



Assessment of Raman spectroscopy as a tool for the non-destructive identification of organic minerals and biomolecules for Mars studies

J. Jehlička^{a,*}, H.G.M. Edwards^b, P. Vitek^a

^a Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Prague, Czech Republic

^b Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK

ARTICLE INFO

Article history:

Received 13 March 2008

Received in revised form

5 May 2008

Accepted 13 May 2008

Available online 27 May 2008

Keywords:

Organic minerals

Mars

Raman spectroscopy

Evenkite

Idrialite

Oxalates

Terpenoids

Mellite

Fichtelite

Hartite

Hoelite

Kladnoite

β -Carotene

ABSTRACT

Several characteristic geological features found on the surface of Mars by planetary rovers suggest that a possible extinct biosphere could exist based on similar sources of energy as occurred on Earth. For this reason, analytical instrumental protocols for the detection of biomarkers in suitable geological matrices unequivocally have to be elaborated for future unmanned explorations including the forthcoming ESA ExoMars mission. As part of the Pasteur suite of analytical instrumentation on ExoMars, the Raman/LIBS instrument will seek elemental and molecular information about geological, biological and biogeological markers in the Martian record. A key series of experiments on terrestrial Mars analogues, of which this paper addresses a particularly important series of compounds, is required to obtain the Raman spectra of key molecules and crystals, which are characteristic for each biomarker. Here, we present Raman spectra of several examples of organic compounds which have been recorded non-destructively—higher *n*-alkanes, polycyclic aromatic hydrocarbons, carotenoids, salts of organic acids, pure crystalline terpenes as well as oxygen-containing organic compounds. In addition, the lower limit of β -carotene detection in sulphate matrices using Raman microspectroscopy was estimated.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Investigations of the Martian surface by the NASA MER rovers *Opportunity* and *Spirit* confirmed the presence of mineral phases which are likely to originate in liquid water including sulphate minerals and haematite (Squyres et al., 2004; Squyres and Knoll, 2005; Wang et al., 2006). It is generally supposed that at some period in the Martian history, there were conditions suitable for sustaining the presence of liquid water, whether this be surface standing water or groundwater or as subsurface aquifers. Liquid water is viewed as a key prerequisite for evolving life, thus at least some regions on Mars may have been considered favourable for life sustenance for some periods of time in the Martian history. For various reasons, Mars has been identified as a prime target in the Solar System to search for evidence of life, extant or extinct, and one of these is its proximity to Earth, making it a desirable target for remote robotic missions. Within the payload designed by ESA

and NASA for future missions focusing on Mars's astrobiology, Raman spectroscopy will be a key non-destructive analytical tool (separately and in combination with LIBS or fluorescence) for the *in situ* identification of both organic and inorganic compounds relevant to life detection on the Martian surface or near subsurface. Therefore, it is important to perform a series of Earth-based Raman spectroscopic studies of some key samples, where organic compounds reflecting biological activity can be recognized within the geological record. In this respect, because of the harsh conditions that now pertain on Mars and that have been predicted to have existed there for some time, the analytical protocols for the detection of biomolecules for the recognition of past or present life must involve not only major biomolecules such as chlorophyll, carotenoids and the anti-desiccative and photoprotective suites of complex organic molecules synthesized by organisms as part of their survival strategies, but also the decomposition and degradation products of these molecules as identified in the record of terrestrial analogues.

Investigations of endolithic communities from extreme habitats on Earth have demonstrated that Raman spectroscopy is an excellent tool to detect various types of biomolecules that have been produced by particular microorganisms as part of their

* Corresponding author. Tel.: +420 2 2195 1503.
E-mail addresses: jehlicka@natur.cuni.cz (J. Jehlička),
H.G.M.Edwards@bradford.ac.uk (H.G.M. Edwards).

survival strategy in these extreme environments (see Wynn-Williams and Edwards, 2000a, b; Edwards et al., 2004, 2005a, b, c; Villar et al., 2005; Villar and Edwards, 2006). Photoprotective pigments provide an important group of such biomolecules which are produced as a response to harmful UV radiation and act as UV-screening compounds (parietin, scytonemin, for example), or indirectly as antioxidants (carotenoids) to quench the reactive oxygen species responsible for cellular damage; for a detailed review, see Edwards et al. (2005a). The recent discovery of evaporitic rocks on Mars is not the only evidence of liquid water in the Martian geological history. Brines or evaporites may also be suitable habitats for various halophilic (osmophilic) organisms or provide the last refuge for extinct life (Mancinelli et al., 2004). Recently, Marshall et al. (2007) showed that resonance Raman spectroscopy is a powerful tool for the identification of carotenoids in halophilic archaea.

Raman microspectroscopy permits us to obtain information which is not easily obtained by other analytical methods. Its advantage consists in the possibility of evaluating the spectral characteristics non-destructively, using an objective lens of an optical microscope. This allows the identification of individual parts of complex geological materials, organic compounds in the neighbourhood of minerals, at the interfaces between minerals and within micrometric inclusions in inorganic or organic minerals. The spatial resolution of the majority of Raman microspectrometers is in practice about 2 μm . When using 1064 nm lasers for near-infrared (NIR) Fourier transform (FT) Raman spectroscopic studies without a microscope, a particular advantage consists especially in the strong reduction of fluorescence emission from many organic materials for which the Raman spectra are too weak to be registered by using 466, 532, 633 or 785 or 852 nm lasers in the presence of strong background fluorescent emission from the organic materials (Edwards et al., 2003). The non-destructive microanalytical advantage of Raman spectroscopy is particularly useful for the assessment of the biomolecular information that is expected to accrue from the interrogation of a planetary surface and subsurface geology by remote rover laboratories because of the heterogeneity of the specimens available. In this respect, although here we are dealing with pure crystalline organic minerals, the sampling footprints are of the order of microns in diameter, which is similar to those of naturally occurring residues of degraded organics in niche areas that have been reported in terrestrial geological systems (Edwards et al., 2003, 2005c). In contrast, the preliminary experiments with carotene/gypsum mixtures reported here address the sensitivity of the detection of Raman spectral signatures of a biomolecular marker “impurity” in a sulphate mineral deposit.

Raman spectroscopy has also been used to identify several highly specific structural units and functional groups contained within complex mixtures of fossil resins (Brody et al., 2001; Winkler et al., 1998; Jehlička et al., 2004). Even if Raman spectroscopy does not allow the complete identification of all chemical species contained in these complex materials, as gas chromatography–mass spectrometry (GC–MS) generally does, significant bonds and functional groups nevertheless can be identified—and with the added advantage of preservation of the specimen without prior treatment. IR and Raman spectra of natural oxalates (Edwards et al., 1997; Frost and Weier, 2003) from different environments have been obtained and interpreted. Edwards et al. (1992, 1997) and Prieto et al. (2000) studied the occurrence of oxalates at the biogeochemical interface between rocks and lichens by FT-Raman spectroscopy. Humboldtine (ferrous oxalate), glushinskite (magnesium oxalate), moolooite (copper oxalate), natroxalate (sodium oxalate) and oxammite (ammonium oxalate) are less common natural oxalates. Their

Raman spectra have been measured and interpreted recently by Frost and Weier (2003) and Frost (2004). More recently, the Raman spectra of the organic minerals idrialite evenkite, kladnoite, hoelite were obtained and interpreted (Jehlička et al., 2006a, b, 2007a, b), and a comprehensive review of the application of Raman spectroscopy to study organic minerals is given by Jehlička and Edwards (2008) (Table 1).

The primary goal of this paper is to evaluate Raman spectroscopy for the detection of organic minerals and key biomolecules with high relevance for exobiological studies on Mars and potentially elsewhere. Here, we are not focussing on water and OH groups in minerals, which is the major theme of other research groups. In this paper, we present two different approaches of Raman spectroscopic analysis to detect biogenic compounds, relevant for Mars’s astrobiology. First, crystalline organic minerals originating from biogenic processes, and which have been subjected to various degrees of degradation in the terrestrial environment, were investigated using a bench Raman microspectrometer. Second, the Raman spectroscopic study of β -carotene in experimentally prepared mixtures with gypsum was performed in order to evaluate the potential of Raman microspectroscopy to detect this biomarker in low content in an evaporitic matrix, which is considered as a likely habitat for possible Martian biota (Rothschild, 1990; Mancinelli et al., 2004).

Table 1
Review of the main Raman bands of organic minerals

Mineral	Composition	Main Raman bands
Evenkite	C ₂₄ H ₅₀	2883 , 2848, 1464, 1441 , 1295, 1171, 1133, 1062 cm ⁻¹
Karpatite	C ₂₄ H ₁₂	3042, 3060 , 1628, 1618, 1596, 1449, 1437, 1368, 1351, 1340, 1221, 1026 cm ⁻¹
Idrialite	C ₂₂ H ₁₄	3049, 2891, 1617 , 1579, 1393 , 1375, 1367, 1301, 1017 , 825, 752 , 710 , 642, 611, 579 cm ⁻¹
2,3-Benzothiophene	C ₈ H ₆ S	3050 , 1560 , 1498 , 1320, 1020 , 800 , 706 , 492, 220 cm ⁻¹
Dibenzothiophene	C ₁₂ H ₈ S	3076 , 3053 , 3023, 2993, 2628, 2618, 1597 , 1556, 1317 , 1309, 1232, 1132, 1023 , 701 , 495, 407, 284, 215 cm ⁻¹
Whewellite	Ca(C ₂ O ₄)·H ₂ O	3248, 1630, 1491, 1463 , 896, 866, 503, 193, 139 cm ⁻¹
Mellite	Al ₂ C ₆ (COO) ₆ ·16H ₂ O	3250, 1550, 1469 , 1390, 1344, 1226 , 812, 774, 327, 245, 180 , 164, 120 cm ⁻¹
Mellitic acid	C ₆ (COOH) ₆	1676 , 1427, 1333, 1199, 1192, 737, 172, 104 cm ⁻¹
Fichtelite	C ₁₉ H ₃₄	2864 , 1442 , 1302, 1247 , 836, 717 and 533 cm ⁻¹
Hartite	C ₂₀ H ₃₄	2942 , 2921 , 1480, 1441 , 1310, 1287, 1208 , 1145 , 1041, 792 , 729 , 693, 527 cm ⁻¹
Hoelite	C ₁₄ H ₈ O ₂	3076, 1665 , 1597, 1317, 1176 , 1146, 1030 , 767, 475, 238 cm ⁻¹
Kladnoite	C ₆ H ₄ (CO) ₂ NH	3085, 3046, 1755 , 1606, 1165, 1142, 1012 , 743 , 641, 549, 260, 200, 163 cm ⁻¹

Strong Raman bands are shown in bold.

Download English Version:

<https://daneshyari.com/en/article/1782291>

Download Persian Version:

<https://daneshyari.com/article/1782291>

[Daneshyari.com](https://daneshyari.com)