Vibrational Spectroscopy 87 (2016) 67–80

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Distinguishing in situ stromatolite biosignatures from silicification and dolomitisation using short wave, visible-near and thermal infrared spectroscopy: A mars analogue study

Sureyya H. Kose[a,*], Simon C. George[a], Ian C. Lau[b]

[a] Department of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia
[b] CSIRO, Australian Resources Research Centre (ARRC), 26 Dick Perry Avenue Kensington, WA 6151, Australia

ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 10 September 2016
Accepted 12 September 2016
Available online 13 September 2016

Keywords:
Infrared spectroscopy
Weathering
Mars
Pilbara
Stromatolites

ABSTRACT

The search for life on Mars has relied on infrared spectroscopy from orbit and in situ rovers to detect chemical signals akin to those found within stromatolites on Earth. Carbonate and hydrothermally altered mineral signals were detected on small rock units within the Nili Fossae region, and in small concentrations within the Gusev Crater region, but these minerals were likely a product of dolomitisation rather than an indicator of stromatolitic precipitation. To date, no studies have been undertaken to investigate the effect of weathering processes such as dolomitisation and silicification, which may obscure mineralogical signals that may be associated with stromatolites during in situ spectroscopic detection. This study investigates the capacity that short-wave, visible-near, and thermal infrared spectrometers have in detecting minerals in the oldest known and heavily weathered stromatolites of the Pilbara Craton, Western Australia. A diversity of mineral signals in stromatolitic samples can be distinguished from dolomitisation and silicification in even the oldest rock units, when fresh surfaces are scanned multiple times by a short-wave infrared capable spectrometer, with a minimum spectral resolution of 7 nm. It is expected that this approach will significantly inform and direct the interpretation of carbonate signals within the heavily weathered Noachian rock units on Mars.

1. Introduction

To date, the most extensive Mars analogue studies have been those undertaken by Brown et al. [1,2] where in situ PIMA II (Portable Infrared Mineral Analyser) and hyperspectral aerial scans were conducted over the Trendall locality stromatolites within the Strelley Pool Formation, in the Pilbara Craton of NW Australia. The findings from these studies indicate that carbonates could be detected by the hand-held PIMA II spectrometer, but not by aerial hyperspectral detectors. The aerial survey was conducted with the assumption that the stromatolite-hosting North Pole Dome area had minimal low grade metamorphism and a minimal weathering rind, either of which would obscure possible biogenic signals. Nevertheless, the principal minerals detected in the aerial survey were kaolinite, chlorite, talc, muscovite, and hornblende [1]. The findings demonstrated, at best, that these minerals provided a good indication of high magnesium lava flows (komatiites) and hydrothermal alteration 'hot spots', both suggested to be optimum environments for the emergence of life on Earth [1]. In recent years, trace amounts of carbonate have been detected in Martian dust and Martian meteorites [2]. Aerial observations by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and terrestrial observations by the Mars Exploration Rover (MER) Spirit have detected Mg-carbonate and Mg-phyllosilicate bearing rock units in the Nili Fossae region [3] and the Gusev crater region of Mars [4]. The Nili Fossae Mg-carbonates were interpreted by Brown et al. [2] to be partially dolomitised magnesite, and the Mg-phyllosilicates to be talc-carbonates that have been produced by hydrothermal alteration processes during an earlier, possibly warmer, more hydrous and CO_2 rich Martian environment. The emphasis within current Mars analogue research is that abiogenic processes produced the carbonates detected on the Martian surface, rather than the alternative hypothesis that the carbonates were precipitated by living organisms. It was noted, however, that the hydrothermal alteration processes that occurred on Mars are similar to those recorded within the Warrawoona Group rock units in the North Pole Dome area of the Pilbara Craton [2]. Importantly,

* Correspondence to: Department of Chemistry, Curtin University, WA 6102, Australia.
E-mail address: sureyya.kose@curtin.edu.au (S.H. Kose).

http://dx.doi.org/10.1016/j.vibspec.2016.09.007
0924-2031/

Mars carbonates detected in the Nili Fossae region are from the Noachian (4.1–3.7 Ga) period, the time equivalent of Earth's Archean period. Thus it is timely to consider the difficulty of detecting carbonate minerals in the Archean on Earth, as an analogue to inform and direct the interpretation of carbonate signals within the heavily weathered Noachian rock units on Mars.

The present study aims to determine the extent to which old age, weathering, or the depositional environment contributes to the ability to successfully detect carbonate signatures. If weathering adversely affects the detection of biologically-derived carbonate precipitates, a secondary aim is to determine which spectral detector would best distinguish between stromatolitic signatures and weathered minerals that may obscure evidence for biogenicity. In this study, stromatolite samples were taken from the 3.48 Ga Dresser Formation, which hosts the oldest known stromatolites, the 3.38 Ga Strelley Pool Formation which contains well preserved stromatolites, and the younger 2.7 Ga Tumbiana Formation which contains unambiguous and especially well preserved stromatolites. The Dresser Formation stromatolites were formed in a hydrothermal environment [5] similar to the age and environment of the Nili Fossae region of Mars. The Strelley Pool stromatolites were formed in a shallow marine environment [6,7] and the Tumbiana Formation stromatolites in a lacustrine environment [8,9].

The specific aims of this study were:

1. To obtain a range of stromatolite samples from three different environments and age groups (listed above) that are suitable to use as Martian analogue materials.
2. To determine the spectral and mineralogical diversity of the stromatolitic samples using Visible-Near-Short-Wave, Short-Wave, and Thermal Infrared spectroscopy (VNIR-SWIR, SWIR and TIR).
3. To assess whether the spectral signals are affected by various weathering processes by scanning both their fresh and weathered surfaces.
4. To determine which instrument is best for detecting carbonate and associated signals in weathered samples. Not only the instruments, but where their spectral range intersects will be compared. The PIMA II and the ASD FieldSpec3 both measure the SWIR region of the EM spectrum. To this end, the SWIR regions of the PIMA II and the ASD FieldSpec3 instruments will also be compared. A great difference in the results of the SWIR spectra from each instrument is not expected, however, particular SWIR minerals may manifest in one spectrometer than the other due to spectrometer strengths coupled with a mineral's mixed characteristics. We present the SWIR results for each instrument separately to account for this eventuality.

2. Spectroscopy – a background

Spectroscopy involves shining an energy source onto a target object and measuring the reflected or scattered electromagnetic waves (EM) or radiation. All objects have a unique spectral signature when absorbing, reflecting, or emitting EM waves. A mineral's unique spectral signature will depend on its chemical properties (e.g. how molecule vibrations behave when interacting with an incident EM source), structural arrangement (e.g. the crystal lattice structure of quartz), absence or presence of certain metal ions (usually $Fe^{2+/3+}$, Cr^{3+}, Cu^{2+}, $Ni^{2+,}$ Al), moisture content (OH stretching), grain size, colour, or hardness [10]. Rock forming minerals are particularly detectable in the infrared range of the EM spectrum. These include the Visible-Near Infrared (390–1300 nm), Short Wave Infrared (1300–2500 nm) and Thermal Infrared (6000–15000 nm) [10,11]. The spectral intervals used in this paper correspond with Australian geoscience standards. For readers outside the remote sensing community, the spectral interval equivalents are Visible (390–780 nm or 25640–12820 cm^{-1}), Near-Infrared (780–2500 nm or 12820–4000 cm^{-1}), the Short-Wave interval within the NIR range (780–1050 nm or 12820–9525 cm^{-1}), and the Mid infrared (2500–25000 nm or 4000–400 cm^{-1}). The chemical signatures most sought after when examining stromatolites for biogenicity are the bio-essential elements: carbon, nitrogen, sulphur, phosphorous, oxygen and hydrogen [12]. The minerals corresponding to the aforementioned chemical signatures are carbonates, such as calcite, ankerite, saponite, siderite, biologically metabolized sulphides (pyrite), iron oxides (Haematite) and iron oxyhydroxides (goethite) [5,13,14].

Infrared spectroscopy can utilise the infrared range of the electromagnetic spectrum, the sun, or halogen bulbs as a light source. In recent decades, a variety of spectrometers have been utilised in Mars analogue studies. Raman spectroscopy, which is able to utilise a range of light sources including near ultraviolet lasers [15], has been useful in finding bio-essential signals within the Strelley Pool Formation stromatolites. These signals include sulphur in association with pyrite, and carbon, nitrogen and phosphorous enrichments [16–19,14]. SWIR spectroscopy, in particular, has detected carbonates (calcite and siderite) – key indicators to support a biological origin of stromatolites – from samples at the Trendall locality (also part of the Strelley Pool Formation) and the Dawn of Life Trail [1,20,5]. The Dresser Formation stromatolites have yielded similar results to the above with the application of hyperspectral imaging (infrared spectroscopy using a combination of VNIR-TIR Infrared bandwidths). The spectral scans were performed on drill core samples taken from approximately 4 km south of the Buick locality stromatolites [21]. Iron chlorites, magnesium chlorites, calcite, dolomite, ankerite and siderite carbonates were detected. A drill core study of stromatolites from the Meentheena member of the Tumbiana Formation yielded the identification of cell-like organic globules closely related to aragonite, a biogenic carbonate mineral [22].

2.1. Stromatolites

Stromatolites offer a unique insight into how life developed on Earth, and their old age and scarcity makes them both highly significant and highly contentious [23]. The application of novel techniques, such as Raman and infrared spectroscopy, has provided strong support for the biogenic hypothesis, with many researchers agreeing on the biogenicity of Archean stromatolites [16,6,24,1,25–29]. Raman and infrared instruments have been recognised as important for studying organic carbon in stromatolites [30]. For example, CRISM is being used by the Mars Reconnaissance Orbiter as it searches for mineralogical indications of past and present water on Mars, and a Raman capable spectrometer (SHERLOC) will be installed on the rover for the 2020 mission to Mars which will search for signs of life [31,32]. There is much interest in searching for stromatolites on Mars, as they may be the Martian equivalent of the ancient, heavily weathered and contentious Archean stromatolites on Earth.

3. Instrument characteristics

3.1. PIMA II spectrometer

The PIMA II system developed by Integrated Spectronics Pty Ltd was utilised in this study. The PIMA II and software were provided by the CSIRO Australian Resources Research Centre (ARRC) in Kensington, Perth, Western Australia. The equipment included a personal laptop with PIMA SP Acquisition Version 2.2 software. The PIMA II is a short-wave infrared spectrometer that can detect