Palygorskite: Crystallochemistry by Spectroscopy

Palygorskite and Sepiolite are phyllosilicates with many industrial applications due to their unusual modulated structure and their lath-like morphology. They have a discontinuous octahedral sheet and consist of alternating 2:1 aluminosilicate modules (ribbons) and hydrated channels. Progressive dehydration distorts the crystal and reveals a variety of inner and outer surface sites with different reactivity and accessibility. The largest known palygorskite deposits in Europe are in the Ventzia basin (Grevena, W. Macedonia, Greece). In the famous Maya Blue pigment palygorskite acts as substrate for the insertion and one-dimensional confinement of indigo molecules.

Modular structure of Palygorskite (left) and Sepiolite (right) viewed along the c-axis. H$_2$O in the channels is not shown.

The rich unit cell structure, its dependence on hydration, as well as the variable occupation of the octahedral sites by Mg, Al, or Fe, make the crystallochemical characterization of palygorskite very challenging. In close collaboration with Geohellas SA, we employ Near-Infrared (NIR) spectroscopy with 2$^{\text{nd}}$ derivative analysis to study palygorskite in a non-destructive manner, explore the stability regime of this mineral, and provide links between structure and properties.

*American Mineralogist* *91*, 1125-1133 (2006)
*Clays and Clay Minerals* *55*, 543-553 (2007)
The OH stretching overtone spectra of palygorskite exhibit discrete signatures of the various types of structural hydroxyl groups of the octahedral sheet.

Measuring the NIR band intensities of palygorskite allows for the quantification of its dioctahedral and trioctahedral fraction and composition according to the formula

\[ y\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_2 \cdot (1-y)\text{[xMg}_2\text{Fe}_2\cdot \text{(1-x)Mg}_2\text{Al}_2\text{]}\text{Si}_8\text{O}_{20}(\text{OH})_2 \]

The NIR predictions have been benchmarked against single particle Analytical Electron Microscopy data in collaboration with the University of Salamanca (M. Suarez), the Complutense University of Madrid (E. Garcia-Romero) and ESRF (M. Sanchez del Rio).


Contact
G. D. Chryssikos and V. Gionis
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., Athens 11635, Greece

Tel.: +30 210 7273819 and 7273820
FAX: +30 210 7273794
Email: gdchryss@eie.gr, vgionis@eie.gr