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Raman and reflectance spectroscopy of serpentinites and related hydrated silicates: Effects of physical properties and observational parameters, and implications for detection and characterization on Mars

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ABSTRACT

Raman and high-resolution reflectance spectrometers will play an increasingly important role in future surface exploration of Mars. We undertook a study of the 532 nm Raman and 0.35–2.5 μm reflectance spectral properties of a suite of terrestrial serpentinites and related rocks from the Southern Quebec Ophiolite Belt, Canada in order to: (1) determine what factors control the appearance of their Raman and reflectance spectra; and (2) enable more robust analysis of Raman and reflectance observational data for Mars to be provided by future Mars landed missions. We examined the effects of surface texture, presence of weathered surfaces, sample heterogeneity, grain size (whole rock versus powder) on Raman and reflectance spectra, and of integration time on the Raman spectra. The Raman spectra are characterized by strong induced fluorescence, however they usually still allow the strongest peaks of the major silicate phase (serpentine, tremolite-actinolite, or talc) to be identified. The different serpentine polymorphs (antigorite, chrysotile, lizardite) can also normally be identified by differences in some Raman peak positions. Only a few of the accessory phases are recognizable in the Raman spectra. There is no systematic difference relating the presence or absence of Raman peaks between whole rock and powder spectra. Increasing integration time can allow weak Raman peaks to be more confidently recognized. Reflectance spectra are dominated by the numerous absorption bands of serpentine or talc, making these phases easily identifiable, but also making accessory phases difficult to identify. Factors such as tetrahedrally-coordinated Fe^{3+}, mixed valence Fe (Fe^{2+}/Fe^{3+}), and the presence of octahedrally coordinated Fe^{2+} in serpentine can also be recognized. As in the Raman spectra, accessory phases are generally not identifiable in the reflectance spectra due to low abundance, weak absorption bands, or because their absorption bands are overlapped by the stronger hydrated silicate absorption bands. In the reflectance spectra the presence of magnetite can be recognized by a lowering of reflectance and a negatively-sloped spectrum. The presence of other opaque phases may be inferred from a lowering of reflectance. Reflectance spectroscopy is generally superior to Raman spectroscopy for identifying the presence of serpentine because of the aforementioned induced fluorescence seen in some of the Raman spectra. Raman and reflectance spectra do not always allow for identification of the same accessory phases, demonstrating their complementarity for analysis of hydrated silicate-dominated rocks.

1. Introduction

Raman spectroscopy is finding an increasing number of applications in planetary exploration, particularly for Mars. This is due to its ability to uniquely identify a wide range of minerals and organic molecules that are, or may be, present on, or relevant to, Mars (e.g., Jorge-Villar and Edwards, 2006; De Gelder et al., 2007; Alajtal et al., 2010; Edwards et al., 2013). Raman spectroscopy also has operational advantages, such as the ability to acquire data at variable stand-off distances (Sharma et al., 2003), in daylight (Misra et al., 2005), and to use time-gating to separate induced fluorescence from Raman excitation (Sharma, 2007).

Raman spectroscopy has a number of additional potential benefits for Mars exploration. These include the fact that it is usually non-destructive and is sensitive to molecular species that may be hard to detect using reflectance or emission spectroscopy (Smith and Dent, 2005). It is also of importance because of its ability to detect and discriminate minerals

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indicative of more clement conditions in the past, such as products of oxidation and aqueous alteration of igneous rocks (Wang et al., 1998). The importance of Raman spectroscopy for Mars surface exploration is highlighted by the fact that Raman spectrometers have been selected for flight on the 2020 European Space Agency (ESA) ExoMars rover: the Raman Laser Spectrometer (RLS) (Rull et al., 2013). The 2020 NASA Mars rover will also include two Raman-capable instruments: SuperCam (Maurice et al., 2015) and SHERLOC (Beegle et al., 2014).

Similarly, ultraviolet to near-infrared reflectance spectroscopy is also gaining increasing importance for Mars surface exploration. Three high spectral resolution reflectance spectrometers have been selected for flight on the ESA 2020 ExoMars rover: ISEM (Infrared Spectrometer for ExoMars): Korablev et al. (2014)); MA_MISS (Mars Multispectral Imager for Subsurface Studies): De Angelis et al. (2014); and MicrOmega: Pilorget and Bibring (2013). The NASA Mars 2020 rover will also include high spectral resolution reflectance spectroscopy capabilities with the SuperCam instrument with wavelength coverage from ~0.4 to 0.8 and ~1.1–2.6 μm (Clegg et al., 2015; Fouchet et al., 2015).

Identification and characterization of water-bearing minerals continues to be a high priority for future Mars missions (Mustard et al., 2013). This is due to many factors, including their possible association with astrobiology. Serpentinites represent one species of hydrated minerals that is of particular importance to astrobiology and Mars exploration. Their importance includes the fact that serpentinization from anhydrous precursors results in the production of hydrogen, which can sustain microbial communities (e.g., Kelley et al., 2001; Sleep et al., 2004; Kelley et al., 2005; Schulte et al., 2006; Cardace and Hoehler, 2009; Russell et al., 2010; McCollom and Seewald, 2013), and that methane which may be associated with serpentinization has tentatively been identified on Mars (e.g., Formisano et al., 2004; Krasnopolsky et al., 2004; Oze and Sharma, 2005; Mumma et al., 2009; Webster et al., 2015). Methanogens are commonly viewed as primitive organisms that would be relevant to searching for evidence of incipient primitive life forms on Mars (Woese, 1987; Ueno et al., 2006). Serpentinization can also result in the formation of mixed valence Fe species (Andreani et al., 2013; Greenberger et al., 2015), which provides a potential energy source for microbes. Areas where serpentinization is occurring are also commonly viewed as a favorable habitat for life to have evolved (e.g., Schulte et al., 2006; Lang et al., 2012; Muntener, 2010).

While the landing site of the NASA Mars 2020 rover is not yet determined, the short list includes two sites, Jezero crater and northeast Syrtis, where some combination of serpentine precursors (olivine), serpentinites, or phases associated with serpentinization (carbonates, talc-carbonate) are present (Ehlmann et al., 2008, 2010; Brown et al., 2010; Goudge et al., 2015; Bramble et al., 2017). As described more fully below, serpentines can be discriminated from other phyllosilicates, and serpentine polymorphs (antigorite, chrysotile, lizardite) discriminated from one another, on the basis of unique spectral features in the 0.3–2.5 μm range (e.g., King and Clark, 1989; Clark et al., 1990) Bishop et al., 2008a).

To date, four candidate landing sites have been recommended for the ExoMars 2018 rover: Oxia Planum 1, Mawrth Vallis, Hypanis Vallis West, and Aram Dorsum (LSSWG, 2014). The proposed Oxia Planum and Mawrth Vallis landing sites are characterized by extensive exposures of Mg/Fe phyllosilicates (likely saponite, nontronite and/or vermiculite) and other hydrated silicates (likely Al-rich clays such as kaolinite and montmorillonite), as well as hydrated silica, jarosite, and bassanite (Bishop et al., 2008b, 2013; Farrand et al., 2009; Loizeau et al., 2010; Wray et al., 2010). Serpentinite has also been identified in this region (Ehlmann et al., 2010). The mineralogy of the proposed Hypanis Vallis West landing site is not well-constrained. The proposed landing ellipse includes fan-shaped deposits of probable fluvial origin as well as impact and volcanic materials (Di Achille et al., 2006, 2007; Hauber et al., 2009). The proposed Aram Dorsum landing site is characterized by an inverted channel of probable fluvial origin, and various channel deposits with depositional fans/deltas. CRISM spectroscopic data show only limited evidence for poorly-constrained phyllosilicate outcrops (LSSWG, 2014).

We undertook a multifaceted examination of the Raman and reflectance spectroscopic properties of serpentinites for a number of reasons: their astrobiological importance, their presence on Mars, and the possibility that serpentinites may be encountered by the next generation of Raman and reflectance spectrometer-equipped rovers. Our investigation focused on examining the range of primary and accessory minerals that could be detected in serpentinites and related rock types using a 532 nm excitation source (the same wavelength as the ExoMars, 2018 Raman spectrometer and 2020 Mars rover SuperCam). We focused on how the following variables affect Raman spectra: surface texture, weathered surfaces, sample heterogeneity, grain size (whole rock versus powder), and integration time. We also looked at the relative capabilities of Raman versus reflectance spectroscopy.

2. The 2018 ExoMars and Mars 2020 Raman and reflectance spectrometers

2.1. The ExoMars RLS and Mars 2020 SuperCam and SHERLOC Raman systems

The planned ExoMars RLS incorporates an extremely lightweight, compact, energy efficient laser that will produce a beam with an output power of 300 mW (Rull et al., 2012). It will use a 532 nm laser to excite samples, and will cover a range of ~150-3800 cm^{-1}, with a resolution of ~6 cm^{-1} (Rull et al., 2012). It will produce irradiance between 0.8 and 1.2 kW/cm^2 (Rull et al., 2012). The laser spot size will be approximately 50 μm on the target, to be compatible with the sizes of individual grains that will be studied (<400 μm; Rull and Martinez-Frias, 2006; Rull et al., 2012). The Raman instrument should have the capability to auto-integrate, therefore each sample should be examined using optimal integration times which balance high integration times while avoiding detector saturation.

The Sample Preparation and Distribution System (SPDS) on the ExoMars lander will be used to introduce samples to the RLS, which is mounted on the rover deck. The SPDS incorporates a 2 m long drill which will be responsible for collecting rock and soil samples (Richter et al., 2013). Once the samples are obtained, they are transported to the Crushing Station where they will be reduced to a powder with a maximum grain size of 400 μm (Schulte et al., 2010). These powdered samples will be distributed to the Powder Sample and Dosing Distribution Center (PSDDC), where a specific amount of the sample (0.1 mL) is measured then distributed to a sample carousel in the Powder Sample Handling System (PSHS) (Schulte et al., 2010). A flattening tool will be used within the PSHS to prepare a flat surface for each powdered sample (Schulte et al., 2010).

The SuperCam Raman spectrometer on Mars 2020 willuse a frequency doubled 532 nm laser (10 Hz, 10 mJ/pulse) to collect Raman spectra up to 12 m from the rover (Clegg et al., 2015). Raman spectra will be collected from ~150 to 4200 cm^{-1} with a 0.67 mrad FOV and 10 cm^{-1} spectral resolution. Time gating will be used to separate Raman from fluorescence emissions (Clegg et al., 2015). The SHERLOC instrument (Scanning Habitable Environments with Raman & Luminescence for Organics and Chemicals) will illuminate samples with a 248.6 nm deep-ultraviolet laser at a spot size of <100 μm, along with contextual imaging, and record induced fluorescence and Raman excitation. It will operate over a 7 × 7 mm area (Beegle et al., 2014; Abbey et al., 2017).

2.2. The 2018 ExoMars and Mars 2020 rover reflectance spectrometers

The ExoMars 2018 rover will be equipped with three main passive reflectance spectrometers. The ISEM instrument is a narrow field of view (1°) mast-mounted spectrometer that measures reflectance spectra from 1.15 to 3.3 μm with <25 cm^{-1} spectral resolution (Korablev et al., 2014) and is boresighted with the PanCam imager. The Ma_MISS spectrometer