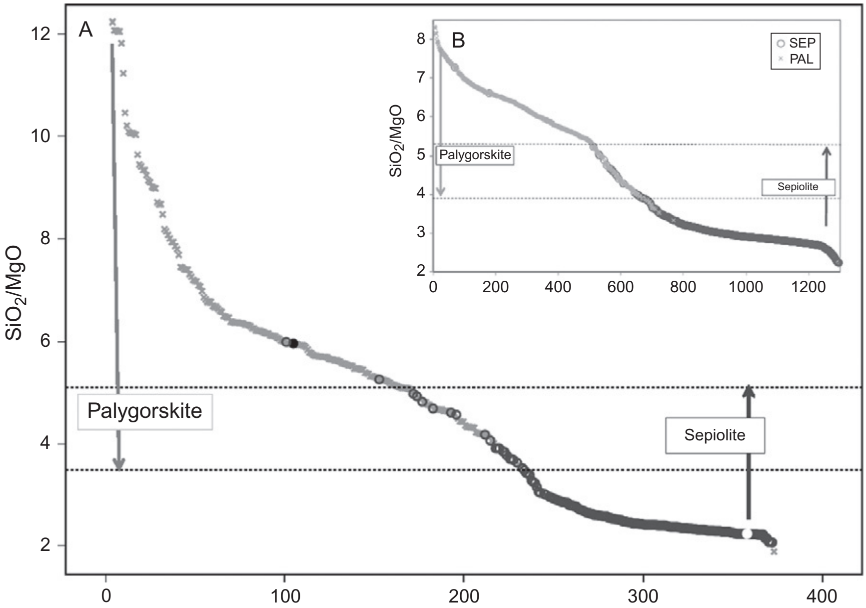

FIGURE 9 SiO_2/MgO ratios ordered from the largest to the smallest values: (A) from the References 1 and (B) from AEM analysis (García-Romero and Suárez, 2010).

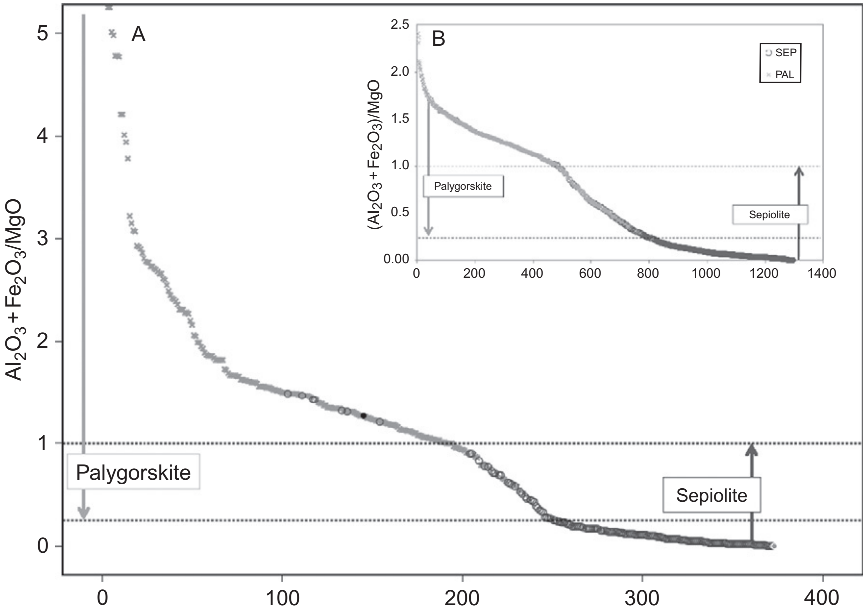

FIGURE 10 $Al_2O_3+Fe_2O_3/MgO$ ratios ordered from the largest to the smallest values: (A) from the references[1] and (B) from AEM analysis (García-Romero and Suárez, 2010).

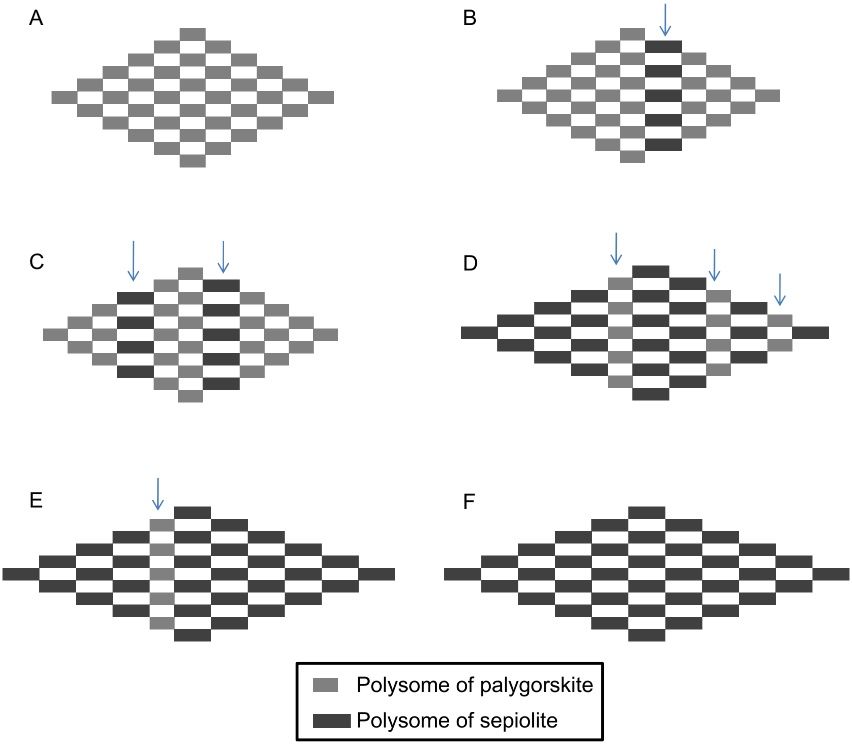

FIGURE 11 Structural scheme for the sepiolite–palygorskite polysomatic continuous series. (A) palygorskite, (B) palygorskite with a small proportion of sepiolite polysomes, (C) palygorskite with sepiolite polysomes, (D) sepiolite with palygorskite polysomes, (E) sepiolite with a small proportion of palygorskite polysomes, (F) sepiolite.

of them very rich in Mg, both by HRXRD and by AEM, and found no evidence of impurities, especially sepiolite, in the diffraction patterns. If there are no impurities in the sample, the high Al or Mg content has to be explained due to its crystallochemical features.

References to Mg-rich palygorskite are more frequent than Al-sepiolite, and the arrangement of octahedral cations has been studied by IR spectroscopy. Chahi et al. (2002) proposed a trioctahedral arrangement of Mg based on the 3680 cm^{-1} peak in the FTIR spectra. However, Garcia-Romero et al. (2004) did not find this peak in the very rich in Mg palygorskite from Esquivias. They proposed a possible distribution of the excess of Mg without Mg_3–OH bonds but with local excess of the octahedral charge. A later and more detailed study of this and other palygorskites (Chryssikos et al., 2009) showed that most palygorskites have a trioctahedral fraction that can be expressed by using the formula suggested by Gionis et al. (2007). The possibility of polysomatism in sepiolite–palygorskite was referred to by

Ferraris et al. (2005). In addition, Krekeler et al. (2005) proposed the existence of polysomes with different widths (2, 3, 4 or 5 tetrahedral chains) in order to explain the transformation of smectite into palygorskite.

Therefore, a polysome of one of these minerals could contain a 2:1 ribbon, and it is to say half unit cell (Figure 1). Taking into account the possibility of the existence of sepiolite polysomes intergrowth in the palygorskite structure, a small portion of sepiolite polysomes produces a high portion of Mg, causing a small loss of crystallinity. If this polysomatic model, which was suggested for palygorskite with an excess of Mg, is taken into account, then, in the same way, the existence of Al-sepiolite could also be explained with the presence of palygorskite polysomes in the sepiolite structure. It is feasible to wonder about the existence of all possibilities in the continuous series, from the purest and the most exclusive magnesic sepiolite, to the purest palygorskite, with all intermediate compositions. These compositions could include palygorskite with different portions of sepiolite polysomes grading into sepiolite with all possible portions of palygorskite polysomes, as shown in the simplified scheme in Figure 11.

This structural scheme for the sepiolite–palygorskite polysomatic continuous series could explain all the compositions found and all of the types of the two minerals. Type I palygorskite is a pure palygorskite without sepiolite polysomes (Figure 11A). Type II, the most common palygorskite, with a small excess of Mg, corresponds to a palygorskite with a small amount of sepiolite polysomes (Figure 11B). Type III, the Mg-rich palygorskite, is a palygorskite with a high proportion of sepiolite polysomes (Figure 11C). The Al-rich sepiolite is a sepiolite with a high proportion of polysomes palygorskite (Figure 11D). On the other hand, a small portion of palygorskite polysomes in the sepiolite (Figure 11E) is almost a pure sepiolite from chemical data because it causes a small effect on the chemical composition of the crystal.

The existence of a “certain type of transition” between the two minerals has been considered since the first studies were performed on the chemical composition of these minerals. Martin Vivaldi and Linares Gonzales (1962) did not use the term polysome but referred to it when they pointed out the possible existence of a mineral formed by a random intergrowth of the two types of structures. They found a mineral “that has intermediate properties between those of attapulgite and sepiolite… a broad line in the 10–12 Å region with a central value at 11 Å. It seems, then, logical to imagine that the rotation of tetrahedra suitable to give sepiolite or attapulgite structures is produced at random, thus giving about 50 percent of each structure for the mineral. This would account for the 110 reflections at 11 Å and the b axis having an average value between those for sepiolite and attapulgite”. This is the only reference found to a mineral with a reflection at 11 Å, which would imply periodicity for the *2 + 3 silicate chains unities*, or polysomes, like in Figure 12A, to produce the diffraction peak. If polysomes are random, as suggested in Figure 11 B–E, the only expected effect in the XRD patterns is

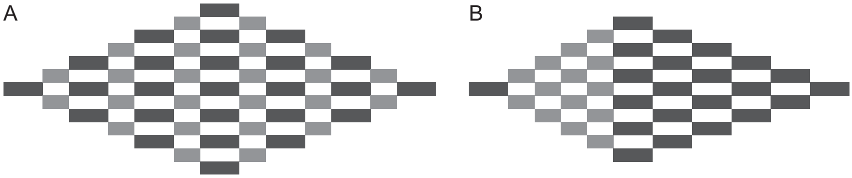

FIGURE 12 Structural schemes for (A) the regular sepiolite–palygorskite intergrowth. (B) Clusters of sepiolite and palygorskite polysomes in a crystal.

a broader peak corresponding to the loss of crystal perfection. Another possibility for the arrangement of the polysomes is to occur in clusters with discrete domains of the two minerals (Figure 12B). They would appear in XRD patterns as a mixture of the two minerals because the two regions of the crystal would diffract separately.

Therefore, the overlapping chemical compositions could be considered as intergrowths of the two minerals in all possible proportions.

6. OPEN QUESTIONS

All of the previously stated points to the complexity of the sepiolite and palygorskite crystallochemistry and some questions regarding the chemical composition of these minerals remain open. First, the polysomatic model before exposed has to be supported by HRTEM and electron diffraction data. In addition, Al-rich palygorskite, or palygorskite Type IV, is not uncommon in nature (García-Romero and Suárez, 2010; Suárez et al., 2009), and could be explained from the point of view of its composition, by intergrowth of pure dioctahedric polysomes in palygorskite. These new types of polysomes could be formed by units of more than three tetrahedral chains as shown by Krekeler et al. (2005). The possibility of intergrowth with laminar structures or close relationships with the inosilicates remains yet to be studied in detail.

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