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Time-dependent degradation of biotic carbonates and the search for past life on Mars

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Searching for traces of extinct and/or extant life on the surface of Mars is one of the major objectives for remote-sensing and *in-situ* exploration of the planet. In the present paper we study the infrared (IR) spectral modifications induced by thermal processing on differently preserved calcium carbonate fossils, in order to discriminate them from their abiotic counterparts.

The main conclusion of this study is that the degree of alteration of the fossils, derived from IR spectral analysis, seems to be well correlated with the sample age, and that terrestrial fossils after a billion years are so altered that it becomes impossible to trace their biotic origin. Since it is reasonable to assume that the putative Martian fossils should be at least 3.5 billion years old, this would imply that our spectroscopic method could not be able to detect them, if their degradation rate were the same as that we have found in usual conditions for the terrestrial fossils. However, due to the different climate evolution of the two planets, there is the possibility of having two different degradation rates, much lower for Mars than for Earth, especially if the fossils are embedded in a protective layer, such as a clay deposit. In this case IR spectroscopy, coupled with thermal processing, can be a useful tool for discriminating between abiotic and biotic (fossil) carbonate samples collected on the Martian surface.

1. Introduction

Environmental conditions favourable for the emergence of life similar to that on Earth, must have been present on Mars during the first part of its history, lasting for about 0.5–1 Gyr after its formation. These conditions probably included a dense atmosphere (Pollack et al., 1987), relatively mild temperatures (Carr, 1996; Paige, 2005), liquid water on the surface with subsequent formation of extensive sulphate and/or carbonate rock layers in paleolake basin sediments (Carr, 1996). Actually, magnesium and calcium sulphates have been identified by Mars Express and Opportunity in various small areas of the planet (Bibring et al., 2005; Squyres et al., 2006). On the other hand, apart from the identification of small quantities of carbonates in the Martian dust (Pollack et al., 1990; Lellouch et al., 2000; Bandfield et al., 2003), no carbonate deposits have been found so far on Mars (McKay and Nedell, 1988; Christensen et al., 2001; Bibring et al., 2005; Stockstill et al., 2005, 2007; Jouglet et al., 2007).

In addition to the obvious assumption that massive carbonate deposits never formed on Mars, many other hypotheses have been proposed in order to explain why remote-sensing instruments have not identified such deposits (for a detailed discussion on the subject see Craddock and Howard, 2002). In particular Bullock and Moore (2007) have suggested that extensive volcanism, present in the first part of Mars history, most likely injected large amounts of SO_2 into the atmosphere of the planet. Efficient photochemical conversion of SO_2 to H_2SO_4 would have caused widespread sulphuric acid/water clouds, similar to those seen on Venus today. Acid atmospheric precipitation from these clouds would have added sulphur, but no cations to Martian waters, lowering their pH. Carbonates would not be stable under these conditions, and would have rapidly decomposed to CO_2, while sulphates would have precipitated with the available cations, Ca^{2+} and Mg^{2+}. In this scenario, the widespread presence of sulphates on Mars would preclude the presence of massive carbonate deposits. According to Bandfield (2008), however, this conclusion does not consider that multiple aqueous environments could be present on the planet at the same time. In other words, the presence of sulphate deposits in various Martian areas should not preclude the presence of carbonate deposits in other regions or even in the same areas, if deposition occurred in different epochs with different environmental conditions.

In any case it is not unreasonable to think 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). If this were the case, traces of extinct life could be present on the planet in form of fossils in some geologic layer and these

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fossil marks, in principle, could be detectable (Banfield et al., 2001). In the framework of Mars exploration, searching for these traces is a major objective, even if the detection of a biosignature is not a straightforward process, in particular in the case of microfossils. In fact, the simple morphology of microfossils can be mimicked by abiological mineral microstructures, so that discriminating between true microbial fossils and microscopic pseudofossils can be difficult (Schopf and Walter, 1983; Mendelson and Schopf, 1992). For this reason, Cabane et al. (2004) and Stalport et al. (2005, 2007) have proposed differential thermal analysis (DTA) as a useful tool to differentiate between abiotic minerals and biominerals. In particular Stalport et al. (2005, 2007) have used DTA coupled to thermogravimetric analysis (DTA-TG) to determine the thermal behaviour of calcium carbonate ($CaCO_3$) samples. These compounds, produced on Earth by abiotic process as well as by biological activity, are mainly present in two polymorphic forms: aragonite and calcite. According to Mackenzie (1970), the classical DTA of aragonite, a metastable state of $CaCO_3$, shows two peaks: the first one (rather weak) appears at a temperature $T_1 = 400$–$500\,^{\circ}C$ (depending on the experimental device and conditions) and is related to the endothermic transformation of aragonite into calcite, the stable state of $CaCO_3$. The second more intense peak at $T_2 = 800$–$900\,^{\circ}C$, corresponds to the decomposition of calcite into solid calcium oxide (CaO) and gaseous CO_2. Cabane et al. (2004) have found that under the same experimental conditions the temperatures T_1 and T_2 for the case of the abiotic $CaCO_3$ are higher than those observed for the biotic one, due to the structural fragility of the latter. They claim, therefore, that it may be possible to discriminate between biotic and abiotic origin of the carbonate under study. These results are in agreement with those obtained by Stalport et al. (2005) who have investigated several terrestrial calcite samples of various origins. These authors have used DTA coupled to thermogravimetric analysis (DTA-TG) to determine the thermal behaviour of the samples. They have found that the thermal degradation of abiotic calcite starts at a temperature at least 40 °C higher than the degradation temperature of any investigated biotic calcite. Consequently, Stalport et al. (2005) conclude that the analysis of Martian minerals by DTA-TG represents a promising approach to detect evidence of past biological activity on Mars in the case of a Martian *in-situ* study or in a sample return mission.

Another approach, alternative and/or complementary to DTA, has been suggested by our group. In two previous works (D'Elia et al., 2006; Orofino et al., 2007—hereinafter Paper I), we used infrared (IR) transmission spectroscopy in order to analyse the reaction to heat treatments of biotic and abiotic particulate samples mainly composed of calcium carbonate. We found that, after thermal processing, it is possible to distinguish, by means of IR spectroscopy, abiotic carbonate samples from their biotic counterparts. In particular, for biological carbonates, like fresh aragonite shells and relatively young aragonite and calcite fossils (younger than 30 Myr), we observed a different spectral behaviour compared to that of minerals. All the mid-IR (MIR; 2000–$400\,cm^{-1}$ or 5–$25\,\mu m$) spectra of biotic samples thermally processed at 485 °C show the onset of the characteristic CaO band, a broad absorption feature centred at about $330\,cm^{-1}$ ($30\,\mu m$; Farmer, 1974). It is worthwhile to note that at this temperature we can observe the beginning of the transformation from $CaCO_3$ to CaO (via CO_2 release), which, as already mentioned, becomes complete at higher temperature (800–1000 °C). On the contrary, for minerals of abiotic origin, the variations between the spectra of unprocessed specimens and those processed at 485 °C, are much smaller and often not detectable.

However, after these studies, the question remained open about the applicability of our method to more ancient fossils. This is a crucial point since the hypothetical Martian fossils are expected to be much older than the fossils analysed in Paper I. In fact it is likely that the initial conditions favourable for life, with a thick atmosphere able to allow mild temperature and abundant liquid water on the surface of the Red Planet, lasted only 1 Gyr or less (Pollack et al., 1987; Carr, 1996), so that we can expect to find fossils, if any, at least 3.5 Gyr old.

In the present work we extend our study to the analysis of ancient fossils, dating back to more than a billion years, focusing our attention to the appearance and evolution of the CaO band. In the next section, the analysed samples are shortly discussed and the methodological approach is reported along with the experimental results. Finally, in Section 3, the astrobiological implications of our results are discussed, and the main conclusions are drawn.

2. Measurements and results

The samples analysed in this work are reported in Table 1. They consist of two fresh aragonite shells (sample 1: *Tellina exigua*; sample 2: *Cardites antiquata*), three recent calcite fossils dating from Pleistocene (sample 3: *Pecten* sp.; sample 4: *Ostrea* sp.; sample 5: *Myriapora Truncata*), four medium aged fossils, of both calcite and aragonite composition, dating from Miocene (sample 6: *Clypeaster* sp.) and Oligocene (sample 7: *Cerithium*; sample 8: *Ampullinopsis crassatin*; sample 9: *Haliotis Lamellosa*), and three old calcite fossils dating from Cretaceous (sample 10: *Rudista*), Devonian (sample 11: *Ortoceras*), and Meso-Proterozoic period (sample 12: fossil stromatolites). We also studied particulate samples of two carbonate rocks, aragonite (sample 13) and calcite (sample 14), of abiotic origin. The former is a high-purity research mineral supplied by Ward's Inc.; the latter is a piece of limestone, collected in a place near Lecce, Italy, and composed of more than 98% of $CaCO_3$ in the calcite polymorphic form (Orofino et al., 2002). Also listed in Table 1 are the locations where the samples have been collected and their estimated geological ages. The beginning and the end of each period/epoch are those established by the International Commission on Stratigraphy (ICS) deputed to the terrestrial stratigraphy on a global scale (Gradstein et al., 2004).

All the samples were ground for approximately 10 min in a mechanical mortar grinder in order to obtain fine powders suitable for IR spectral analyses. The spectra of the two carbonate minerals, aragonite and calcite, are shown in Paper I and compared with those reported by Salisbury et al. (1991) for the same minerals.

As described in Paper I, the thermal processing of the samples was performed by means of a furnace under vacuum and the same analytical procedure was followed for the characterization of the samples listed in Table 1.

When calcium carbonate is submitted to heat treatment, the following well-known decomposition process occurs:

$$CaCO_3 \rightarrow CaO + CO_2$$

This transformation is complete at 800–1000 °C (Stalport et al., 2005, 2007), but it begins at lower temperatures. In this respect, it is important to underline that the temperature, at which the decomposition mechanism begins, 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 (Paper I).

Since the CaO spectrum is characterized by a flat continuum in the MIR and a broad and strong band in the far IR (FIR; 700–$200\,cm^{-1}$ or 14–$50\,\mu m$), we have started our analysis in the latter spectral range and examined the CaO band formation of our