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LETTER

Octahedral cation distribution in palygorskite

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ABSTRACT

The OH speciation of 18 palygorskite samples from various localities were evaluated by near infrared spectroscopy (NIR) and compared to the corresponding octahedral composition derived from independent, single-particle analytical electron microscopy (AEM). NIR gives evidence for dioctahedral-like (AlAlOH, $AlFe^{3+}OH$, $Fe^{3+}Fe^{3+}OH$) and trioctahedral-like (Mg_3OH) species. Therefore, palygorskite can be approximated by the formula $y Mg_5 Si_8O_{20}(OH)_2 \cdot (1 - y)[xMg_2Fe_2 \cdot (1 - x)Mg_2Al_2]Si_8O_{20}(OH)_2$, where x is the Fe content of the dioctahedral component, and y is the trioctahedral fraction. The values of x estimated from the NIR data are in excellent agreement with the $Fe/(^{VI}Al + Fe)$ ratio from AEM ($R^2 = 0.98$, $\sigma = 0.03$), thus suggesting that all octahedral Al and Fe in palygorskite participate in M2M2OH (dioctahedral-like) arrangements. Furthermore, y values from AEM can be compared to NIR ($R^2 = 0.90$ and $\sigma = 0.05$) after calibrating the relative intensity of the Mg_3OH vs. $(Al,Fe)_2OH$ overtone bands using AEM data. The agreement between the spectroscopic and analytical data are excellent. The data show that Fe^{3+} for Al substitution varies continuously in the analyzed samples over a broad range ($0 < x < 0.7$), suggesting that fully ferric dioctahedral palygorskites ($x = 1$) may exist. On the other hand, the observed upper trioctahedral limit of $y = 0.50$ calls for the detailed structural comparison of Mg-rich palygorskite with sepiolite.

Keywords: Palygorskite, Fe-rich, Mg-rich, structure, near infrared spectroscopy, trioctahedral, dioctahedral, composition, AEM, sepiolite