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Ab initio quantum mechanical modeling of infrared vibrational frequencies of the OH group in dioctahedral phyllosilicates. Part II: Main physical factors governing the OH vibrations

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ABSTRACT

The physical factors responsible for the variability observed in OH infrared (IR) fundamentals in dioctahedral phyllosilicates, due to octahedral substitution of Al^{3+} by Mg^{2+}, Fe^{2+}, and Fe^{3+}, are discussed here. The data analyzed consist of experimental frequencies as well as frequencies modeled using Density Functional Theory (DFT) calculations.

The charge of the octahedral cations surrounding the OH is one of the main factors affecting both the OH stretch and the in-plane bend; cationic electronegativity and ionic radius play important roles in the stretch and bend modes, respectively. The mass of the octahedral cations does not affect the OH fundamental vibrations.

The nature of the octahedral cations alone can explain most of the variability observed in the OH in-plane bend, making this fundamental vibration the most suitable for assessing octahedral composition. Discrepancies between modeled and experimental OH stretch frequencies indicate the existence of other factors governing this fundamental vibration. Further DFT calculations indicate that apical O atoms of the tetrahedral sheet with unsatisfied charges due to octahedral and/or tetrahedral substitutions can explain these discrepancies.

The modeling results are utilized to predict the frequency of the OH stretch and in-plane-bend combination band that occurs near 4545 cm^{-1} (2.2 μm) in phyllosilicates. This band can be observed in imaging spectrometer data, allowing for the detection and analysis of phyllosilicates and other minerals in large natural systems. The modeling results confirm that the variability observed in the combination band of dioctahedral phyllosilicates reflects octahedral and, to a certain degree, tetrahedral composition, but not interlayer composition.