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The infrared spectroscopy of biotic and abiotic minerals: its relevance to Mars studies

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Abstract. The evidence of water erosion on Mars is particularly interesting since present climatic conditions are such that liquid water cannot exist at the surface. But, if water was present on the planet in the past, there may have been life, too. Since the discovery of carbonates on Mars also may have very important implications on the possibility that life developed there, we have studied a mineral that can have biotic or abiotic origin: aragonite, a metastable state of calcium carbonate ($CaCO_3$). We have analysed biomineral aragonite, in form of shells, along with crystals of mineral aragonite. Infrared spectroscopy in the 2-25 μm wavelength range shows that, after heat treatment, the biotic samples and the abiotic ones have a different spectral behaviour. The importance of such differences is discussed in the framework of the present exploration of the Planet Mars.

1. Introduction

The suggestion of McKay et al. (1996) that the Martian meteorite ALH84001 has preserved traces of Martian bacteria led to a surge in scientific research on putative Martian forms of life. Indeed the tantalizing possibility that life might once have existed on the red planet has stimulated a lot of work on this subject. However, as it is well know, for life to develop and survive, the presence of liquid water is essential (Irwin & Schulze-Makuch 2001). With its current hyperarid climate, Mars is inhospitable for sustaining any life form. However, data from several robotic (both orbiter and lander) missions have demonstrated convincingly that Mars was once warm and wet enough to allow the presence of abundant liquid water on the surface (Mars Pathfinder Rover team 1997; Phillips et al. 2001; Craddock & Howard 2002). In this scenario, environmental conditions on Mars may have been Earth-like, so that simple forms of life could have developed at the surface or in the underground (McKay & Stoker 1989). If this was the case, traces of extinct life should be present on the planet in form of fossils and microfossils included into some geological layer and these fossil marks, in principle, could be detectable (Banfield et al. 2001).

In this respect Cabane et al. (2001) have proposed, in the framework of the next NASA Mars Science Laboratory, to be launched in 2009, the experiment SAM (Sample Analysis at Mars) devoted to *in situ* analysis of the Martian ground and underground.

One important part of this experiment will be devoted to search, in ground and underground, for organic traces of a past prebiotic chemistry, and, in the best of the cases, of an organized life. The goal will be also to use the so-called Differential Thermal Analysis (DTA) coupled with Gas-Chromatography and Mass

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Spectroscopy in order to differentiate between minerals and biominerals (shells, tests, carapaces, skeletons, etc.). This experimental approach is based on the fact that, if a mineral is produced from the biotic activity of some organism, in general it has not exactly the same properties as its abiotic equivalent, due to the fact that a biomineral is built in a rather shorter time. In a subsequent work Cabane et al. (2004) have performed DTA on some tens milligrams of the crushed shell of a modern gastropod, which consists in aragonite, and on the same mass and granulometry of a particulate sample of hydrothermal abiotic aragonite. According to Mackenzie (1970), the classical DTA of aragonite, a metastable state of calcium carbonate ($CaCO_3$), shows two peaks: the first one, rather weak, appears at a temperature T_1 = 400-500°C (depending on the experimental device and conditions), and it is related to the endothermic transformation of aragonite into calcite, the stable state of $CaCO_3$; the second one, more intense, at T_2 = 800-900°C, corresponds to the decomposition of calcite into solid calcium oxide (CaO) and gaseous CO_2.

Cabane et al. (2004) have found that, in the same experimental conditions, the temperatures T_1 and T_2 in the case of the abiotic mineral are higher than those observed for the biotic one, due to the structural fragility of the latter. For this reason the authors claim that it could be possible to discriminate between a biotic or abiotic origin of the mineral under study.

It is important to note that the structural change of aragonite to calcite and the subsequent decomposition of calcite into CaO, produced by thermal annealing and recorded by DTA, should be detected also by means of infrared (IR) spectroscopy. We have thus started a research program aimed to perform IR spectroscopic analyses, along with morphological and compositional studies using a Scanning Electron Microscope and an Energy Dispersive X-ray spectrometer, directed to examine the reactions to thermal treatments of biotic and abiotic particulate samples composed of $CaCO_3$.

As a first step, in the present work we have analysed recent biomineral aragonite samples (in form of crushed modern sea shells) and crystals of mineral aragonite, in order to confirm the results obtained with DTA by Cabane et al. (2004). As a second step in a forthcoming paper we will study, instead, the spectroscopic behaviour of fossils subjected to the same thermal treatments.

2. Sample preparation and measurements

In order to obtain fine grains for IR transmission measurements, all the samples, both minerals and biominerals, were powdered by means of a mechanical mortar grinder (RM 100 Retsch). A selection of particles in the size range between 20 and 50 μm was then achieved using a mechanical sieve. All transmission measurements have been performed by means of a FT-IR Spectrometer (Spectrum 2000 Perkin Elmer) in the spectral range 2-25 μm with a resolution of 4 cm^{-1}. We used the standard pellet technique with about 0.5 mg of sample grains in 250 mg of potassium bromide (KBr) matrix.

The thermal treatments were performed by placing the materials in a furnace under vacuum at a pressure of about 10^{-5} mbar, at various temperatures.

Fig. 1 reports the transmission spectra concerning grains of commercial mineral aragonite (abiotic) (Ward's research mineral) measured for unprocessed samples, denoted as "T ambient", and for samples of the same material after heat treatment at 420°C and 485°C for 3.5 hours. Fig. 2 shows similar spectra for particles of aragonite of biotic origin obtained after grinding shells of a modern sea bivalvia (Tellina exigua). We note that similar results have been obtained also for another type of biotic aragonite after crushing, a Cardites Antiquata bivalvia. The values of the temperatures for the heat treatment have been chosen according to DTA analysis showing that aragonite of biotic origin is transformed into calcite with a heat treatment at 420°C, before mineral aragonite, which also becomes calcite with a heating process but at an higher temperature of 485°C (Cabane et al. 2004).

Our results shown in Figs. 1 and 2 confirm, by means of a different experimental method,

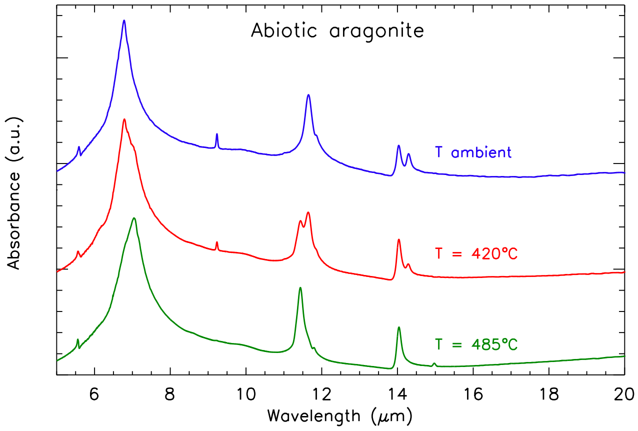

Fig. 1. Abiotic aragonite: before (blue curve) and after thermal process at 420°C (red curve) and at 485°C (green curve). Spectra have been arbitrary scaled for clarity.

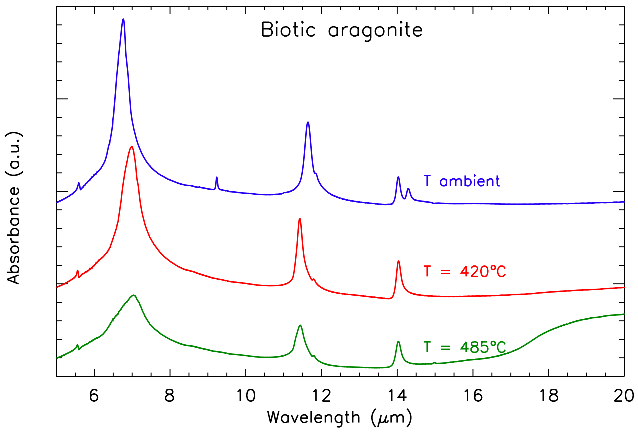

Fig. 2. Biotic aragonite: before (blue curve) and after thermal process at 420°C (red curve) and at 485°C (green curve). Spectra have been arbitrary scaled for clarity.

the same results. In fact, although the starting material is spectroscopically undistinguishable (blue curves) having the same IR spectra as pure aragonite (Salisbury et al. 1992), the heating processes influence differently the original materials. Indeed, abiotic aragonite (Fig. 1) has a transition phase at 420°C, with some changes in the shape and position of the main bands at 6.7 μm, 9.25 μm, 11.5 μm and 14.3 μm and then, at 485°C, it is transformed into calcite (compare green spectrum of Fig.1 to spectra of calcite in Salisbury et al. 1992). On the other hand, biotic aragonite is completely transformed into calcite already at 420°C (red curve in Fig. 2). Further thermal process begins to transform calcite, via CO_2 release from the sample, into calcium oxide (CaO). This is clearly evident in the spectrum of biotic aragonite processed at 485°C (green curve in Fig.2) where the band at 6.7 μm becomes less pronounced while the absorbance beyond 17 μm starts to increase considerably.

In conclusion, thermal processing at 420°C and 485°C of aragonite ($CaCO_3$) induces structural changes of the samples which are transformed into calcite (again $CaCO_3$). However, the process of transformation is faster for biotic samples than for the abiotic mineral.

3. Conclusions

With a detailed spectral analysis we have demonstrated that it is possible to distinguish, not only with DTA and gas-chromatography but also with IR spectroscopy, mineral aragonite from aragonite of recent biological origin. This can be easily understood by the fact that the organic matrix, secreted by the biological organism to create the shell structure, forms a base of fine fibres, overlayed by solid particles of calcium carbonate. The result is that the properties and structure are different from those of the abiotic mineral, in sense that the rapid increase of the crystalline structure developed under biotic conditions makes it less resistant to thermal treatments, compared to samples of abiotic origin. Therefore, the temperatures at which the crystalline structure is modified, are lower for the organic material.

The question now is: do we expect to find recent biotic minerals on Mars? All the experimental and observational studies concerning the red planet show, up to now, that this possibility is highly unlikely. If life existed in the past we can expect "ancient" biotic carbonates which can be investigated to search for a way to be discriminated from similar abiotic minerals. In this context, the result obtained by Cabane et al., that we verified by IR spectroscopy, are unsuited for drawing definitive conclusions. This means that experimental projects designed as sample return or *in situ* analyses and based on DTA coupled with Gas-Chromatography and Mass Spectroscopy and/or IR spectroscopy, could have a very low probability of success.

We are now working on terrestrial carbonates of fossils origin to see how they behave after thermal processing. The aim is to check if it has sense for measurements of the kind discussed in this work, to be proposed as diagnostic on Martian life forms.

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