NEAR INFRARED SIGNATURE OF KAOLINITE: A PROXY FOR ESTIMATING ITS CRYSTALLINITY AND ITS GEOLOGICAL ORIGIN ON EARTH AND MARS.

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Introduction: Kaolinite, a 1:1 dioctahedral phyllosilicate of chemical formula $Al_2Si_2O_5(OH)_4$, has been detected at the martian surface by orbiters in: (i) Al-clay rich materials associated with opaline silica, overlaid by Fe/Mg-clays in inferred pedogenetic paleoprofiles [1,2,3,4], (ii) alone or associated with a great diversity of alteration phases in contexts suggested to be linked to hydrothermal activity [5,6,7]. On Earth, kaolinite forms through pedogenesis/surface weathering, hydrothermal activity, or diagenetic/sedimentary processes [8]. Thus, the occurrences of kaolinite may be of various origins on Mars as well. Kaolinite crystallinity has been suggested to reflect the physicochemical conditions where it forms, and thus its geological conditions of formation [8]. As spectroscopic sensors on Mars cover the Near-Infrared range, we investigated the NIR signatures of terrestrial kaolinite samples from various origins in order to reveal the degrees of crystalline disorder of this clay mineral.

Material and Methods: We analyzed 24 powders of kaolinite samples, for some with well constrained geological origins. XRD data were used to determine their long-range degree of crystalline order as assessed by the Liétard Index (LI) [9]. Infrared reflectance spectra were acquired with a FTIR spectrometer with a mean spectral resolution of 2 cm^{-1}, numerically interpolated with cubic spline functions down to 0.1 cm^{-1}. Kaolinite is distinguished from other phases thanks to the 2.2 µm doublet absorption band (hereafter 4500 cm^{-1} doublet) and the 1.4 µm doublet (hereafter

7000 cm^{-1} doublet) on which we focused our spectral analysis. As these two doublets are composed of numerous superimposed absorption bands [10], we decided to investigate their different spectral contributions through second and third derivative analyses. Each main spectral contribution (SC) is highlighted by positive peaks (or local maxima) in the second derivative NIR spectra: its center position is given by the position of the local maxima and the intensity gives an estimation of the SC shape. We calculated a spectral criterion called the Sharpened Peak Width (SPW) as a proxy of the Full Width at Half Maximum (FWHM) of each SC by subtracting the positions of local maxima and minima in the 3rd derivative spectra. The results of the spectral criteria were then compared to the LI values.

Results: LI values of our samples vary from 0.52 to 1.37. LI variations are not linked to the geological origins of the samples. In our sampling set, disordered kaolinites are exclusively formed by continental weathering at low-temperature and in sedimentary/diagenetic contexts. Conversely, well-ordered kaolinite can form either by hydrothermal activity, continental weathering or diagenetic processes.

Second derivative analyses permit us to highlight 27 main SCs: 15 for the 4500 cm^{-1} doublet (SC1-15, **Fig 1A**), and 12 for the 7000 cm^{-1} doublet (SC16-27, **Fig 1B**). Visual inspection of the **Fig 1** shows that the SC8, SC11, SC20, SC23 and SC24 (related to inner-surface Al-OH vibrations) exhibit "rainbow fan" patterns when spectra are colored according to the LI values. Such patterns indicate that
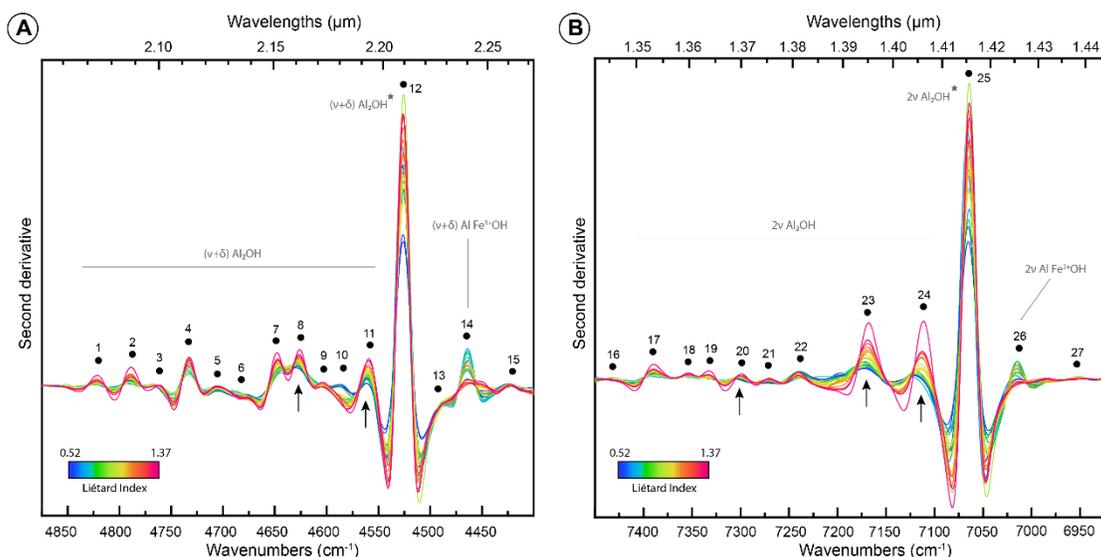

Fig 1. Second derivative spectra of the two absorption bands at 4500 cm^{-1} (A) and 7000 cm^{-1} (B) of terrestrial kaolinites. Spectra are colorized according to the Liétard Index LI values that increase with the crystalline order. Vibrations modes: ν = OH-stretching; δ = OH-bending. The black stars indicate absorptions associated to the inner-hydroxyl vibrations. Black dots indicate spectral contributions SC that were found through second derivative analysis. Black arrows point to remarkable "rainbow fan" distribution features caused by second derivative intensity regularly increasing with Liétard Index.

the spectral properties of these SCs (position and shape) vary in relation with the kaolinite crystallinity.

For some SCs related to inner-surface Al-OH vibrations, the center positions, extracted using the second derivative position of local maxima, exhibit shifts (4.0 to 11 cm^{-1}) that correlate strongly with the LI values with R^2=0.68-0.87 for SC3,7,8,1,20,23,24 (**Fig 2A,B**). Similar trends are observed for the second derivative local maxima intensities of the SC1,2,5,7,8,11,17,18,20,21,23,24 with R^2 ranging from 0.60 to 0.95, still mainly for SCs related to inner-surface Al-OH vibrations (**Fig 2C**). The SCs related to inner Al-OH vibrations (SC12&SC25) are almost fixed in terms of positions (shifts < 2 cm^{-1}) and no relationship with LI values are observed. Although the second derivative local maxima intensities variations of theses SCs are among the highest, they are not strongly correlated with LI values (R^2 < 0.50). However, these SCs show the most correlation with LI regarding SPW variations calculated using third derivatives (R^2 = 0.69-0.72), despite the SPW variations are lower than 2.5 cm^{-1} (**Fig 2D**). Only inner-surface Al-OH related SC4,5,18 show R^2 ranging from 0.49 to 0.61 between SPW variations and LI values.

We used the same methodology on the same spectra resampled at the CRISM resolution, but we did not observed sufficient spectral variations that could be indicative of different degrees of crystalline order. Thus, the use of this type of methodology to determine the kaolinite degree of crystalline order needs to be done with a sufficiently fine spectral resolution.

Discussion and Conclusions: By using 2nd and 3rd derivative curves of the 4500 cm^{-1} (2.2 µm) and 7000 cm^{-1} (1.4 µm) absorption regions of kaolinite NIR spectra, we demonstrate that the signature of kaolinite can bring information about its stacking degree. Resulting NIR indices could be related to shifts in position of some of the SCs as well as the second derivative intensity of local maxima. These two parameters are shown to be mostly correlated for the inner-surface Al-OH vibrations. The present data also reveal that the modifications of the spectral properties of the inner Al-OH groups are much weaker than those of inner-surface OH groups because their crystal chemistry environment is more constrained and only slightly affected by stacking defects.

The results on spectral criteria versus geological origin show that the crystallinity of kaolinite can be used as a proxy to determine its geological origin only in a very limited extent. Even if the crystallinity is not a categorical proxy for the geological environment of a kaolinite-bearing deposit, it nevertheless makes it possible to give indications on the most probable geological processes. Indeed, based on our sampling, we can propose that a poorly crystalline kaolinite is much more likely to have a sedimentary or pedogenetic origin than a hydrothermal origin.
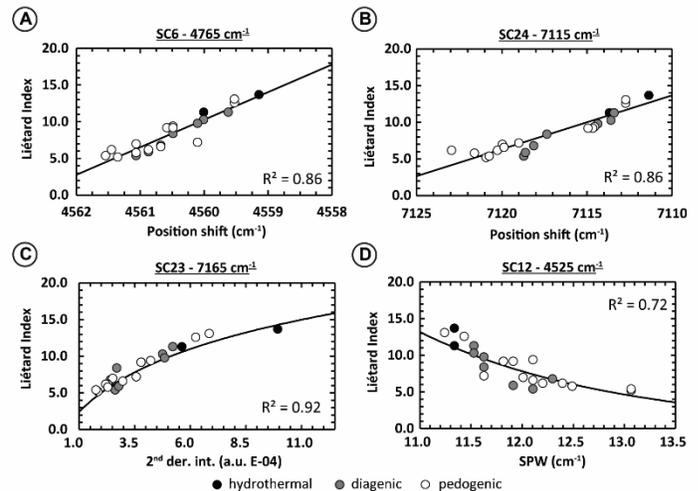

Fig 2. Relationship between the different spectral criteria of different SCs and LI XRD index. (A) Shifts in position of the 4765 cm^{-1} SC6 inner-surface Al-OH vibration, (B) Shifts in position of the 7115 cm^{-1} SC24 inner-surface Al-OH vibration, (C) Intensity variation of the 7165 cm^{-1} SC23 inner-surface Al-OH absorption, (D) Intensity Variation of the (C) SPW variation of the 4525 cm^{-1} SC12 inner Al-OH vibration.

Kaolinite has been remotely detected from orbit at Jezero crater and Oxia Planum, the two next Mars 2020 and Exo-Mars 2022 landing sites [11,12]. As the two rovers will be equipped with NIR spectrometers, in-situ measurements should permit to obtain kaolinite spectra of good quality. Combined with other NIR spectral criteria dedicated to other hydrated minerals, commonly associated to kaolinite (e.g. opaline silica, [13,14,15,16]), the proposed methodology should help to constrain the origin of kaolinite, and hence contribute to the reconstitution of the geological history of these two Mars' sites.

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