REACTIVE IRON MINERAL PHASES MAY PRESERVE ORGANIC CARBON ON MARS: IMPLICATIONS FOR RAMAN SPECTROSCOPY

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Introduction: Over 20% of organic carbon in sediments on Earth is bound to reactive iron mineral phases [1]. These reactive iron minerals occur as nanoparticulate and X-ray amorphous phases, which are challenging to characterize. On Mars, reactive iron mineral phases are abundant in sedimentary rocks and have been identified as iron-rich X-ray amorphous material in Gale crater with the Curiosity rover [2,3] and as nanophase iron oxides in Gusev crater with the Spirit rover and at Meridiani Planum with the Opportunity rover [4-7]. Reactive iron minerals are metastable and their presence indicates only a limited diagenetic overprint [8]. They therefore offer a high potential for the preservation of organic compounds as potential biosignatures. Both the Perseverance rover and the upcoming ExoMars Rosalind Franklin rover use Raman spectroscopy for mineral identification [9-11], and it is important that they can identify reactive iron mineral phases and distinguish them from their well-crystalline counterparts. In this study, we investigate Mars-relevant samples with both temperature-dependent Mössbauer spectroscopy and Raman spectroscopy. Low-temperature Mössbauer spectroscopy can identify reactive iron mineral phases [12,13] and can thus help to optimize Raman spectroscopy parameters to enable their characterization.

Methods: Mössbauer and Raman spectroscopy measurements were carried out on samples from a core of an active pockmark in the North Sea – The Scanner Pockmark. Pockmarks are circular depressions in the ocean floor, indicating fluid flow from a methane rich subsurface [14]. Whilst not formally identified on the Martian surface, pockmarks are morphologically similar to small craters so could be misidentified [15,16]. The occurrence of pockmarks on Mars could explain the controversial methane detected by various authors [16]. Mössbauer spectroscopy was used to quantify iron mineralogy and Raman spectroscopy used to quantify overall mineralogy and composition with results presented in this abstract.

Mössbauer Spectroscopy was carried out on a non-magnetic, brown nodule found at a depth of 1.64 cm. The sample was ground into a fine grey powder with a mortar and pestle. Approximately 100 mg of the powder was then placed into an acrylic sample holder which was subsequently placed into a Wissel transmission Mössbauer spectrometer (Wissel, Germany) at the University of Stirling. Spectra were collected at 4.2 K, 77 K and room temperature, with low temperatures achieved with a closed-loop helium gas cryostat (Ice-Oxford, UK). Spectral evaluation was carried out using the Voigt-based fitting routing of Recoil (University of Ottawa, Canada).

Raman spectroscopy was carried out on a second non-magnetic, brown nodule from the same depth as the nodule used for Mössbauer analysis. This nodule was similarly ground to a fine grey powder with a pestle and mortar. Analysis was carried out on the Exo-Mars Raman Laser Spectrometer simulator at the University of Leicester, UK [17].

Results: Mössbauer Spectroscopy identified nanophase ferric oxide (npOx) and Fe-phosphate doublets at room temperature which continue to be seen as the temperature decreases (Figure 1). Superparamagnetic goethite is identified at 77 K with a sextet identified as lepidocrocite appearing at 4.2 K (Figure 1).

Raman spectroscopy identified carbonate, quartz, phosphate, feldspar, anatase and haematite within the sample (Figure 2).

Discussion: Mössbauer spectroscopy is a powerful tool for the investigation of iron minerals but it is limited to iron-bearing mineral phases. Raman spectroscopy can identify a much greater range of minerals plus organic substances. Reactive iron minerals are opaque in visible wavelengths and therefore need a higher laser intensity to achieve good signal-to-noise for identification in Raman spectra. However, laser power is capable of rapid transformation of iron minerals, especially when poorly crystalline like the samples examined here [18]. Our comparison of Mössbauer and Raman data suggests that nanophase goethite and lepidocrocite were transformed into haematite by the Raman laser. Transformation to haematite can then cause further issues as the fluorescence of haematite can overwhelm the organic carbon signal at certain wavelengths [19]. A careful optimization of laser intensity and other instrument parameters is thus necessary to be able to identify reactive iron species. An accurate identification of reactive iron mineral phases is important for the Perseverance rover to be able to assess the biosignature preservation potential of samples under consideration for collection and subsequent return to Earth. It is equally important for the ExoMars rover where accurate knowledge of iron mineralogy is important to select the optimal operational mode for the MOMA instrument investigating organic carbon molecules [20]: The presence of iron minerals during pyrolysis can reduce the detecta-

bility of certain organic compounds, but this effect depends on the specific iron minerals present and is mitigated in the presence of clay minerals [21,22].
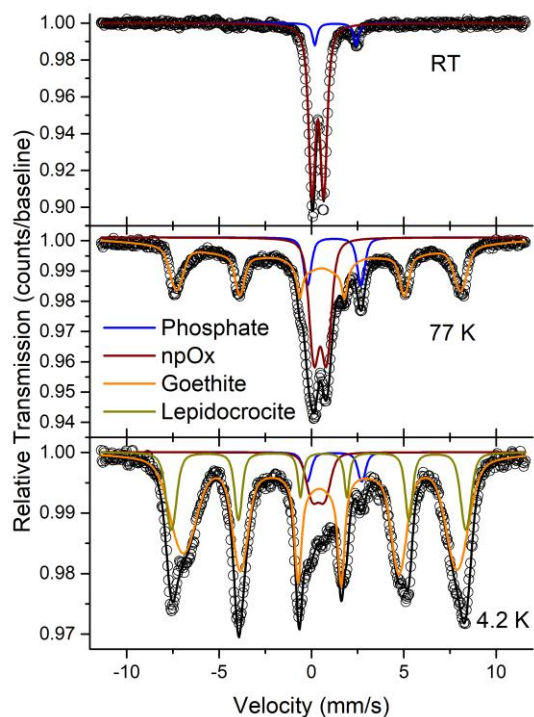
Figure 1: Mössbauer spectra taken at different temperatures with circles indicating data points
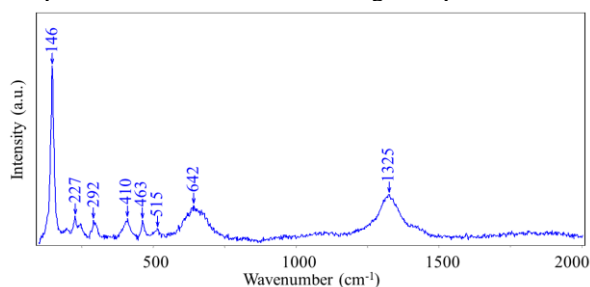
Figure 2: Raman spectrum showing peaks correlating to anatase (146, 515, 642 cm⁻¹) and haematite (227, 292, 410, 463, 1325 cm⁻¹)

Conclusions: Samples from an active pockmark in the North Sea have been analysed with Mössbauer and Raman spectroscopy. Differences in iron mineralogy between the 2 analytical techniques are observed. These differences can be explained due to transformation of the iron minerals by the laser of the Raman spectrometer.
This study highlights the need for caution to be taken when analysing poorly crystalline iron oxides with

Raman spectroscopy. This is especially important ahead of the launch of ESA's ExoMars rover Rosalind Franklin and results from NASA's Mars 2020 rover Perseverance begin to be released to the public as both rovers have Raman spectrometers onboard.

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