

Trioctahedral entities in palygorskite: Near-infrared evidence for sepiolite-palygorskite polysomatism

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Abstract: The mixed dioctahedral-trioctahedral character of Mg-rich palygorskite has been previously described by the formula $y\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot (1-y)[x\text{Mg}_2\text{Fe}_2 \cdot (1-x)\text{Mg}_2\text{Al}_2]\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4$, where y is the trioctahedral fraction of this two-chain ribbon mineral with an experimentally determined upper limit of $y \approx 0.5$ and x is the Fe^{III} content in the M2 sites of the dioctahedral component. Ideal trioctahedral ($y = 1$) palygorskite is elusive, although sepiolite $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4$ with a similar composition, three-chain ribbon structure and distinct XRD pattern is common. A set of 22 samples identified by XRD as palygorskite and with variable composition ($0 < x < 0.7$, $0 < y < 0.5$) were studied to extrapolate the structure of an ideal trioctahedral ($y = 1$) palygorskite and to compare this structure to sepiolite. Near-infrared spectroscopy was used to study the influence of octahedral composition on the structure of the TOT ribbons, H_2O in the tunnels and surface silanols of palygorskite, as well as their response to loss of zeolitic H_2O . All spectroscopic evidence suggests that palygorskite consists of discrete dioctahedral and trioctahedral entities. The dioctahedral entities have variable structure determined solely by $x = \text{Fe}^{\text{III}}/(\text{Al} + \text{Fe}^{\text{III}})$ and their content is proportional to $(1-y)$. In contrast, the trioctahedral entities have fixed octahedral composition or ribbon structure and are spectroscopically identical to sepiolite. The value of d_{200} in palygorskite follows the regression $d_{200} (\text{Å}) = 6.362 + 0.129x(1-y) + 0.305y$, $R^2 = 0.96$, $\sigma = 0.013 \text{ Å}$. When extrapolated to $y = 1$, d_{200} is identical to sepiolite. Based on this analysis, we propose that palygorskite samples with non-zero trioctahedral character should be considered as members of a polysomatic series of sepiolite and (dioctahedral) palygorskite described by the new formula $y'\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot (1-y')[x'\text{Mg}_2\text{Fe}_2 \cdot (1-x')\text{Mg}_2\text{Al}_2]\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4$, with $0 < x' = x < 0.7$ and $0 < y' = y/(2-y) < 0.33$.

Key-words: palygorskite, sepiolite, XRD, near-infrared spectroscopy, dioctahedral, trioctahedral, polysomatism.

1. Introduction

Phyllosilicate minerals of the palygorskite-sepiolite group have a layer structure with alternating 2:1 ribbons (modules, Fig. 1) and tunnels containing zeolitic H_2O parallel to the c axis. This modulation is due to the periodic inversion of the apical oxygen atoms of the tetrahedra every two silicate chains in palygorskite, or three in sepiolite, causing the discontinuity of the octahedral sheet. The different periodicity of the silicate chain inversion allows for the clear distinction of palygorskite from sepiolite by X-ray diffraction ($d_{110} \approx 10.4$ and 12.1 Å , respectively). The microstructure of these clays produces interesting absorption and rheological properties with applications in

industry and materials science (Singer, 1989). For example, the Mayas used palygorskite in preparing the Maya Blue pigment, essentially exploiting the principles of molecular insertion and one-dimensional confinement to fabricate hybrid nanomaterials (van Olphen, 1966; Gómez-Romero & Sánchez, 2005).

Both palygorskite and sepiolite were originally described as magnesian and trioctahedral ($\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4$, Bradley, 1940; $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4$, Brauner & Preisinger, 1956, respectively). Later studies made evident that palygorskite is mainly dioctahedral with four octahedral ions per 8 Si and with about half of the Mg substituted by Al or Fe (Drits & Aleksandrova, 1966; Drits & Sokolova, 1971; Serna *et al.*, 1977; Güven *et al.*, 1992).