

## A NEW APPROACH TO COMPOSITIONAL LIMITS FOR SEPIOLITE AND PALYGORSKITE

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**Abstract**—Most bulk chemical analyses of sepiolite and palygorskite available in the literature are erroneous because samples analyzed are admixtures of minerals that are difficult to separate or identify by other techniques. Some chemical analyses performed on selected individual particles by energy dispersive X-ray analysis (EDX) are also influenced by the same problem. Chemical analyses are summarized for sepiolite and palygorskite reported in the literature (bulk and EDX analyses). The analyses are evaluated by comparison to three sepiolite and three palygorskite pure samples analyzed by EDX techniques. Results indicate that sepiolite is a true trioctahedral mineral, very pure (near end-member) with negligible structural substitution and with eight octahedral positions filled with magnesium, close to the theoretical formula  $Mg_3Si_{12}O_{30}(OH)_4(OH_2)_4(H_2O)_8$ . Palygorskite is intermediate between di- and trioctahedral phyllosilicates. The octahedral sheet contains mainly Mg, Al, and Fe with a R<sup>2</sup>/R<sup>3</sup> ratio close to 1, and with four of the five structural positions occupied. The theoretical formula is close to  $(Mg_2R_{2-3+□_1})(Si_{8-x}Al_x)O_{20}(OH)_2(OH_2)_4 \cdot R^{2+}_{x/2}(H_2O)_4$ , where  $x = 0-0.5$ . Sepiolite and palygorskite are thus more compositionally limited than previously reported.

**Key Words**—Chemical Composition, Palygorskite, Sepiolite.

### INTRODUCTION

Most chemical data reported for clay minerals are the result of bulk analyses. These analyses are affected because of both crystallochemical variations and admixed contaminants (other clay minerals and associated minerals). Generally contaminants are very difficult to isolate and detection by X-ray diffraction (XRD) is difficult also. Similar problems exist for fibrous clay minerals, sepiolite, and palygorskite. The most frequent admixtures in sepiolite and palygorskite are smectites, illite, chlorite, quartz, feldspars, carbonates, zeolites, and iron and silica gels. They may contribute elements to the analyses which can be interpreted erroneously as part of the clay mineral structure.

Microanalyses of selected individual particles were published for both palygorskite (Paquet, 1983; Paquet *et al.*, 1987; Aqrawi, 1993; Chahi *et al.*, 1993; Suarez *et al.*, 1994; López Aguayo and González López, 1995) and sepiolite (Post, 1978; Paquet *et al.*, 1987; Bastida *et al.*, 1994; He *et al.*, 1996). These analyses have given a more accurate chemical composition of these minerals. Generally, such samples contain many other minerals because they were not purified prior to analysis. Also, the reproducibility of energy dispersive X-ray analyses (EDX) was not very good.

This paper reassesses the chemical limits of the sepiolite and palygorskite group minerals. The octahedral content is critically reviewed from chemical analyses published previously. Bulk analyses and selected particle analyses from EDX scanning-transmission electron microscopy are considered. Also, new EDX analyses of six samples are presented. We show that

the chemical composition of sepiolite and palygorskite is more limited than previously reported because these analyses probably consider elements from impurities as structural contributions to the sepiolite or palygorskite formula.

### MATERIALS AND METHODS

We selected 28 bulk chemical analyses of palygorskite, 33 of sepiolite, eight EDX analyses of individual palygorskite particles, and three analyses of sepiolite particles from the literature. The structural formulae, most calculated from bulk chemical analyses, and their sources are presented in Tables 1 and 2. Those calculated from EDX analyses are tabulated in Tables 3 and 4. We also used the EDX analyses from Paquet *et al.* (1987) (52 palygorskites and 24 sepiolites) and bulk analyses (50 sepiolites and 20 palygorskites) from Martín Vivaldi and Cano (1956). Other analyses found in the literature were rejected because: 1) they were incomplete, 2) the methods of chemical analyses used were not well described, or 3) the results clearly showed substantial impurities.

Three palygorskites and three sepiolites (Table 5) were selected for additional analyses. They are well-described and representative materials from occurrences previously studied. Chemical analyses were performed using a Si (Li) energy-dispersive (EDX) spectrometer (Link system, ISIS instrument) mounted with a pentafet detector with a Be thin window (ATW) and coupled to a scanning electron microscope (JEOL, JSSM-5400), operated at 20 kV. Samples of sepiolite were prepared by cutting a fragment and coating it with Au. Palygorskite samples were first treated using the dodecylammonium treatment (Abudelgawad *et al.*,

Table 1. Sepiolite structural formulae deduced from selected bulk analyses.

(1) $(\text{Si}_{11.82}\text{Al}_{0.10}\text{Fe}^{3+}_{0.08})(\text{Mg}_{7.73})\text{Ca}^{2+}_{0.08}\text{Na}^{+}_{0.51}\text{K}^{+}_{0.03}$	Mid-Atlantic Ridge (Hathaway and Sachs, 1965)
(2) $(\text{Si}_{11.93}\text{Al}_{0.07})(\text{Al}_{0.01}\text{Fe}^{3+}_{0.03}\text{Mg}_{7.96})\text{Ca}^{2+}_{0.03}\text{Na}^{+}_{0.03}$	Goles, South Serbia (Maksimovic and Radukic, 1961)
(3) $(\text{Si}_{11.67}\text{Al}_{0.22}\text{Fe}^{3+}_{0.11})(\text{Mg}_{7.39}\text{Mn}_{0.53})\text{Cu}^{2+}_{0.13}$	Little Cottonwood, Utah, USA (Nagy and Bradley, 1955)
(4) $(\text{Si}_{11.78}\text{Al}_{0.22})(\text{Al}_{0.03}\text{Fe}^{3+}_{0.01}\text{Mg}_{7.90})\text{Ca}^{2+}_{0.13}$	Kuzuu District, Japan (Imai <i>et al.</i> , 1969)
(5) $(\text{Si}_{11.87}\text{Fe}^{3+}_{0.13})(\text{Fe}^{3+}_{0.03}\text{Mg}_{7.90}\text{Ca}^{2+}_{0.13})$	Madriat, Sistrerie (Caillère, 1934a)
(6) $(\text{Si}_{11.80}\text{Al}_{0.16}\text{Fe}^{3+}_{0.04})(\text{Fe}^{3+}_{0.45}\text{Fe}^{2+}_{0.14}\text{Mg}_{7.19})\text{Ca}^{2+}_{0.11}$	Ampandrandava, Madagascar (Caillère, 1936)
(7) $(\text{Si}_{11.68}\text{Al}_{0.24}\text{Fe}^{3+}_{0.08})(\text{Fe}^{3+}_{0.53}\text{Fe}^{2+}_{0.13}\text{Mg}_{7.24})\text{Ca}^{2+}_{0.11}$	Vasko (Caillère, 1951)
(8) $(\text{Si}_{11.63}\text{Al}_{0.37})(\text{Al}_{1.47}\text{Fe}^{3+}_{0.37}\text{Mg}_{4.98})\text{Ca}^{2+}_{0.11}$	Eskişehir, Turkey (Cetisli and Gedikbey, 1990)
(9) $(\text{Si}_{11.70}\text{Al}_{0.26}\text{Fe}^{3+}_{0.04})(\text{Fe}^{3+}_{0.06}\text{Mg}_{7.60}\text{Ti}^{2+}_{0.02})\text{Ca}^{2+}_{0.26}\text{K}^{+}_{0.16}$	Amboseli, Kenya (Hay and Stoessell, 1984)
(10) $(\text{Si}_{11.64}\text{Al}_{0.36})(\text{Al}_{1.49}\text{Fe}^{3+}_{0.37}\text{Fe}^{2+}_{0.44}\text{Mg}_{4.95})\text{Ca}^{2+}_{0.45}\text{NH}_4^{+}_{0.45}$	Tintinara, South Australia (Rogers <i>et al.</i> , 1956)
(11) $(\text{Si}_{11.84}\text{Al}_{0.16})(\text{Al}_{0.79}\text{Fe}^{3+}_{0.12}\text{Mg}_{6.04})\text{Ca}^{2+}_{0.09}\text{Na}^{+}_{0.24}\text{K}^{+}_{0.36}$	Vallecas, Spain (Galán and Castillo, 1984)
(12) $(\text{Si}_{11.96}\text{Al}_{0.04})(\text{Al}_{0.40}\text{Fe}^{3+}_{0.10}\text{Mg}_{7.04})\text{Ca}^{2+}_{0.11}\text{Na}^{+}_{0.10}\text{K}^{+}_{0.01}$	Yuncillos, Toledo, Spain (Galán and Castillo, 1984)
(13) $(\text{Si}_{12.01})(\text{Al}_{0.05}\text{Fe}^{3+}_{0.05}\text{Mg}_{7.32})\text{Ca}^{2+}_{0.46}\text{Na}^{+}_{0.05}$	Ballarat, Inyo County, California (Post and Janke, 1984)
(14) $(\text{Si}_{11.80}\text{Al}_{0.11}\text{Fe}^{3+}_{0.09})(\text{Fe}^{3+}_{0.37}\text{Mg}_{7.51})\text{Ca}^{2+}_{0.05}$	Itukaichi, Tokyo, Japan (Nagata and Sakae, 1975)
(15) $(\text{Si}_{11.62}\text{Al}_{0.38})(\text{Al}_{0.04}\text{Fe}^{3+}_{0.06}\text{Ti}_{0.02}\text{Mg}_{7.72})\text{Ca}^{2+}_{0.16}\text{Na}^{+}_{0.08}\text{K}^{+}_{0.13}$	Toledo, Spain (López González <i>et al.</i> , 1981)
(16) $(\text{Si}_{11.78}\text{Al}_{0.22})(\text{Al}_{0.41}\text{Fe}^{3+}_{0.08}\text{Mg}_{6.94})\text{Ca}^{2+}_{0.32}\text{Na}^{+}_{0.11}\text{K}^{+}_{0.13}$	Nye County, Nevada (Güven and Carney, 1979)
(17) $(\text{Si}_{11.58}\text{Al}_{0.42})(\text{Al}_{0.11}\text{Fe}^{3+}_{0.13}\text{Mg}_{7.53})\text{Ca}^{2+}_{0.19}\text{Na}^{+}_{0.13}\text{K}^{+}_{0.11}$	Vallecas, Spain (Fukushima and Okamoto, 1987)
(18) $(\text{Si}_{12.02})(\text{Al}_{0.47}\text{Fe}^{3+}_{0.07}\text{Mg}_{6.89}\text{Ti}_{0.02})\text{Ca}^{2+}_{0.11}\text{Na}^{+}_{0.12}\text{K}^{+}_{0.16}$	Vallecas, Spain (Galán, 1987)
(19) $(\text{Si}_{11.88}\text{Al}_{0.12})(\text{Al}_{0.29}\text{Fe}^{3+}_{0.08}\text{Mg}_{7.36})\text{Ca}^{2+}_{0.12}\text{Na}^{+}_{0.05}$	Vallecas, Spain (Vicente Rodríguez <i>et al.</i> , 1994)
(20) $(\text{Si}_{11.75}\text{Al}_{0.21})\text{K}^{+}_{0.06}\text{Na}^{+}_{0.08}$	Ninetyeast Ridge, Indian Ocean (Argast, 1989)
(21) $(\text{Si}_{11.28}\text{Al}_{0.72})(\text{Al}_{0.05}\text{Fe}^{3+}_{0.26}\text{Mg}_{7.44})\text{Ca}^{2+}_{0.21}\text{Na}^{+}_{0.51}$	U.S.S.R. (Teodorovitch, 1961)
(22) $(\text{Si}_{11.96}\text{Al}_{0.04})(\text{Al}_{0.20}\text{Fe}^{3+}_{0.10}\text{Ti}_{0.01}\text{Mg}_{7.44})\text{Ca}^{2+}_{0.05}\text{Na}^{+}_{0.02}\text{K}^{+}_{0.07}$	Ankara, Turkey (Inukai <i>et al.</i> , 1994)
(23) $(\text{Si}_{12.05})(\text{Al}_{0.05}\text{Fe}^{3+}_{0.01}\text{Mg}_{7.78})\text{Ca}^{2+}_{0.03}$	Southwest Konya, Anatolia, Turkey (Yeniyol, 1986)
(24) $(\text{Si}_{11.99}\text{Al}_{0.01})(\text{Al}_{0.68}\text{Fe}^{3+}_{0.12}\text{Ti}_{0.01}\text{Mg}_{6.45})\text{Ca}^{2+}_{0.09}\text{Na}^{+}_{0.22}\text{K}^{+}_{0.25}$	Vallecas, Spain (Komarneni <i>et al.</i> , 1986)
(25) $(\text{Si}_{11.72}\text{Al}_{0.28})(\text{Al}_{0.48}\text{Fe}^{3+}_{0.15}\text{Ti}_{0.04}\text{Mg}_{6.50})\text{Ca}^{2+}_{0.22}\text{Na}^{+}_{0.51}\text{K}^{+}_{0.25}$	Ash Meadows, Nevada (Komarneni <i>et al.</i> , 1986)
(26) $(\text{Si}_{12.16})(\text{Al}_{0.02}\text{Fe}^{3+}_{0.02}\text{Fe}^{2+}_{0.01}\text{Mg}_{7.28})\text{Ca}^{2+}_{0.01}$	Valdemoro, Spain (He <i>et al.</i> , 1996)
(27) $(\text{Si}_{11.95}\text{Al}_{0.05})(\text{Al}_{0.10}\text{Fe}^{3+}_{0.06}\text{Mg}_{7.76})\text{Ca}^{2+}_{0.03}\text{K}^{+}_{0.06}$	Vicalvaro, Madrid, Spain (Robertson and Stot, 1974)
(28) $(\text{Si}_{11.38}\text{Al}_{0.52}\text{Fe}^{3+}_{0.10})(\text{Fe}^{3+}_{0.06}\text{Fe}^{2+}_{0.01}\text{Ti}_{0.03}\text{Mg}_{7.89})\text{Ca}^{2+}_{0.05}\text{Na}^{+}_{0.18}\text{K}^{+}_{0.26}$	Amboseli, Kenya (Stoessell and Hay, 1978)
(29) $(\text{Si}_{11.83}\text{Al}_{0.08}\text{Fe}^{3+}_{0.08})\text{Ca}^{2+}_{0.13}\text{Na}^{+}_{0.15}$	Yavapai Country, Arizona, USA (Kauffman, 1943)
(30) $(\text{Si}_{11.95}\text{Al}_{0.05})(\text{Fe}^{3+}_{0.08}\text{Mg}_{7.69})\text{Ca}^{2+}_{0.21}$	Karasawa Mine, Japan (Takahashi, 1966)
(31) $(\text{Si}_{11.49}\text{Al}_{0.33}\text{Fe}^{3+}_{0.18})(\text{Fe}^{3+}_{0.37}\text{Ti}_{0.03}\text{Mg}_{7.61})\text{Ca}^{2+}_{0.01}\text{K}^{+}_{0.01}$	Mullion, Cornwall, England (Midgley, 1964)
(32) $(\text{Si}_{12})(\text{Al}_{0.16}\text{Fe}^{3+}_{0.36}\text{Ti}_{0.02}\text{Cr}_{0.07}\text{Ni}_{0.04}\text{Mg}_{6.99})\text{Ca}^{2+}_{0.03}\text{Na}^{+}_{0.02}\text{K}^{+}_{0.02}$	Yagca formation, Turkey (Yalçın and Bozkaya, 1995)
(33) $(\text{Si}_{11.99}\text{Al}_{0.01})(\text{Al}_{0.06}\text{Fe}^{3+}_{0.02}\text{Ni}_{0.03}\text{Mg}_{7.84})\text{Ca}^{2+}_{0.01}\text{K}^{+}_{0.01}$	Eskişehir, Turkey (Yalçın nad Bozkaya, 1995)

(2) from Hathaway and Sachs (1965); (3) and (6) from Caillère and Hènin (1972); (4) and (10) from Jones and Galán (1988); (5) from Martín Vivaldi and Cano Ruiz (1953); (14) from Imai and Otsuka (1984); (21) from Ispording, (1984); (29) and (30) from Newman and Brown (1987).

1985). All sepiolites and treated palygorskites were studied by XRD and no other crystalline phase were detected. We performed 20 analyses on three samples each of sepiolite and palygorskite, for a total of 60 analyses on each mineral. The fibers were analyzed at a magnification of 10–20,000 $\times$ , with a window or spot system, and a count time of 50 s. The element abundances were calculated from peak areas with a ZAF computer program and expressed as oxide weight percentage. Detection limits were <1% (Mackinnon, 1993).

To achieve comparability of the data, all the calculated formulae were based on the model of Drits and Sokolova (1971) for palygorskite:  $(\text{Mg}_{5-y-z}\text{R}_y\text{Ca}^{2+}\square)_n(\text{Si}_{8-x}\text{R}_x\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\text{R}^{2+}_{(x-y+2z)/2}(\text{H}_2\text{O})_4$  and the model of Brauner and Preisinger (1956) for sepiolite:  $(\text{Mg}_{8-y-z}\text{R}_y\text{Ca}^{2+}\square)_n(\text{Si}_{12-x}\text{R}_x\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4\text{R}^{2+}_{(x-y+2z)/2}(\text{H}_2\text{O})_8$ . Formulae were calculated on the basis of 32 oxygens for sepiolite and 21 for palygorskite. Squares in the formulae mean vacant octahedral sites.

Octahedral compositions were also calculated on the basis of three octahedral positions for one-half the unit cell ( $\text{Al}^{3+} + \text{Fe}^{3+} + \text{Fe}^{2+} + \text{Mg}^{2+}$  per six positive charges per half unit cell) for plotting on the diagram from Paquet *et al.* (1987). Moles of MgO per 100 g and moles of XO (moles of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO}$  expressed as MgO) per 100 g were calculated for representation on the diagram from Martín Vivaldi and Cano (1956). For EDX analyses, total structural iron was considered as  $\text{Fe}^{3+}$  because the elemental analysis technique does not distinguish between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In general, little or no  $\text{Fe}^{2+}$  is present in standard chemical analyses of the bulk fraction. Summaries of the calculations are contained in Tables 6 to 10 and plotted on Figures 1 to 4.

## RESULTS AND DISCUSSION

### Sepiolite

Based on Brauner and Preisinger (1956) for sepiolite, the number of octahedral cations for bulk analyses

Table 2. Palygorskite structural formulae deduced from selected bulk analyses.

(1) $(\text{Si}_{7.80}\text{Al}_{0.20})(\text{Al}_{1.51}\text{Fe}^{3+}_{0.38}\text{Mg}_{2.22}\text{Ti}_{0.11}\text{K}^{+}_{0.09})$	Attapulugus, Georgia, USA (Bradley, 1940)
(2) $(\text{Si}_{7.82}\text{Al}_{0.18})(\text{Al}_{1.57}\text{Fe}^{3+}_{0.20}\text{Fe}^{2+}_{0.03}\text{Mg}_{2.04}\text{Ca}^{2+}_{3.84}\text{Ca}^{2+}_{0.36})$	Kuzuu District, Toshigi Pref. Japan (Imai <i>et al.</i> , 1969)
(3) $(\text{Si}_{7.61}\text{Al}_{0.39})(\text{Al}_{2.26}\text{Fe}^{3+}_{0.23}\text{Mg}_{1.43}\text{Ti}_{3.92}\text{X}_{0.04})$	Bakkasetter, Shetland Isles, Scotland (Stephen, 1954)
(4) $(\text{Si}_{7.50}\text{Al}_{0.50})(\text{Al}_{1.62}\text{Fe}^{3+}_{0.34}\text{Fe}^{2+}_{0.16}\text{Mg}_{1.78}\text{Ca}^{2+}_{3.84}\text{Ca}^{2+}_{0.34})$	Tafraout, Morocco (Caillère and Henin, 1957)
(5) $(\text{Si}_{7.88}\text{Al}_{0.12})(\text{Al}_{0.95}\text{Ti}_{0.10}\text{Fe}^{3+}_{0.42}\text{Mg}_{2.81}\text{Ca}^{2+}_{4.28})$	Mt. Flinders, Queensland, Australia (Rogers <i>et al.</i> , 1954)
(6) $(\text{Si}_{7.81}\text{Al}_{0.19})(\text{Al}_{1.40}\text{Fe}^{3+}_{0.48}\text{Mn}_{0.05}\text{Mg}_{1.99}\text{Ca}^{2+}_{3.92}\text{Ca}^{2+}_{0.04}\text{Na}^{+}_{0.32}\text{K}^{+}_{0.06})$	Eastern Saudi Arabia (Shadfan <i>et al.</i> , 1985)
(7) $(\text{Si}_{7.8}\text{Al}_{0.2})(\text{Al}_{1.13}\text{Fe}^{3+}_{0.87}\text{Mg}_{1.83}\text{Ca}^{2+}_{3.83}\text{Ca}^{2+}_{0.14}\text{Na}^{+}_{0.03}\text{K}^{+}_{0.23})$	Timsanpalli, Deccan, India (Siddiqui, 1984)
(8) $(\text{Si}_{7.66}\text{Al}_{0.34})(\text{Al}_{1.52}\text{Fe}^{3+}_{0.15}\text{Mg}_{2.65}\text{Ca}^{2+}_{4.32}\text{Ca}^{2+}_{0.04}\text{K}^{+}_{0.04})$	Mao Kou Limestone, Sichuan province, China (Zheng, 1991)
(9) $(\text{Si}_{8.05})(\text{Al}_{1.68}\text{Fe}^{3+}_{0.10}\text{Mg}_{2.20}\text{Ca}^{2+}_{3.98}\text{Ca}^{2+}_{0.02})$	Anhui province, China (Zheng, 1991)
(10) $(\text{Si}_{7.85}\text{Al}_{0.15})(\text{Al}_{1.15}\text{Fe}^{3+}_{0.38}\text{Ti}_{0.08}\text{Mg}_{2.55}\text{Ca}^{2+}_{4.14})$	Jiansu province, China (Zheng, 1991)
(11) $(\text{Si}_{7.98}\text{Al}_{0.21})(\text{Al}_{1.29}\text{Fe}^{3+}_{0.37}\text{Fe}^{2+}_{0.03}\text{Mg}_{1.96}\text{Ca}^{2+}_{3.65}\text{Ca}^{2+}_{0.32})$	Attapulugus, Georgia, USA (Bradley, 1940)
(12) $(\text{Si}_{7.89}\text{Al}_{0.11})(\text{Al}_{1.87}\text{Fe}^{3+}_{0.16}\text{Mg}_{1.91}\text{Ca}^{2+}_{3.94}\text{Ca}^{2+}_{0.05}\text{Na}^{+}_{0.03})$	Metaline Falls, Washington. (Huggins <i>et al.</i> , 1962)
(13) $(\text{Si}_{7.64}\text{Al}_{0.36})(\text{Al}_{1.73}\text{Fe}^{3+}_{0.63}\text{Mg}_{1.45}\text{Ca}^{2+}_{3.81}\text{Ca}^{2+}_{0.08})$	Jordan Valley, Israel (Wiersma, 1970)
(14) $(\text{Si}_{7.79}\text{Al}_{0.21})(\text{Al}_{1.52}\text{Fe}^{3+}_{0.31}\text{Ti}_{0.05}\text{Mg}_{1.89}\text{Ca}^{2+}_{3.77}\text{Ca}^{2+}_{0.31}\text{K}^{+}_{0.05}\text{Na}^{+}_{0.08})$	Attapulugus, Georgia (Robertson, 1961)
(15) $(\text{Si}_{7.43}\text{Al}_{0.57})(\text{Al}_{1.58}\text{Fe}^{3+}_{0.65}\text{Mg}_{1.66}\text{Ca}^{2+}_{3.89}\text{Ca}^{2+}_{0.06}\text{Na}^{+}_{0.14}\text{K}^{+}_{0.21})$	Bercimuel, Segovia, Spain (Suarez <i>et al.</i> , 1991)
(16) $(\text{Si}_{7.35}\text{Al}_{0.65})(\text{Al}_{1.29}\text{Fe}^{3+}_{0.47}\text{Mg}_{2.20}\text{Ca}^{2+}_{3.96}\text{Ca}^{2+}_{0.20}\text{Na}^{+}_{0.45}\text{K}^{+}_{0.12})$	Umm Radhuma, Saudi Arabia (Dahab and Jarjarah, 1989)
(17) $(\text{Si}_{7.66}\text{Al}_{0.34})(\text{Al}_{1.48}\text{Ti}_{0.03}\text{Fe}^{3+}_{0.46}\text{Mg}_{2.01}\text{Ca}^{2+}_{3.98}\text{Ca}^{2+}_{0.05}\text{Na}^{+}_{0.13}\text{K}^{+}_{0.15})$	Bercimuel, Segovia (Suarez <i>et al.</i> , 1995)
(18) $(\text{Si}_{7.58}\text{Al}_{0.42})(\text{Al}_{0.87}\text{Fe}^{3+}_{0.81}\text{Ti}_{0.08}\text{Mg}_{2.42}\text{Ca}^{2+}_{4.18}\text{Ca}^{2+}_{0.08}\text{Na}^{+}_{0.03}\text{K}^{+}_{0.08})$	Yagca formation, Turkey (Yalçın and Bozkaya, 1995)
(19) $(\text{Si}_{7.50}\text{Al}_{0.50})(\text{Al}_{1.68}\text{Fe}^{3+}_{0.54}\text{Mg}_{1.77}\text{Ca}^{2+}_{3.99}\text{K}^{+}_{0.27})$	(Millot <i>et al.</i> , 1977)
(20) $(\text{Si}_{7.79}\text{Al}_{0.21})(\text{Al}_{1.06}\text{Fe}^{3+}_{0.56}\text{Ti}_{0.02}\text{Mg}_{2.46}\text{Ca}^{2+}_{4.10}\text{Ca}^{2+}_{0.06}\text{Na}^{+}_{0.03}\text{K}^{+}_{0.06})$	Kizilyalak formation, Turkey (Yalçın and Bozkaya, 1995)
(21) $(\text{Si}_{7.70}\text{Al}_{0.30})(\text{Al}_{1.27}\text{Fe}^{3+}_{0.63}\text{Ti}_{0.06}\text{Mg}_{2.06}\text{Ca}^{2+}_{4.02}\text{Ca}^{2+}_{0.06}\text{Na}^{+}_{0.05}\text{K}^{+}_{0.06})$	Ugurlu formation, Turkey (Yalçın and Bozkaya, 1995)
(22) $(\text{Si}_{7.86}\text{Al}_{0.14})(\text{Al}_{2.11}\text{Fe}^{3+}_{0.22}\text{Mg}_{1.12}\text{Ca}^{2+}_{3.45}\text{Ca}^{2+}_{0.43})$	Taodeni, Algeria (Caillère, 1934b)
(23) $(\text{Si}_{7.64}\text{Al}_{0.36})(\text{Al}_{2.27}\text{Fe}^{3+}_{0.23}\text{Mg}_{1.40}\text{Ca}^{2+}_{3.90}\text{Ca}^{2+}_{0.02})$	Bakkasetter, Shetland (Stephen, 1954)
(24) $(\text{Si}_{7.61}\text{Al}_{0.39})(\text{Al}_{1.81}\text{Mg}_{2.52}\text{Ca}^{2+}_{4.33}\text{Ca}^{2+}_{0.04})$	Dogniaska, USSR (Fersmann, 1913)
(25) $(\text{Si}_{7.33}\text{Al}_{0.67})(\text{Al}_{2.37}\text{Mg}_{1.69}\text{Ca}^{2+}_{4.06}\text{Ca}^{2+}_{0.08})$	Permsk, USSR (Fersmann, 1913)
(26) $(\text{Si}_{7.99}\text{Al}_{0.01})(\text{Al}_{1.62}\text{Fe}^{3+}_{0.05}\text{Fe}^{2+}_{0.45}\text{Ti}_{0.05}\text{Mg}_{1.90}\text{Ca}^{2+}_{4.07}\text{K}^{+}_{0.08})$	Northwestern Transvaal, South Africa (Botha and Huhes, 1992)
(27) $(\text{Si}_{8.04})(\text{Al}_{1.05}\text{Fe}^{3+}_{0.08}\text{Mg}_{2.75}\text{Ca}^{2+}_{3.88}\text{Ca}^{2+}_{0.08})$	Dornboom, South Africa (Heystek and Schmidt, 1953)
(28) $(\text{Si}_{7.52}\text{Al}_{0.48})(\text{Al}_{2.08}\text{Fe}^{3+}_{0.17}\text{Mg}_{1.37}\text{Ti}_{0.04}\text{Mn}_{0.01}\text{Ca}^{2+}_{3.67}\text{Ca}^{2+}_{0.15}\text{Na}^{+}_{0.16}\text{K}^{+}_{0.30})$	Padasjoki, Finland (Linqvist and Laitakari, 1981)

(1–5) from Newman and Brown (1987); (11) from Imai and Otsuka (1984); (12) and (13) from Weaver and Pollard (1973); (14) and (27) from Ispording (1984); (19) from Suarez *et al.* (1994); (22–25) from Caillère and Hènin (1972).

lies between 6.95–8.11 (average 7.72) for eight holes, or between 2.6–3.02 on the basis of three octahedral positions (one-half unit cell) (Table 6). Cations are mainly Mg with some Al,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , Ti, and occasional  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ .  $^{\text{VI}}\text{Mg}$  varies between 4.96–8.1, and  $^{\text{VI}}(\text{R}^2 + \text{R}^3)$  from 0 to 2.28.

The above limits for total octahedral cations are very similar to those derived from EDX data (6.93–8.5) published by Paquet *et al.* (1987) but slightly more restricted for  $^{\text{VI}}\text{Mg}$  (5.6–8.5) and  $^{\text{VI}}(\text{R}^2 + \text{R}^3)$  (0–1.8). Other EDX analyses from the literature account for less octahedral variation:  $^{\text{VI}}\text{R}$  from 7.61 to 7.87,  $^{\text{VI}}\text{Mg}$  from 6.05 to 7.73, and  $^{\text{VI}}(\text{R}^2 + \text{R}^3)$  from 0 to 1.8. Our EDX analyses on sepiolite show no structural Al

and Fe, and an octahedral occupancy close to 8 (Tables 5 and 6; Figures 1 through 4) for more than 90% of the analyses. The presence of some Al, Fe, K, or Ca in a small number of the determinations was due to minor impurities. These elements were excluded from the calculations for sepiolite.

Graphical representation of the EDX analyses (Figure 2) from the literature on the diagram from Paquet *et al.* (1987) shows that sepiolite analyses (except one) are in the trioctahedral domain proposed by those authors (with  $>2.1$  Mg per half unit cell). This limit is lower for the bulk analyses (1.86) probably because most of the other analyses were performed on impure samples containing free silica (quartz), illite, and other

Table 3. Sepiolite structural formulae deduced from selected EDX analyses.

(1) $(\text{Si}_{11.80}\text{Al}_{0.20})(\text{Al}_{0.16}\text{Fe}^{3+}_{1.66}\text{Mg}_{6.05}\text{Ca}^{2+}_{7.87}\text{Ca}^{2+}_{0.09}\text{Na}^{+}_{0.07})$	Tarragona, Spain (Bastida <i>et al.</i> , 1994)
(2) $(\text{Si}_{12.05})(\text{Al}_{0.05}\text{Mg}_{7.56}\text{Ca}^{2+}_{7.61}\text{Na}^{+}_{0.24}\text{K}^{+}_{0.02})$	Two Crows, Las Vegas, USA (Post, 1978)
(3) $(\text{Si}_{11.49}\text{Al}_{0.11}\text{Mg}_{7.73}\text{Ca}^{2+}_{1.02}\text{Na}^{+}_{0.08}\text{K}^{+}_{0.13})$	Valdemoro, Spain (He <i>et al.</i> , 1996)

Table 4. Palygorskite structural formulae deduced from selected EDX analyses.

(1) $(\text{Si}_{7.60}\text{Al}_{0.40})(\text{Al}_{1.22}\text{Fe}^{3+}_{0.39}\text{Mg}_{1.75})_{3.36}\text{K}^{+}_{0.17}$	Iberian Range, Spain (López Aguayo and González López, 1995)
(2) $(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{1.57}\text{Fe}^{3+}_{0.47}\text{Mg}_{1.93})_{3.97}\text{K}^{+}_{0.22}$	Iberian Range, Spain (López Aguayo and González López, 1995)
(3) $(\text{Si}_{7.71}\text{Al}_{0.29})(\text{Al}_{1.79}\text{Fe}^{3+}_{0.62}\text{Mg}_{1.32})_{3.73}\text{K}^{+}_{0.46}$	Iberian Range, Spain (López Aguayo and González López, 1995)
(4) $(\text{Si}_{7.58}\text{Al}_{0.42})(\text{Al}_{1.67}\text{Fe}^{3+}_{0.69}\text{Mg}_{1.45})_{3.81}\text{K}^{+}_{0.21}$	Iberian Range, Spain (López Aguayo and González López, 1995)
(5) $(\text{Si}_{7.85}\text{Al}_{0.15})(\text{Al}_{1.86}\text{Fe}^{3+}_{0.20}\text{Mg}_{1.81})_{3.87}\text{K}^{+}_{0.10}\text{Ca}^{2+}_{0.07}$	Morocco (Paquet, 1983)
(6) $(\text{Si}_{7.61}\text{Al}_{0.39})(\text{Al}_{0.82}\text{Fe}^{3+}_{0.54}\text{Ti}_{0.10}\text{Mg}_{2.60})_{4.06}\text{Ca}^{2+}_{0.21}\text{Na}^{+}_{0.09}\text{K}^{+}_{0.19}$	Mesopotamia (Aqrawi, 1993)
(7) $(\text{Si}_{7.51}\text{Al}_{0.49})(\text{Al}_{1.04}\text{Fe}^{3+}_{0.70}\text{Mg}_{2.43})_{4.17}\text{Ca}^{2+}_{0.14}\text{K}^{+}_{0.13}$	Bercimuel, Segovia, Spain (Suarez <i>et al.</i> , 1994)
(8) $(\text{Si}_{7.93}\text{Al}_{0.07})(\text{Al}_{1.34}\text{Fe}^{3+}_{0.28}\text{Mg}_{2.48})_{4.10}$	Jbel Rhassoul, Morocco (Chahi <i>et al.</i> , 1993)

Table 5. EDX analyses of sepiolites and palygorskites selected for this paper.

	V	N	C	CR	CB	B
SiO <sub>2</sub>	69.31 ± 0.21	69.15 ± 0.59	69.33 ± 0.75	67.87 ± 0.89	70.34 ± 0.92	71.64 ± 0.60
Al <sub>2</sub> O <sub>3</sub>	n.d.	(a)	(c)	12.89 ± 0.81	15.00 ± 0.86	11.00 ± 1.19
Fe <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	(d)	6.83 ± 0.85	4.38 ± 1.23	4.92 ± 0.69
MgO	30.69 ± 0.21	30.85 ± 0.52	30.67 ± 0.85	12.41 ± 0.87	10.28 ± 1.14	12.44 ± 1.31
K <sub>2</sub> O	n.d.	n.d.	(e)	(g)	n.d.	n.d.
CaO	n.d.	(b)	(f)	n.d.	n.d.	n.d.
	100.00	100.00	100.00	100.00	100.00	100.00

(V) $(\text{Si}_{12.04})\text{Mg}_{7.93}$	Sepiolite from Vallecas, Spain, described by Galán and Castillo (1984)
(N) $(\text{Si}_{12.00})\text{Mg}_{7.98}$	Sepiolite from Nevada, USA, described by Post (1978)
(C) $(\text{Si}_{12.03})\text{Mg}_{7.94}$	Sepiolite from Calatayud, Spain, described by Mayayo <i>et al.</i> (1996)
(CR) $(\text{Si}_{7.71}\text{Al}_{0.29})(\text{Al}_{1.43}\text{Fe}^{3+}_{0.56}\text{Mg}_{2.10})_{4.09}$	Palygorskite from Ciudad Real, Spain, described by Sánchez and Galán (1995)
(CB) $(\text{Si}_{7.86}\text{Al}_{0.14})(\text{Al}_{1.84}\text{Fe}^{3+}_{0.40}\text{Mg}_{1.71})_{3.95}$	Palygorskite from Castelo Branco, Portugal, described by Dias <i>et al.</i> (1997)
(B) $(\text{Si}_{8.05})(\text{Al}_{1.46}\text{Fe}^{3+}_{0.41}\text{Mg}_{2.09})_{3.96}$	Palygorskite from Bercimuel, Segovia, Spain, described by Suarez <i>et al.</i> (1995)

n.d.: not detected.

(a) detected in 3 analyses, range: 0.96–3.58.

(c) detected in 6 analyses, range: 0.66–2.90.

(e) detected in 7 analyses, range: 0.11–0.35.

(g) detected in 7 analyses, range: 0.44–0.96.

Total analyses on each sample: 60.

(b) detected in 4 analyses, range: 0.44–2.04.

(d) detected in 7 analyses, range: 0.55–2.39.

(f) detected in 3 analyses, range: 0.23–0.30.

Table 6. Octahedral and tetrahedral occupancy ranges for bulk and EDX analyses of sepiolites and palygorskites (in bracket mean value).

		Bulk analyses	EDX analyses by Paquet <i>et al.</i> (1987)	Other EDX analyses from literature	EDX analyses for this paper
Sepiolite	<sup>VI</sup> R	6.95–8.11 (7.72)	6.93–8.5	7.61–7.87 (7.74)	7.93–7.98 (7.95)
	<sup>VI</sup> Mg	4.96–8.1 (7.36)	5.6–8.5	6.05–7.73 (7.11)	7.93–7.98 (7.95)
	<sup>VI</sup> (R <sup>2</sup> + R <sup>3</sup> )	0–2.28 (0.32)	0–1.8	0–1.8 (0.62)	0
	<sup>IV</sup> (Al + Fe <sup>3+</sup> )	0–0.72 (0.19)	—	0–0.2 (0.10)	0
Palygorskite	<sup>VI</sup> R	3.45–4.33 (3.96)	2.63–4.63	3.36–4.17 (3.88)	3.95–4.09 (4.00)
	<sup>VI</sup> Mg	1.12–2.82 (2.00)	0.83–3.08	1.32–2.60 (1.97)	1.71–2.10 (1.96)
	<sup>VI</sup> (R <sup>2</sup> + R <sup>3</sup> )	1.12–2.50 (1.96)	1.5–2.66	1.46–2.41 (1.91)	1.87–2.24 (2.04)
	<sup>IV</sup> (Al + Fe <sup>3+</sup> )	0–0.67 (0.29)	—	0.07–0.49 (0.30)	0–0.29 (0.14)

<sup>VI</sup>R = All octahedral cations.

<sup>VI</sup>(R<sup>2</sup> + R<sup>3</sup>) = Octahedral cations other than Mg. They are mainly Al and Fe<sup>3+</sup>.

→

Figure 1. Sepiolite and palygorskite bulk analyses selected from the literature (except data from Martín Vivaldi and Cano, 1956), and EDX analyses of this paper, plotted on Paquet *et al.* (1987) diagram. ○ palygorskite: bulk analyses from the literature; △ sepiolite: bulk analyses from the literature; \* EDX results for palygorskite (this paper); + EDX results for sepiolite (this paper); --- conventional; — proposed by Paquet *et al.* (1987).

Table 7.  $^{VI}(\text{Al} + \text{Fe})$  and  $^{VI}\text{Mg}$  per half unit cell (on the basis of three octahedral positions) of bulk and EDX analyses of sepiolites plotted on Paquet *et al.* (1987) diagram.

Sample	$^{VI}(\text{Al} + \text{Fe})$ / half unit cell	$^{VI}\text{Mg}$ /half unit cell	Sample	$^{VI}(\text{Al} + \text{Fe})$ / half unit cell	$^{VI}\text{Mg}$ /half unit cell
<sup>1</sup> From Table 1					
1	0.00	2.86	18	0.20	2.59
2	0.01	2.99	19	0.14	2.76
3	0.00	2.77	20	0.00	3.02
4	0.02	2.97	21	0.12	2.79
5	0.01	2.97	22	0.12	2.79
6	0.45	2.70	23	0.02	2.92
7	0.25	2.72	24	0.30	2.42
8	0.86	1.87	25	0.24	2.44
9	0.02	2.85	26	0.02	2.73
10	0.87	1.86	27	0.06	2.91
11	0.34	2.27	28	0.03	2.96
12	0.19	2.64	29	0.00	2.95
13	0.04	2.75	30	0.04	2.89
14	0.14	2.82	31	0.14	2.86
15	0.04	2.90	32	0.20	2.62
16	0.19	2.61	33	0.02	2.96
17	0.09	2.83			
<sup>2</sup> From Table 3					
1	0.69	2.27	3	0.00	2.90
2	0.02	2.84			
<sup>3</sup> From Table 5					
1	0.00	2.98	3	0.00	2.98
2	0.00	2.99			

Table 8.  $^{VI}(\text{Al} + \text{Fe})$  and  $^{VI}\text{Mg}$  per half unit cell (on the basis of 3 octahedral positions) of bulk and EDX analyses of palygorskites plotted on Paquet *et al.* (1987) diagram.

Sample	$^{VI}(\text{Al} + \text{Fe})$ / half unit cell	$^{VI}\text{Mg}$ /half unit cell	Sample	$^{VI}(\text{Al} + \text{Fe})$ / half unit cell	$^{VI}\text{Mg}$ /half unit cell
<sup>1</sup> From Table 2					
1	1.14	1.33	15	1.34	1.00
2	1.08	1.23	16	1.06	1.32
3	1.50	0.86	17	1.17	1.21
4	1.24	1.07	18	1.00	1.45
5	0.82	1.69	19	1.34	1.06
6	1.13	1.20	20	0.97	1.48
7	1.20	1.10	21	1.14	1.24
8	1.00	1.59	22	1.40	0.67
9	1.07	1.32	23	1.50	0.84
10	0.92	1.52	24	1.09	1.51
11	1.02	1.18	25	1.42	1.02
12	1.22	1.15	26	1.27	1.14
13	1.42	0.87	27	0.68	1.65
14	1.10	1.14	28	1.35	0.82
<sup>2</sup> From Table 4					
1	0.97	1.05	5	1.27	1.09
2	1.22	1.16	6	0.82	1.56
3	1.45	0.79	7	1.05	1.46
4	1.42	0.87	8	0.98	1.49
<sup>3</sup> From Table 5					
1	1.19	1.26	3	1.12	1.25
2	1.34	1.02			

<sup>1</sup> Table 1, bulk analyses.

<sup>2</sup> Table 3, EDX analyses from literature.

<sup>3</sup> Table 5, EDX analyses for this paper.

<sup>1</sup> Table 2, bulk analyses.

<sup>2</sup> Table 4, EDX analyses from literature.

<sup>3</sup> Table 5, EDX analyses for this paper.

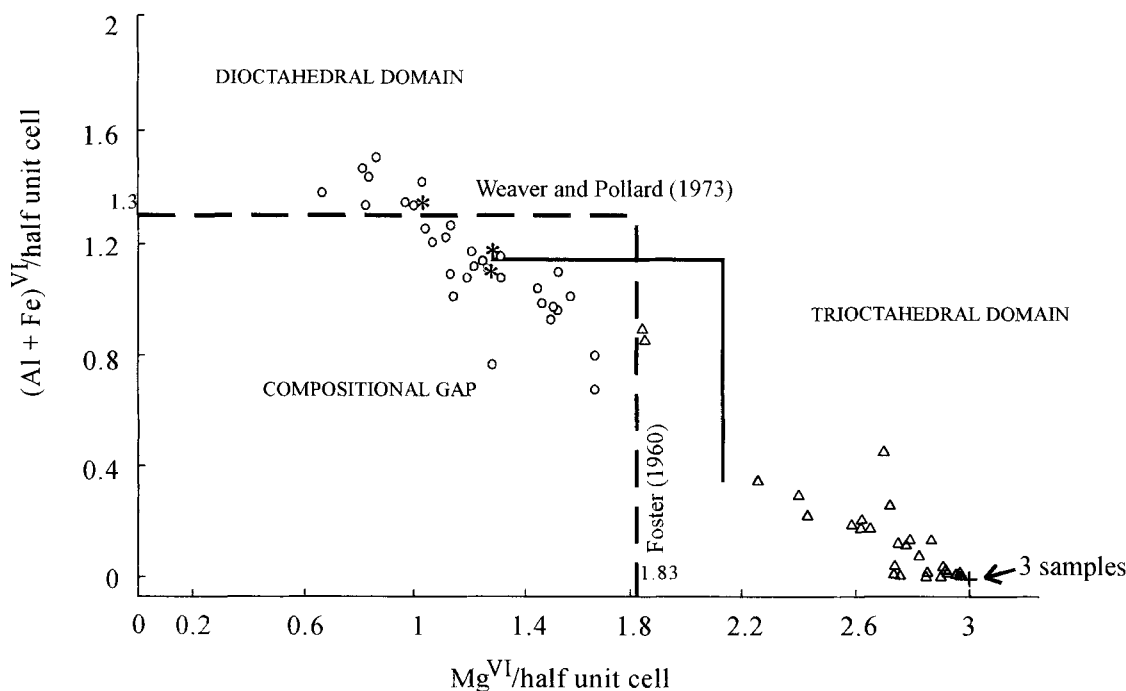


Table 9. Moles of MgO and XO per 100 g of bulk and EDX analyses of sepiolites, plotted on Martín Vivaldi and Cano (1956) diagram.

Sample	Moles of MgO per 100 g	Moles of XO per 100 g	Sample	Moles of MgO per 100 g	Moles of XO per 100 g
<sup>1</sup> From Table 1					
1	0.60	0.02	18	0.59	0.05
2	0.63	0.01	19	0.57	0.05
3	0.56	0.07	20	0.77	0.03
4	0.59	0.03	21	0.58	0.12
5	0.60	0.02	22	0.61	0.05
6	0.53	0.10	23	0.60	0.005
7	0.54	0.13	24	0.52	0.09
8	0.68	0.003	25	0.51	0.10
9	0.58	0.04	26	0.63	0.04
10	0.37	0.29	27	0.57	0.02
11	0.51	0.11	28	0.61	0.07
12	0.58	0.06	29	0.61	0.02
13	0.56	0.01	30	0.56	0.01
14	0.56	0.08	31	0.55	0.12
15	0.72	0.07	32	0.58	0.07
16	0.66	0.08	33	0.60	0.01
17	0.56	0.06			
<sup>2</sup> From Table 3					
1	0.51	0.40	3	0.72	0.01
2	0.64	0.006			
<sup>3</sup> From Table 5					
1	0.76	0.00	3	0.76	0.00
2	0.76	0.00			

Table 10. Moles of MgO and XO per 100 g of bulk and EDX analyses of palygorskites, plotted on Martín Vivaldi and Cano (1956) diagram.

Sample	Moles of MgO per 100 g	Moles of XO per 100 g	Sample	Moles of MgO per 100 g	Moles of XO per 100 g
<sup>1</sup> From Table 2					
1	0.26	0.34	15	0.19	0.46
2	0.23	0.30	16	0.26	0.43
3	0.16	0.44	17	0.22	0.35
4	0.21	0.43	18	0.30	0.41
5	0.35	0.27	19	0.26	0.54
6	0.26	0.37	20	0.31	0.36
7	0.21	0.39	21	0.26	0.42
8	0.29	0.30	22	0.13	0.39
9	0.26	0.28	23	0.16	0.44
10	0.27	0.26	24	0.30	0.33
11	0.22	0.31	25	0.20	0.45
12	0.23	0.34	26	0.28	0.43
13	0.18	0.48	27	0.35	0.19
14	0.24	0.37	28	0.16	0.43
<sup>2</sup> From Table 4					
1	0.27	0.44	5	0.27	0.44
2	0.28	0.47	6	0.30	0.30
3	0.19	0.55	7	0.35	0.47
4	0.21	0.57			
<sup>3</sup> From Table 5					
1	0.31	0.49	3	0.31	0.39
2	0.26	0.48			

<sup>1</sup> Table 1, bulk analyses.

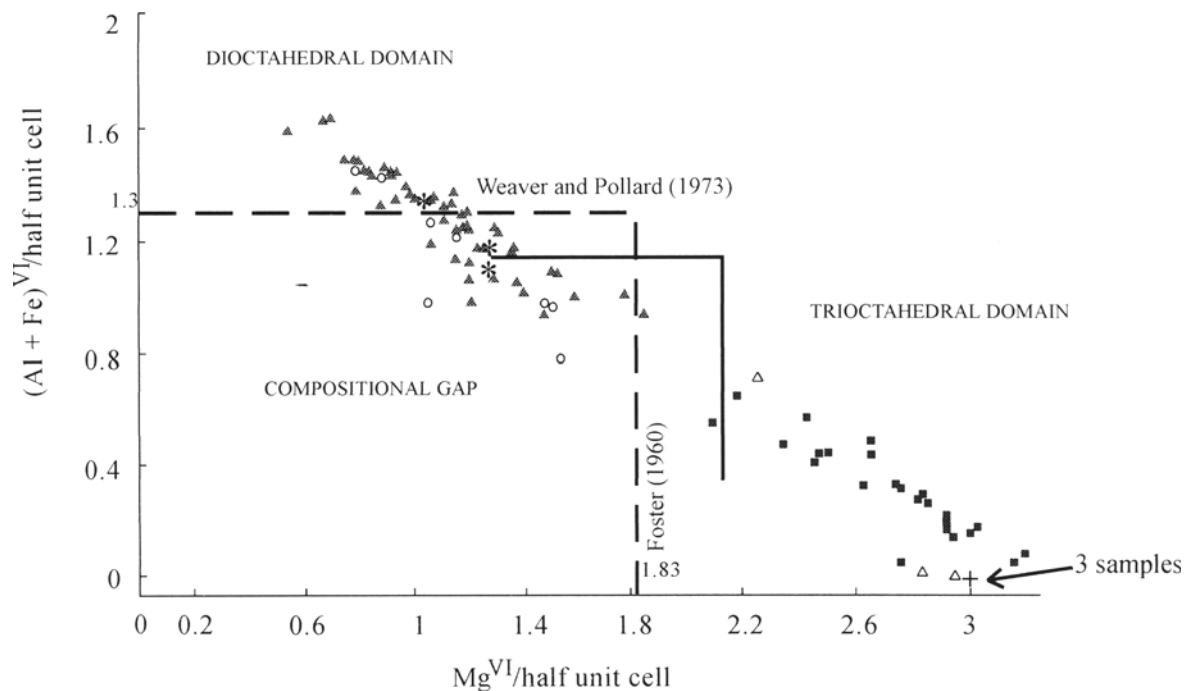
<sup>2</sup> Table 3, EDX analyses from literature.

<sup>3</sup> Table 5, EDX analyses for this paper.

<sup>1</sup> Table 2, bulk analyses.

<sup>2</sup> Table 4, EDX analyses from literature.

<sup>3</sup> Table 5, EDX analyses for this paper.



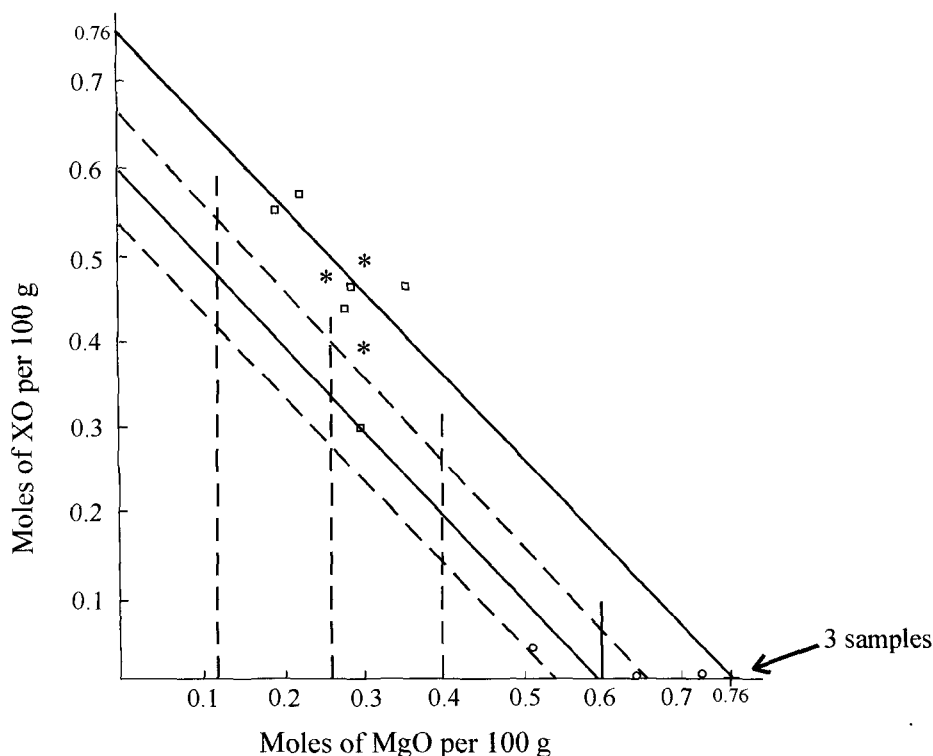


Figure 3. Sepiolite and palygorskite EDX analyses from the literature (except data from Paquet *et al.*, 1987) and this paper, plotted on Martín Vivaldi and Cano (1956) diagram. XO = moles of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO}$  expressed as MgO. □ Palygorskite: EDX analyses from the literature; ○ Sepiolite: EDX analyses from the literature; \* EDX results for palygorskite (this paper); + EDX results for sepiolite (this paper).

admixtures (see Table 7; Figure 1). Octahedral substitution can reach to 0.69 in the EDX analyses from the literature (0.67 after Paquet *et al.*, 1987) but in our analyses it is negligible and cannot be detected by the EDX technique (Figure 2). Since tetrahedral substitution is also negligible, chemical composition of sepiolite corresponds to a very pure magnesium silicate, and we propose for this mineral the following formula instead of that given by Brauner and Preisinger (1956):  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4(\text{H}_2\text{O})_8$ .

In contrast, EDX data for sepiolite plotted on the diagram of Martín Vivaldi and Cano (1956) are mainly shifted to higher MgO values, and those obtained by us are exactly 0.76 (Figure 3; Table 9), whereas the bulk analyses occupy a similar position to those given by Martín Vivaldi and Cano (1956), as shown in Figure 4.

#### Palygorskite

In the model of Drits and Sokolova (1971) for palygorskite the sum of octahedral cations for bulk analyses ranges from 3.45 to 4.33 with  $\text{VI}(\text{Al} + \text{Fe})$  between 1.12–2.5 for five octahedral sites (Table 6). The bulk analyses of palygorskite plotted on Figure 1 illustrate that the octahedral occupants have variable quantities of Mg, Al, and Fe. No palygorskite lies within the conventional octahedral divalent cation limit proposed by Foster (1960) for the trioctahedral minerals (total divalent cations must exceed 1.83 per half unit cell in trioctahedral phases), but many of them are within the dioctahedral domain proposed by Weaver and Pollard (1973) (total cations must exceed 1.3 per half unit cell in dioctahedral phases).

More than 30% of the published EDX analyses of palygorskite are between dioctahedral and trioctahed-

←

Figure 2. Sepiolite and palygorskite EDX analyses from the literature and this paper, plotted on Paquet *et al.* (1987) diagram ■ Sepiolite (Paquet *et al.*, 1987); ▲ Palygorskite (Paquet *et al.*, 1987); ○ Palygorskite: EDX analyses from the literature; △ Sepiolite: EDX analyses from the literature; \* EDX results for palygorskite (this paper); + EDX results for sepiolite (this paper); --- conventional; — proposed by Paquet *et al.* (1987).

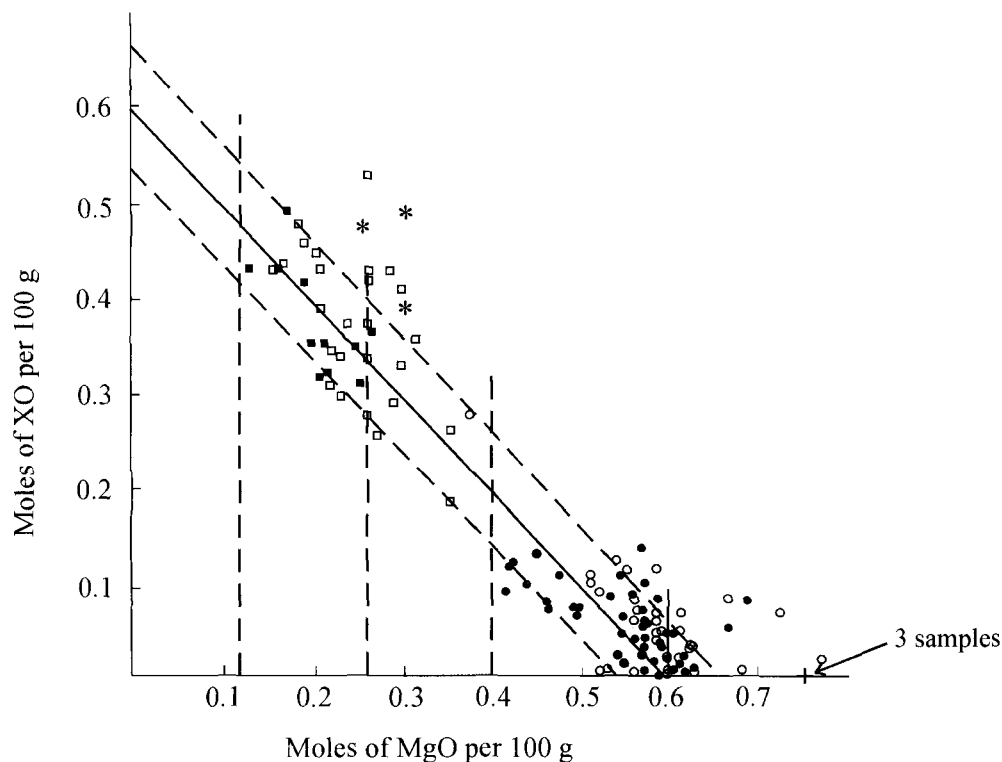


Figure 4. Sepiolite and palygorskite bulk analyses from literature and EDX analyses of this paper, plotted on Martín Vivaldi and Cano (1956) diagram. XO = moles of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO}$  expressed as MgO. ■ palygorskite (Martín Vivaldi and Cano, 1956); ● sepiolite (Martín Vivaldi and Cano, 1956); □ palygorskite: bulk analyses from the literature; ○ sepiolite: bulk analyses from the literature; \* EDX results for palygorskite (this paper); + EDX results for sepiolite (this paper).

ral (Figure 2) even when the limit (1.12) of Paquet *et al.* (1987) is accepted, instead of the more restrictive one (1.3) of Weaver and Pollard (1973). Considering our three palygorskite samples, two of the average chemical compositions are dioctahedral and one is in the gap between regions of dioctahedral and trioctahedral (Figures 1 and 2).

Palygorskite analyses (six positive charges per half unit cell) from Paquet *et al.* (1987) show a large range of variability ( $^{VI}\text{Mg}$ : 0.5–1.85,  $^{VI}(\text{Al} + \text{Fe}^{3+})$ : 0.9–1.6) but our data and from others (Table 8) are more limited ( $^{VI}\text{Mg}$ : 0.87–1.56, average 1.18;  $^{VI}(\text{Al} + \text{Fe}^{3+})$ : 0.82–1.45, average 1.16).

In summary, octahedral cations fill four of the five octahedral sites, and the average ratio  $\text{Mg}/(\text{Al} + \text{Fe}^{3+})$  is close to 1 (Table 6), indicating palygorskite is an intermediate di-trioctahedral mineral (Figures 1 and 2).

Tetrahedral substitution is very low, in general <0.5 atoms of  $\text{Al} + \text{Fe}^{3+}$  for eight tetrahedral sites. For our samples, tetrahedral substitution is <0.3 atoms of Al without any  $\text{Fe}^{3+}$ . Also, in our analyses of very pure palygorskite samples, only Si, Al, Fe, and Mg were detected. Other cations, such as Ca, K, and Na as found in other analyses of palygorskite, probably occur as impurities (calcite, illite) and they are not exchange cations, if our results are generalized. Taking

into account our results and the above data, we propose for palygorskite the following formula instead of that given by Drits and Sokolova (1971):  $(\text{Mg}_x\text{R}_2^{3+}\square_1)(\text{Si}_{8-x}\text{Al}_x)\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\text{R}^{2+}_{x/2}(\text{H}_2\text{O})_4$ , where  $x = 0$ –0.5.

In a diagram of Martín Vivaldi and Cano (1956), palygorskite analyses are distributed around the line intersecting the abscissa and ordinate at 0.6 (Figure 4). In our results, they are also aligned along a straight line with the same slope but intersecting the abscissa and ordinate at 0.76 (Figure 3). For bulk analyses plotted on this diagram, there is no apparent composition gap between palygorskite and sepiolite (Figure 4). If only our EDX analyses are considered, a gap can be recognized as Martín Vivaldi and Cano originally proposed. However, limits are 0.76 and 0.3 moles of MgO per 100 g (Figure 3) instead 0.4 and 0.26 (Martín Vivaldi and Cano, 1956), probably because they used bulk chemical analyses.

## CONCLUSIONS

Most bulk palygorskite and sepiolite chemical analyses available in the literature are sufficiently in error that there is an apparent variability of compositional data that does not actually exist. Such variability is caused by impurities that are difficult to separate and



these admixtures are difficult to evaluate. Similar problems occur with some chemical analyses performed on individual particles by EDX. When it is possible to concentrate palygorskite and sepiolite and to carry out analyses of many particles, the results are more reproducible, and the average result can be used to represent the “real” chemical composition.

Our results indicate that sepiolite is a true trioctahedral mineral that is near end-member in composition, with only negligible substitution. Sepiolite has eight octahedral sites filled with Mg. Palygorskite is intermediate between di- and trioctahedral phyllosilicates. The octahedral sheet mainly contains Mg, Al, and Fe with a  $R^2/R^3$  ratio close to 1, and four of the five octahedral sites occupied.

According to Martín Vivaldi and Cano (1956), a compositional gap exist in Mg content between sepiolite and palygorskite (0.76–0.3 moles of MgO per 100 g). The possibility of octahedral sheet “continuity” in relation to the number of vacancies, as proposed by Martín Vivaldi and Cano (1956), should be revised on the basis of these new crystallochemical data.

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