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► **To cite this version:**

M. Pineau, F. Baron, M. Mathian, Laetitia Le Deit, B. Rondeau, et al.. Estimating kaolinite crystallinity using near-infrared spectroscopy. 51st Lunar and Planetary Science Conference, Mar 2020, The Woodlands, Houston, Texas, United States. hal-02507615

HAL Id: hal-02507615

<https://hal.science/hal-02507615v1>

Submitted on 13 Mar 2020

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ESTIMATING KAOLINITE CRYSTALLINITY USING NEAR-INFRARED SPECTROSCOPY.

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Introduction: Observations of clays on Mars by orbiters and rovers have shown that the planet experienced climatic conditions enabling the existence of liquid water at the surface during the Noachian [1,2]. The occurrence of extensive exposures of Fe/Mg-smectites-rich material covered by Al-phylosilicates-rich material like kaolinite associated to opaline silica are inferred to be pedogenetic paleoprofiles, major witnesses of this former more clement climate [3,4,5,6]. Kaolinite has also been detected in other contexts that could be linked to hydrothermal activity [7,8,9]. Kaolinite is a 1:1 dioctahedral phyllosilicate of chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ that crystallizes in the triclinic crystal system. On Earth, kaolinite forms through chemical alteration/weathering of Al/Si-bearing silicates like feldspars or micas. It is found in various contexts including pedogenesis/surface weathering, hydrothermal, magmatic, sedimentary and metamorphic contexts, which highlights that its formation conditions include a wide range of pH, temperature and pressure [10]. Thus, the occurrences of kaolinite may be of various origins on Mars as well. Different degrees of crystalline order (or crystallinity) indicate different conditions of formation, although these conditions remain unspecified. It has been suggested that the degree of crystalline order of kaolinite could be a proxy of its temperature of formation [10]. As spectroscopic probes on Mars cover the near-infrared spectrum, 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 33 powders of kaolinite samples, for some with well constrained geological origins. X-Ray Diffraction (XRD) data were used to determine their long range degree of crystalline order as assessed by the Liétard Index (R2) that is calculated after the ratio of the $1\bar{3}1$ and 131 peak intensities [11]. Infrared reflectance spectra were acquired with a FTIR spectrometer with a mean spectral resolution of 2 cm^{-1} . Because kaolinite is detected on Mars using the $2.2\ \mu\text{m}$ doublet absorption band (hereafter 4500 cm^{-1} doublet) [12], we focused on this absorption band and the $1.4\ \mu\text{m}$ doublet (hereafter 7000 cm^{-1} doublet). As these two doublets are composed of numerous superimposed absorption bands [13], we decided to investigate their different spectral contributions through secondary derivative analysis. Each main spectral contribution is highlighted by positive peaks (or local maxima) in the second derivative NIR spectra and their positions are compared to the R2 Liétard index values, related to the crystalline order, obtained by XRD measurements.

Results: R2 Liétard index of our samples vary from 0.26 to 1.37. R2 variations are not linked to the geological origins of the samples. Indeed, several samples from the same context and origin show contrasted R2 values (e.g. from 0.26 to 0.98 for the sedimentary kaolinites of the “Bassin des Charentes”, France).

NIR observations revealed specific features in the 4500 and 7000 cm^{-1} absorption bands that differ from one sample to another. The observed variations are mainly localized in the high-frequency parts of the two doublets, within the $4550\text{--}4650$ and $7100\text{--}7250\text{ cm}^{-1}$ spectral ranges. They consist in the sharpening of the bands with the increasing degree of crystalline order (**Fig 1**; the 7000 cm^{-1} absorption is chosen as an example). We also observed supplementary absorptions on the high-frequency side of the two doublets that are diagnostic of octahedral cations (Cr^{3+} and Fe^{3+}) substituting for Al^{3+} in the kaolinite structure [14,15].

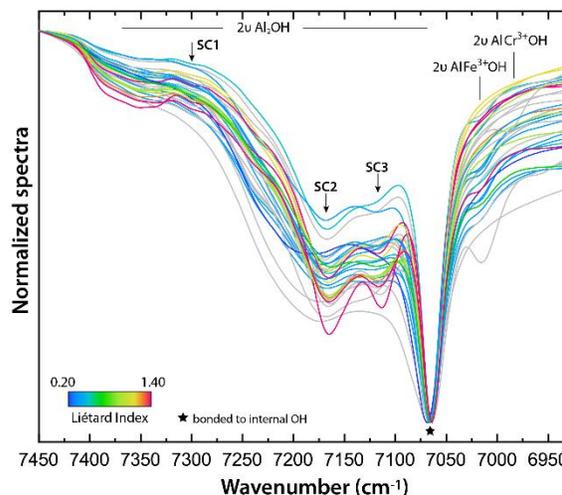


Fig 1. Reflectance spectra of the 7000 cm^{-1} doublet ($1.4\ \mu\text{m}$) of terrestrial kaolinite samples. Spectra are colorized according to the Liétard Index values that increase with the crystallinity order. Grey spectra are for kaolinite samples that were not analyzed through XRD measurements. Black arrows indicate spectral contributions that shift according to the crystallinity of the samples.

Second derivative analyzes show that, for the two doublets, several spectral contributions shift from a sample to another. These contributions are referred as SC1, SC2 and SC3, pointed by dark arrows in **Fig 1** and **Fig 2**. We observed that the spectral contribution with the largest shifts related to crystallinity is SC3, the $7115\text{--}7125\text{ cm}^{-1}$ contribution. Especially, the variations of the position of this contribution seem to be closely linked to variations of the

sample degree of crystalline order as indicated by the R2 Liétard index, with a correlation coefficient close to 0.85 (Fig 3). We also observed that the Al-OH vibrations (related to Al atoms bonded to internal hydroxyls groups) at 4525 and 7065 cm^{-1} do not show any shift, regardless of the considered sample, even samples with Fe^{3+} or Cr^{3+} .

We used the same methodology on the same spectra resampled at the CRISM resolution, but we did not observe 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.

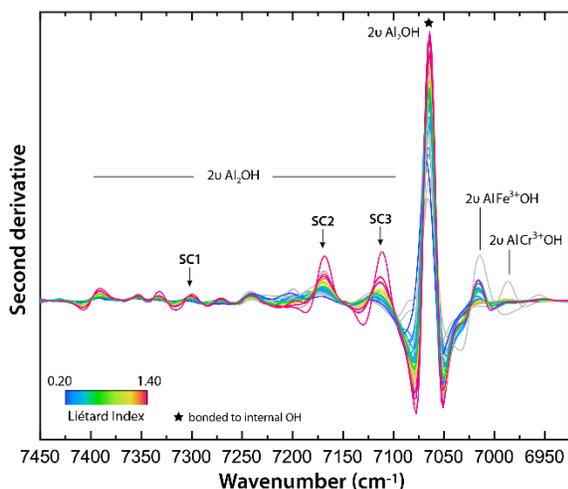


Fig 2. Secondary derivative spectra of the 7000 cm^{-1} doublet (1.4 μm) of terrestrial kaolinite samples. Spectra are colored according to the Liétard Index values that increase with the degree of crystalline order. Grey spectra indicate kaolinite samples that were not analyzed through XRD measurements. Black arrows indicate spectral contributions that shift according to the crystallinity of the samples.

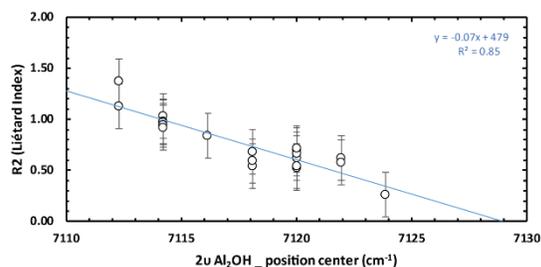


Fig 3. Diagram illustrating the relationship between the crystallinity of kaolinite and its near-infrared signature as seen through the representation of the Liétard Index values as a function of the position shift of the 7120 cm^{-1} peak position.

Discussion and Conclusions: In this study, we demonstrate that the NIR signature of kaolinite can bring information about its crystallinity. Also, we observed that the crystallinity of a kaolinite sample may not be used as a proxy to identify its geological origin. However, varying degrees of crystalline order indicate different conditions and/or mechanisms of formation. They may indicate different geochemical microenvironment, pH, kinetics or even different primary minerals. Indeed, the ordering of kaolinite may be favored by its formation through the weathering of micas: their crystalline sheets acting as templates, whereas the weathering of feldspar in the same conditions may provide lower degrees of crystalline order.

The application of the present methodology to determine the kaolinite crystallinity is still difficult for orbital measurements on Mars due to several factors including: (i) the insufficient spectral resolution of current imaging spectrometers, (ii) the low signal-to-noise ratio of CRISM spectra in the case of the absorption band located at 7000 cm^{-1} , and (iii) the possible interference with different hydrated phases favored by low spatial resolution.

Near future Mars missions will send rovers on Mars (ESA's ExoMars Rosalinda Franklin rover, and NASA's Mars2020 rover) equipped with spectrometers with better spectral resolutions [16,17]. Detection of kaolinite at the two landing sites by CRISM observations has been done recently [18,19]. New observations of these outcrops with the in-situ instruments will help to determine their precise mineralogy, the crystallinity of the kaolinite, and possibly a hint of the primary minerals that were present before kaolinitization.

Acknowledgments: We acknowledge the support from the Agence Nationale de la Recherche (ANR, France) under the contract ANR-16-CE31-0012 entitled Mars-Prime and the Centre National de la Recherche Scientifique (CNRS, France).

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