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Physical characterization of biominerals of Martian interest

A. Blanco, M. D'Elia, D. Licchelli, V. Orofino, S. Fonti

Physics Department, University of Lecce, Via Arnesano, 73100 Lecce
e-mail: armando.blanco@le.infn.it

Abstract. In order to obtain mineralogical information and to determine if life ever existed on the surface of Mars, next space missions have the purpose to perform *in-situ* analyses or recover samples of the Martian ground, and to bring them back to Earth. The aim is determining the mineralogical and chemical composition of these samples for studying the Martian geology and possible past or present biology. In this framework, laboratory research on biotic and abiotic minerals of exobiological interest can allow to characterize possible discriminating factors useful to distinguish the biological origin from the mineral one. We have investigated the physical properties of calcium carbonate ($CaCO_3$), which could be expected on Mars. The polymorphs of $CaCO_3$, aragonite and calcite, are interesting because on Earth these compounds are produced by abiotic process as well as by biological activity. We performed infrared transmission spectroscopic analyses aimed to examining the behaviour after heating biotic and abiotic particulate samples composed of calcium carbonate (mineral, fresh biotic and recent fossil aragonite), in order to discriminate their origin. Here we present the results of our spectroscopic and thermal studies focused also on carbonates linked to primitive terrestrial living organisms (fresh stromatolites) to understand whether and how the different biomineralization can influence the structure and composition of the samples.

Key words. exobiology – Mars – spectroscopy

1. Introduction

The environmental conditions on Mars may have been Earth-like (Carr, 1996). Observations show now a cold and dry planet with a very thin atmosphere and no liquid water on the surface. However, geomorphological evidences indicate that liquid water once was on the Planet and therefore simple forms of life could have developed on the surface or in the underground (McKay and Stoker, 1989).

The future *in-situ* and sample-return space missions have the aim to determine whether life ever existed on Mars, to characterize and study in detail the climate and the geology of the planet, and to prepare for human exploration.

In this framework Cabane et al. (2001) have proposed the SAM (Sample Analysis at Mars) experiment, devoted to *in-situ* analyses of the Martian soil for the next NASA Mars Science Laboratory, to be launched in 2009. One important part of this experiment has the aim to search, on the surface and underground, for traces of a past prebiotic chemistry and, op-

Send offprint requests to: A. Blanco

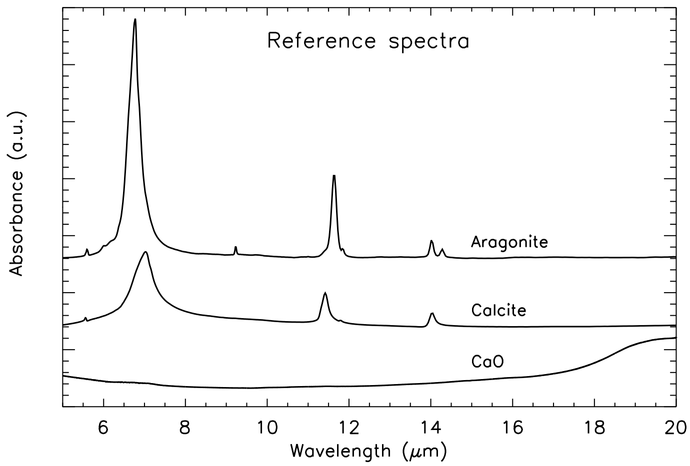

Fig. 1. Reference spectra: abiotic aragonite and calcite (data from Salisbury et al., 1991) and pure CaO grains analysed in our laboratory. In this figure, as well as in all the following figures, the spectra have been arbitrarily scaled for sake of clarity.

timistically, for extant life. A mass spectrometer (MS) associated to a gas chromatograph (GC) will be used as detector to differentiate between abiotic minerals and biominerals, by Differential Thermal Analysis (DTA).

Planning the scientific instruments for *in-situ* analyses and for experiments on the possible specimens of sample-return missions requires preliminary laboratory studies able to test the proposed techniques on terrestrial mineral samples that are analogous to the Martian ones.

Waiting for the final confirmation of the presence of carbonates on Mars, which may have important implications regarding the possibility that life developed there, we studied a mineral that may have either biotic or abiotic origins: aragonite, a polymorph of calcium carbonate ($CaCO_3$). We performed transmission spectroscopy, using a FT-IR spectrometer, in the infrared wavelength range (2-25 μm) focused on examining results of different thermal treatments starting from tested temperatures in DTA experiments (420°C, 485°C and other not shown in this work). As a matter of fact, an endothermic transformation occurs from the metastable aragonite to the more stable form of calcite (another polymorph of $CaCO_3$) and then, at higher temperatures, from calcite into solid calcium oxide (CaO) and gaseous carbon dioxide (CO_2).

Fig. 1 reports the reference spectra of aragonite and calcite (Salisbury et al., 1991) and a laboratory spectrum of pure CaO.

We have also used an optical microscope and a Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray Spectrometer (EDX), in order to morphologically and compositionally characterize the samples.

2. Measurements and results

Sample preparation, thermal treatments and types of measurements are described in Blanco et al. (2005) and in Orofino et al. (2006). Blanco et al. (2005) demonstrated that the spectroscopy and DTA should be helpful in distinguishing minerals from recent biominerals. Comparing the infrared spectra of recent biomineral aragonite and crystals of mineral aragonite, it is evident that the thermal processing at 420°C and 485°C induces different physical changes depending on mineral or biological origin of the samples; as a matter of fact, the process of transformation is faster for ”recent" biotic samples compared to the abiotic mineral.

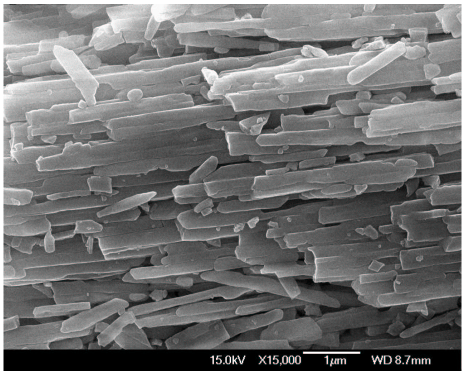

Fig. 2. Aligned crystal of aragonite in an Oligocene fossil.

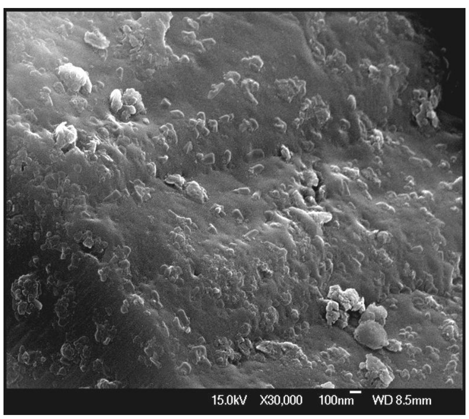

Fig. 3. Mineral aragonite grain morphology.

It would be unreasonable, however, restricting the laboratory experiments to modern biotic samples because, if water and life existed in the past on the surface of Mars, it is more likely to find ancient living forms. For this reason, we studied aragonite fossils dating from Oligocene (23-30 million years ago).

It is known that the organic macromolecules control crystal growth and orientation and we verified that the fossilization process, in the considered samples, did not modify the structure of the biominerals which maintain their microscopic characteristics. Looking at the morphology of analysed fossil biominerals with a Scanning Electron Microscope, it is evident that the crystals are arranged in complex architectures compared with the compact structure of the mineral crystals (Fig. 2 and Fig. 3 respectively). Obviously, SEM analysis is not sufficient to distinguish the biotic samples from the abiotic ones but, in this case, this technique gave us a characterization of the analysed fossil biominerals that helped to distinguish the different physical properties.

The aragonite fossils (*Ampullinopsis crassatina* and *Cerithium sp.* dating back 23-30 million years) were collected in a layer of fossil clay. The very specific environmental conditions allowed preserving the original structure of aragonite so that spectroscopic analysis before the heat treatment shows the characteristic features of this mineral (compare the "T ambient" spectrum in Fig. 4 with that of aragonite in Fig. 1).

After heating at 420°C, the fossil biotic samples change from the metastable form of aragonite to the more stable form of calcite ("T=420°C" spectrum in Fig. 4 shows the same spectral features of calcite in Fig.1). At 485°C the transformation process from $CaCO_3$ to CaO is activated via CO_2 release from the sample; as a matter of fact, looking at the "T=485°C" spectrum in Fig. 4, it is evident the formation of the CaO band that has its maximun at about 30 μm (see CaO spectrum in Fig. 1). As indicated by the spectra, the thermal processing of fossil aragonite induces the same behaviour of "recent" biotic aragonite (Blanco et al., 2005; Orofino et at., 2006). In fact, both fresh and fossil analysed shells have spectra differing considerably from those of the correspondent abiotic specimens heated at the same temperatures. This means that, also in the case of biomineral fossil aragonite, the transformation process takes place at lower temperatures. An explanation could be that the rapid development of the crystalline structure under biotic conditions, makes it less resistant than the abiotic mineral. We note that the fossilization process did not modify, from this point of view, the physical characteristic of the considered biomineral so that the infrared spectroscopy

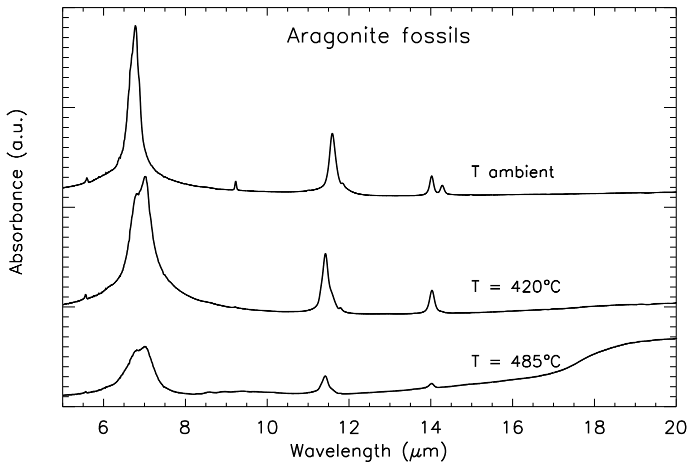

Fig. 4. Spectra of fossils of aragonite (*Ampullinopsis crassatina* and *Cerithium sp.* fossils have the same behaviour) before and after processing at 420°C and 485°C.

is still able to differentiate between the analysed biotic and abiotic samples (Orofino et at., 2006).

Since on Earth there are microfossils almost four billion years old, life must have appeared within one or two hundred million years after Earth cooled enough to host liquid water. Life may have developed readily, perhaps inevitably, given the physical and chemical conditions on the planet. Such conditions could have occurred also on Mars, before it dried and froze. If Mars was once wet and warm, with seas and hydrothermal vents present in some areas of its surface, then we might hope to find primitive life form, particularly in such lacations (McKay and Stoker, 1989).

On Earth, stromatolites are the oldest known fossils, dating back more than 3 billion years. They are colonial structures formed by photosynthesizing cyanobacteria and other microbes. They were the dominant life form on Earth for over 2 billion years. For this reason, while waiting for some fossil stromatolites, we spectroscopically studied fresh stromatolites from Shark Bay in Australia, that have an aragonite structure. The spectrum at T=ambient (i.e. before the thermal process), shown in Fig. 5, indicates that they are composed of aragonite. The feature around 9 μm is due to traces of magnesium sulphate ($MgSO_4$). The SEM morphological analysis confirms the presence of seaweeds while the EDX compositional study reveals the presence of Magnesium, Sulphur and Oxigen. Also in this case the heating process transforms aragonite first into calcite and than into calcium oxide (see the formation of the characteristic feature beyond 20 μm in the spectrum at T=485°C in Fig. 5).

3. Conclusions

Many different areas of investigation may be important in studying Mars, but one of the main goal is the search for a possible microbial activity. For this reason, scientists are actively preparing *in-situ* instrumentation for future landing platforms and they are studying possible techniques for the analysis of samples brought back from Mars. The future missions to Mars, taking advantage of a rich legacy of remote sensing observations, will be able to target a pre-selected site of scientific interest and will address the issue of life on the planet.

In the meantime, laboratory research on biotic and abiotic minerals of exobiological interest can be used to find possible discriminating factors, useful to distinguish the biological origin of a sample from an abiotic formation.

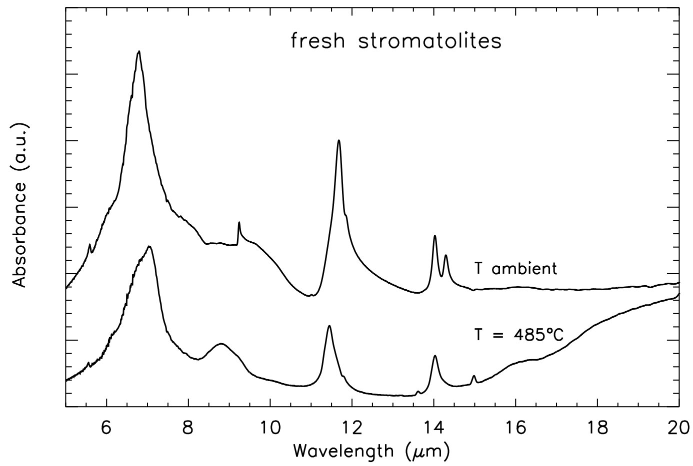

Fig. 5. Spectra of fresh stromatolites before and after processing at 485°C. The band around 9 μm is due to traces of magnesium sulphate.

Cabane et al. (2004) proved that the mass spectrometer coupled with a gas chromatograph (GC), using the Differential Thermal Analysis, can differentiate between abiotic minerals and fresh biominerals. In our work we demonstrated that also the infrared spectroscopy can be a diagnostic tool for discriminating samples of biotic and abiotic origin. This is true not only for minerals and "recent" biomineral (fresh shells and stromatolites) but also for fossils of aragonite. All the organogenetic samples behave in the same way: the changes occur at lower temperatures than those for the abiotic specimens. Indeed, studying the physical properties and examining the behaviour after heating, the endothermic transformation from aragonite to calcite and the following modification of calcite into CaO, is faster for biotic samples than for the abiotic mineral. As a next step, it will be interesting to analyse fossil stromatolites as well as fossils of intermediate geologic epochs (50 - 1000 Myr ago), not only of aragonite composition but also of calcite structure. As a matter of fact, the fossilization process can transform their original composition and we aim to study in depth the changes in spectral behaviour after heat processing of differently preserved biological structures. In future we plan to repeat the measurements (again in the infrared wavelength range) using reflectance spectroscopy, which is more easy to be performed directly *in-situ* on the surface of Mars.

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