



Infrared spectroscopy of microbially induced carbonates and past life on Mars



Armando Blanco^{a,*}, Vincenzo Orofino^a, Marcella D'Elia^a, Sergio Fonti^a, Adelaide Mastandrea^b, Adriano Guido^b, Franco Russo^b

^a Department of Mathematics and Physics "Ennio De Giorgi", University of Salento, Lecce, Italy

^b Department of Earth Sciences, University of Calabria, Rende (CS), Italy

ARTICLE INFO

Article history:

Received 6 September 2012

Revised 8 May 2013

Accepted 18 May 2013

Available online 1 June 2013

Keywords:

Exobiology

Mars

Spectroscopy

ABSTRACT

A number of evidences, as the past presence of water, a denser atmosphere and a mild climate, suggest that on early Mars environmental conditions should have been favourable to the emergence of life. Therefore, if life actually developed on Mars a few hundreds of million years ago, or even more recently, some biomarkers may still be present.

In several previous papers, based on laboratory analysis, we have investigated the modifications induced by thermal processing in the mid-infrared spectra of carbonate samples, in the form of fresh shells and fossils of different ages, skeletal remains of already complex terrestrial life, whose biotic origin is not questionable. In this way we have been able to develop a spectroscopic method for discriminating biotic samples from their abiotic counterparts.

In this work we show that our method can be successfully applied also to microbialites, i.e. bio-induced carbonates deposits, and particularly to stromatolites, the laminated fabric of microbialites, some of which are among the most primitive and oldest traces of biological activity on Earth. This result is of valuable importance since such primitive living organisms can be considered good analogues for putative martian life forms.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

1.1. Scientific background

A great diversity of geomorphological features (Masursky et al., 1977; McCauley, 1978; Carr, 1981, 1996; Goldspiel and Squyres, 1991; Forsythe and Blackwelder, 1998; Cabrol and Grin, 1999; Malin and Carr, 1999; Malin and Edgett, 2000; Craddock and Howard, 2002; Mangold et al., 2004; Ansan and Mangold, 2006) together with the recently studied Mars mineralogy (Christensen et al., 2004; Klingelhöfer et al., 2004; Bibring et al., 2005, 2006; Gendrin et al., 2005; Poulet et al., 2005; Loizeau et al., 2007; Mustard et al., 2008; Wray et al., 2009) are consistent with a scenario where ancient Mars hosted aqueous environments in a variety of geological settings, including impact-induced hydrothermal systems (Newsom, 1980; Gulick and Baker, 1989, 1990; Gulick, 1998; Marzo et al., 2010). This scenario suggests that environmental conditions on early Mars could have been similar to those prob-

ably existing when life emerged on Earth. This has important implications for Mars habitability during the first billion years and on the possibility that simple forms of life could have developed on the surface or in the underground of Mars in the first part of its history (McKay and Stoker, 1989), just as they originated on primitive Earth (Schopf, 1993; Mojzsis et al., 1996).

In upcoming years various space missions will investigate the habitability of Mars and the possibility of extinct or extant life on the planet. A strong impulse in this direction has been given by the recent observations of atmospheric methane (Krasnopolsky et al., 2004; Formisano et al., 2004; Geminale et al., 2008; Mumma et al., 2009; Fonti and Marzo, 2010). Since at present there is no obvious evidence of local volcanism, the most plausible origin of this methane appears to be either the serpentinization of olivine or the presence of methanogenic bacteria, both of which require the presence of a significant subsurface reservoir of liquid water.

On Earth, one of the most common approaches in the search for evidence of fossil life is the identification and characterization of biomarkers linked to organic compounds (Guido et al., 2007, 2011; Preston and Genge, 2010; Preston et al., 2011), although strongly limited by contaminations problems. These biomarkers can be preserved for billions of years, under favourable circumstances, and they provide very important insights into the early

* Corresponding author. Address: Department of Mathematics and Physics "Ennio De Giorgi", University of Salento, C.P. 193, Lecce, Italy. Fax: +39 0832 297505.

E-mail address: Armando.blanco@unisalento.it (A. Blanco).

evolution of life on Earth (e. g. Summons et al., 1999; Brocks et al., 2003). If life was once present on Mars, biomarkers may still exist. However, great care should be taken to distinguish them from meteoritic organic compounds (Benner et al., 2000). In this context, we propose to consider the potential of biotic inorganic compounds (biominerals), since the probability of finding traces of biological activity would certainly be higher if the search is directed towards inorganic materials whose origin can be traced back to some form of life. This is the case of some terrestrial living organisms which are able to produce mineral matrices in the so called biomineralization process (Lowenstam, 1981; Mann, 1983, 2001; Perry et al., 2007; Dupraz et al., 2009; Riding, 2011).

Calcium carbonate minerals (CaCO_3) are particularly interesting, because they can be produced either by abiotic processes or by biologically induced or controlled mineralization (Mann, 2001). Many living organisms on Earth, both prokaryotes and eukaryotes, are able to biomineralize calcite or aragonite and, in fact, the most primitive terrestrial evidence of life are biomineralized carbonates (Schopf, 1993; Westall et al., 2004). On the other hand, it is well known that carbonates are also produced by chemical precipitation following different processes not related to the presence of any life form (Wilkinson and Given, 1986).

Until recently, only a very low percentage of carbonates has been detected in bright martian dust (Bandfield et al., 2003; Boynton et al., 2009; Palomba et al., 2009) and meteorites (Romanek et al., 1994). However, recent findings are demonstrating that carbonates can be more widespread on the planet than previously thought. Ehlmann et al. (2008) found layered sedimentary carbonates overlying olivine deposits near the Isidis Basin, in the Nili Fossae Region. Morris et al. (2010), using the rover Spirit, have identified outcrops rich in Mg–Fe carbonate (16–34 wt%) in the Columbia Hills of Gusev crater with a composition similar to the average composition of the carbonate globules in martian meteorite ALH 84001. Michalski and Niles (2010) have found spectral evidence for deep crustal carbonates rocks exposed by meteor impacts on Mars. These last deposits, that have been buried and metamorphosed, may represent some of the most ancient sedimentary rocks on Mars and also in the entire Solar System. Alternatively, they may be evidence for deep-seated hydrothermal activity in a habitable subsurface environment. In any case, the presence of carbonates deposits, probably precipitated from carbonate-bearing solutions, implies that neutral-to alkaline waters existed at the time of their formation (Kahn, 1985; Schaefer, 1990; Fanale et al., 1992; Ehlmann et al., 2008).

1.2. Previous work and motivations

Martian carbonates could have also been produced, at least partially, by biotic processes in the hypothesis that primitive forms of life have been present on the planet.

In particular, on Earth the polymorphs of CaCO_3 , aragonite and calcite, are produced by abiotic processes as well as by biological activity. According to Mackenzie (1970), when aragonite (a metastable phase of CaCO_3 frequently present in mollusc shells) undergoes heat treatment, an endothermic transformation into calcite (the stable state of CaCO_3) occurs. Then, after further heating, calcite decomposes into solid calcium oxide (CaO) and gaseous carbon dioxide (CO_2).

The latter transformation is complete at 800–1000 °C (Stalport et al., 2005, 2007), but the temperature at which it starts depends on the biotic or abiotic origin of the sample. In the case of recent biominerals, heating at 485 °C for 3.5 h is sufficient to start altering their chemical and/or physical properties, while for minerals of abiotic origin higher temperatures are necessary (see Orofino et al., 2007, 2009, for details).

Fig. 1 shows the transmission spectrum, obtained by Orofino et al. (2007), of a sample of CaO grains, supplied by Sigma–Aldrich Co., and the reference spectra of particulate samples of calcite and aragonite obtained by Salisbury et al. (1991). Orofino et al. (2007, 2009) have studied the effects of thermal processing on the mid-infrared spectra of different samples, from fresh shells to fossils of different ages.

To study the above mentioned transformations Orofino et al. (2007, 2009) performed IR transmission spectroscopy in the range 2000–370 cm^{-1} , focusing their attention mainly on the last part of the spectra (800–370 cm^{-1}). These authors have monitored the decomposition process undergone by all the samples, comparing the spectra taken before and after heating treatment at 485 °C for 3.5 h.

Fig. 2 reports, as an example, the spectra obtained by Orofino et al. (2009) before and after such a treatment for a fresh shell (*Tellina exigua*). It is possible to infer that the sample, before the thermal treatment (solid line) is composed of aragonite, due to the presence of the features at about 1450 cm^{-1} , 1080 cm^{-1} , 870 cm^{-1} and a double peak at 700 cm^{-1} , characteristic of this mineral. The dotted line shows the spectrum obtained for the sample thermally processed at 485 °C. The transformation from the metastable form of aragonite to the more stable form of calcite is indicated by the loss of the feature at 1080 cm^{-1} and of the doublet at 700 cm^{-1} , where it can be observed, instead, a single transmittance minimum. In addition, the ongoing decomposition of CaCO_3 into CaO (and CO_2) can be deduced by the weakening of the bands at 1450 and 870 cm^{-1} and, mainly, by the consistent decrease in transmittance below 800 cm^{-1} , due to the onset of the broad band centred at 330 cm^{-1} , characteristic of CaO (Farmer, 1974), partially shown in Fig. 1.

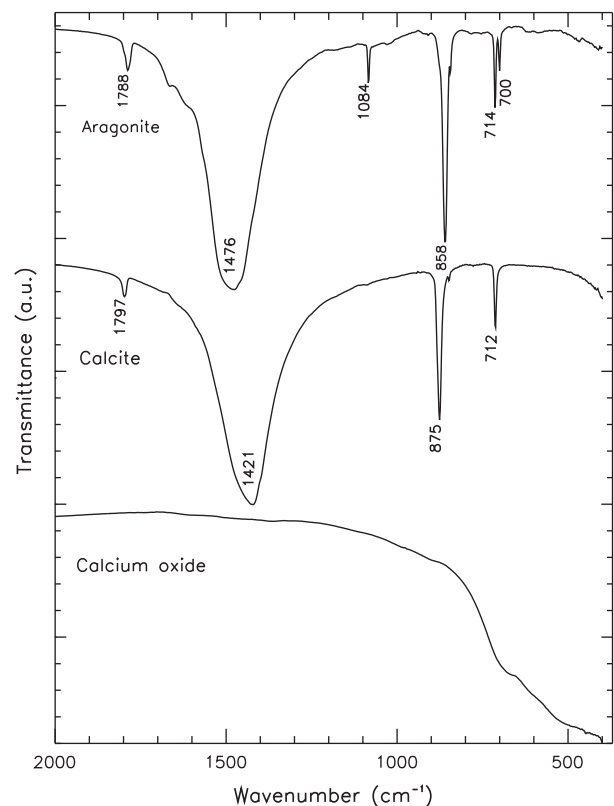


Fig. 1. Reference spectra of aragonite and calcite (data from Salisbury et al., 1991) and pure CaO grains analyzed in our laboratory. The spectra have been arbitrarily scaled for sake of clarity.

Download English Version:

<https://daneshyari.com/en/article/10701289>

Download Persian Version:

<https://daneshyari.com/article/10701289>

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