On the structure of palygorskite by mid- and near-infrared spectroscopy

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Abstract

The OH-structural characteristics of an iron-rich palygorskite from Western Macedonia, Greece (Gr-1) and an aluminous palygorskite from Florida (PFl-1) were examined by combined Fourier-transform near-infrared reflectance (NIR) and mid-infrared attenuated total reflectance (ATR) spectroscopy. Analyses of samples heated from ambient to 130 °C allowed for the development of a self-consistent set of band assignments for the structural and surface OH and H_2O species of both the hydrated and dehydrated forms. The inner octahedral sites of both samples are largely accounted for by dioctahedral AlAlOH, $AlFe^{3+}OH$, and $Fe^{3+}Fe^{3+}OH$ pairs. Band intensities for these pairs are consistent with variations in the concentration of octahedral Fe and Al in the two samples. In addition, both samples display a trace trioctahedral signature in NIR, which may be related to local trioctahedral domains, or the presence of sepiolite in trace amounts, or as intergrowths. A surface H_2O species typical of the hydrated phase was identified via its NIR combination mode at 5317 cm^{-1}. The desorption of this species by heating revealed distinct silanol groups with overtone and combination modes at 7255 and 4575 cm^{-1}, respectively. Mg-coordinated and zeolitic H_2O species are strongly coupled in the hydrated phase and give rise to NIR combination modes at 5190 and 5240 cm^{-1}. The removal of zeolitic H_2O causes the blue shift of the three dioctahedral OH overtones by ca. 20 cm^{-1} and the rearrangement of the coordinated H_2O manifested by the growth of sharp combination modes at ca. 5215 and 5120 cm^{-1}.

Keywords: IR spectroscopy, palygorskite, NIR spectroscopy, Fe-rich, hormite, hydration