RAMAN SPECTROSCOPY OF CLAY STANDARDS AS AN ANALOGUE OF MARTIAN CLAYS.

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Introduction: Clays are finely crystalline, fine-grained, hydrated phyllosilicate minerals with extremely varied chemistry, which are commonly physically mixed with non-phyllosilicate materials in rocks and soils [1]. Not only are they critical components of’ Earth’s geosystem where they form through complex interactions between the lithosphere, hydrosphere, atmosphere and biosphere, but they are also detected on Mars where they likely trace paleoclimatic conditions and in some cases signal habitable environments [ref]. Further, clay could be a valuable natural resource on Mars in the future [2-4] Martian clays characterized in-situ by x-ray diffraction (XRD) [5] or via orbital remote sensing [6] are key components guiding current and future exploration, including sample return. The Perseverance rover is equipped with a Raman spectrometer capable of characterizing clays in-situ, and future missions may also use Raman as a tool. In this work, Raman spectral features of different clay minerals, their Raman spectral patterns, peak positions, and peak widths have been investigated.

Samples and method: Standard clays from the Source Clays Repository of The Clay Minerals Society have been used to study and do mineral identification, including KGa-2 (Kaolinite), KGa-1b (Kaolinite), SHCa-1 (Hectorite), STx-1b Ca-rich Montmorillonite, PFl-1 Palygorskite, and Nontronite (Fe-rich). Pellets were made from the clay powders with die and hydraulic oil press at a maximum load of 5 tons and the load on the die was held 50 seconds to 1 minute. A multi-wavelength inVia Raman spectrometer (Renishaw Company) was used to measure the Raman spectra, using 532-nm excitation (green laser).

Result and discussion:

Raman spectra of clay minerals have bands between 170 and 710 cm^{-1} which are attributed to the SiO_4 and Al_2O_3 lattice. The bands between 840 and 925 cm^{-1} are due to bending vibrations of the structural OH bond [7]. These bands are clearer in montmorillonite and hectorite (Figure 1). Raman spectra of montmorillonite are characterized by three strong bands near 203, 419 and 709 cm^{-1}. The sharp Raman peak at 709 cm^{-1} is due to SiO_4 vibrations and the broader feature near 420 cm^{-1} has been assigned to Si–O–Si (Al) bending modes [6,8]. In Raman spectra of Montmorillonite (STx-1b) an amorphous carbon peak is observed at around 1112 cm^{-1} which may be due to CH bending or C—C bonds in hydrocarbons [9]. Palygorskite is hydrous Mg-enriched clay minerals. Below 700 cm^{-1} there are weak Raman bands around 180 and 258 cm^{-1} which are assigned to silicate sheet deformation [10], however it is complicated to identify the assigned peak due to strong fluorescence. The dominance of 1466 cm^{-1} might be caused by florescence. Hectorite is a trioctahedral smectites with absorption occurring near 688 cm^{-1} by the symmetric stretching modes of the SiO_4 tetrahedra. Another diagnostic pattern near 3681 cm^{-1} is assigned to the antisymmetric stretching modes of the SiO_4 tetrahedra. The band around 925 cm^{-1} occurs due to vibrations of the O–H–O groups [12].

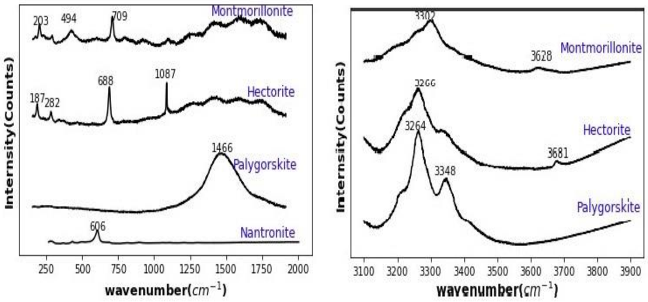

Figure 1. Raman spectra of Clay standards: nontronite, montmorillonite, hectorite, palygorskite in two regions: 100-1800 cm^{-1} and 3100-3900 cm^{-1} region.

Kaolinite exhibits three Raman active OH-stretching modes at 3621, 3652 and near 3696 cm^{-1}. The sharp band at 144 cm^{-1} with [12]. According to Kloprogge, the suggested assignment for this peak is the vibrational modes of Al_2OH of the Al–OH groups. [11]. The details of each band are provided in Table 1.

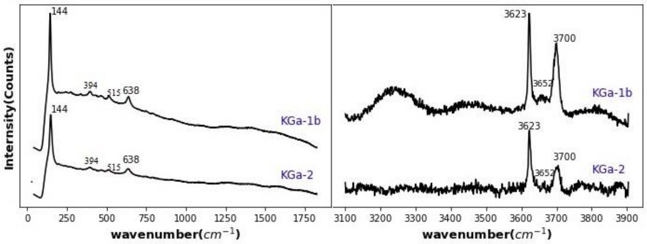

Figure 2. Raman spectra of Kaolinite: KGa-1b and KGa-2 in two regions: 100-1800 cm^{-1} and 3100-3900 cm^{-1} region.

Table 1. Peak positions (in cm^{-1}) of Raman spectra with assignments, chemical phases and FWHM.

Chemical phases	Raman bands (cm^{-1})	FWHM (cm^{-1})	Assignments
Kaolinite (KGa-1b)	144	30.58	O-Al-O symmetric bend?
	638	30.95	Si–O–Al translation
	3623	8.11	Stretching mode inner OH
	3652	-	Stretching mode inner surface OH
	3700	15.71	Stretching mode inner surface OH
Nontronite	430	17.60	H-bonding of OH–O
	606	26.35	-
Montmorillonite (STx-1b)	203	13.51	Structural lattice modes
	419	42.15	-
	709	14.92	Si–Ob–Si
	921	-	Al$_2$OH bending
	3302	30.30	-
	3628	-	-
Hectorite (SHCa-1)	282	14.1	vibration modes of the SiO$_4$ tetrahedra
	688	15.99	symmetric stretching modes of the SiO$_4$
	1087	6.19	vibration modes of the SiO$_4$ tetrahedra
	3680	-	O-H-O vibrations
Palygorskite (PFl-1)	172	5.71	O-Mg-O bend
	212	2.12	SiO$_4$ rotation

Conclusion: Raman spectroscopy is currently and will continue to be an important analytical technique for planetary exploration, including the identification and analysis of clay minerals on Mars. This work explores some of the Raman spectral features of wellknown clay standards for the Clay Minerals Society source clays. Raman active spectral features are in many cases different from the more familiar infrared features of clays. Though previous work has shed light on Raman spectroscopy of clay minerals, these applications are yet to be fully understood and further research is critical for understanding connections between clay structure, chemistry and Raman spectral response.

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