Mem. S.A.It. Suppl. Vol. 16, 101

Memorie della
Supplementi

Preservation of biosignatures in clay-rich systems: implications for Martian exobiology

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Abstract. 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 a recent paper we have studied the infrared (IR) spectral modifications induced by thermal processing on differently preserved carbonate fossils, in order to discriminate them from their abiotic counterparts.
The main conclusion of the study has been 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 billions 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.
In this work we show that our method is quite effective for fossils collected in protective layers of clays and that 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 especially in phyllosilicate-rich regions such as Mawrth Vallis.

Key words. Exobiology – Mars – spectroscopy

1. Introduction

Phyllosilicates have been found abundant and varied on Mars (Bibring et al., 2006; Mustard et al., 2008). Their detection has been reported throughout the most ancient Noachian terrains and, in particular, in two extensive deposits near the outflow channels Mawrth Vallis (Bishop et al., 2008) and Nili Fossae (Mustard et al., 2008). In Mawrth Vallis a common phyllosilicate stratigraphy with nontronite at the bottom, covered by a ferrous phase, then hydrated silica, montmorillonite and kaolinite is observed (Bibring et al., 2005; Poulet et al., 2005; Bishop et al., 2008). Nili Fossae is located west of the large Isidis Basin and contains large outcrops of multiple phyllosilicate minerals such as nontronite, saponite and Fe-rich chlorites (Poulet et al., 2005; Mustard et al., 2008) and also carbonates (Ehlmann et al., 2008). Several smaller phyllosilicate outcrops also occur widespread across the planet often associated with craters, where they are exposed in ancient rocks (Bishop et al., 2007; Buczkowski et al., 2008; Wiseman et al.,

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2008; Marzo et al., 2009), even if their occurrence has been also reported in much younger Hesperian terrains (Fairen et al., 2008; Marzo et al., 2008) which are generally dominated by distinct aqueous alteration products such as sulfates, ferric oxides, and opal (Gendrin et al., 2005; Bibring et al., 2006; Bibring et al., 2007; Milliken et al., 2008). This variety of alteration minerals has been used to suggest that Mars experienced a dramatic, global, environmental change from neutral-alkaline to acidic aqueous conditions. In this hypothesis phyllosilicates were the primary alteration product during the first 1 Gyr on Mars (Bibring et al., 2006). The identification of thick phyllosilicate deposits that contain Fe-rich clays such as nontronite, as in Mawrth Vallis and Nili Fossae, which form under moderate pH and reducing environment (Chevrier et al., 2007) points to conditions potentially favorable to life, as opposed to younger Hesperian terrains, where the assemblage of salts implies environmental conditions that were acidic and oxidizing, with a water activity too low to support terrestrial life (Tosca et al., 2008). Phyllosilicates themselves could have served as reaction centers for organic molecules (Pinnavaia, 1983) and some experiments even suggest that phyllosilicates could have played a role in the origin of life (Lawless, 1986). Moreover, due to the ability of many clay minerals to bind organics, preventing their decay (Butterfield, 1990), phyllosilicate-bearing deposits are a prime target for the 2011 Mars Science Laboratory rover.

Fig. 1. Concentration of macrofossils in the clayey layers of Gagliano del Capo paleosite. The image represents an actual area of 20 cm across.

Fig. 2. Fossil of *Ampullinopsis crassatina*. The shell size is about 7 cm.

2. Preservation of biosignatures and spectral studies

Studies of fossilization processes in modern environments indicate that the preservation of fossil information is controlled by the physical, chemical and biological conditions acting during sedimentation.

With burial, the permeability of fine-grained clay-rich detrital sediments decreases rapidly owing to compaction. In addition to the reduction of permeability, clay may also play an important role in the preservation of biosignatures by binding organic molecules to charged mineral surfaces or incorporating them into clay structures as interlayer cations (Farmer & Des Marais, 1999).

The degradation of organic materials is often assumed to be slower under anaerobic conditions, so the preservation of biosignatures is favoured in rapid burial conditions in fine-grained clay-rich systems and long-term preservation is most successful in phyllosilicate- and silica-bearing host rocks that are resistant to weathering and provide an impermeable barrier for the biosignatures.

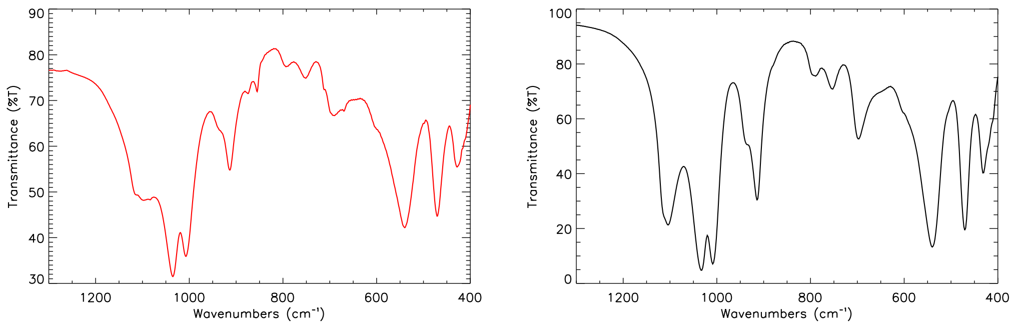

Fig. 3. Transmission spectrum of the Gagliano del Capo clay-rich sediment (right panel) and reference spectrum of kaolinite after Salisbury et al., 1991 (left panel).

In this paper we report on the study of the spectral reaction to thermal processing of differently preserved structures of biotic origin (such as fresh shells, fossils which had a different geological history and/or of different epochs) that has given us relevant information on how the degradation level of the biostructures affects the IR spectral properties of the samples. In particular, we found that terrestrial fossils embedded in a layer of clays, preserve their biomineral characteristics, making much easier their identification by means of our method described in Orofino et al. 2007, 2009.

We focused our attention on the fossils collected in three different clay deposits located at three different sites which are about 30 km apart one from the other in the Salento Peninsula (Southern Italy). In particular, they are two lignite clayey deposits at Gagliano del Capo and Otranto (Bossio et al., 2006), and a greenish-grey sandy clay deposit at Cutrofiano (Margiotta and Varola, 2007). The lignite clayey deposits of Gagliano del Capo (Fig. 1) and Otranto can be dated back to the late Oligocene, as suggested by the presence of the well preserved gastropod *Ampullinopsis crassatina* (Fig. 2) along with ostracodes assemblages, and by the appearance of the depositional environment referable to coastal restricted brackish waters episodically connected with the open sea. Instead, the paleosite of Cutrofiano is one of the most interesting pleistocenic deposits, both for the presence of cetacean odontoceti and misticeti, and for the abundance of several fossilifers association with excellently preserved taxa, notably *Myas truncata* and *Arctica islandica*.

The infrared transmission spectrum of clay-rich sediment in Gagliano del Capo (Fig.3) reveals that it is mainly composed of kaolinite. Kaolinite is one of the phyllosilicates identified by OMEGA in a region of the southern highlands and by CRISM in Nili Fossae and Mawrth Vallis.

All the samples (fresh shells, recent fossils, fossils of more ancient epochs up to 1 billion years, fossils embedded in clay-rich soils listed in Orofino et al. 2009) were ground in a mechanical mortar grinder in order to obtain fine powders suitable for IR spectral measurements and then spectroscopically analysed (in the range of 6500-370 cm^{-1}) before and after a thermal treatment.

Comparing and studying the modifications in the IR spectra of the processed and unprocessed samples between 700 and 400 cm^{-1}, we noted that the level of degradation may be much lower with respect to the standard values if fossils are surrounded by clay minerals (Orofino et al., 2010).

3. Conclusions

Fig. 4 shows the global map of phyllosilicate deposits on Mars (marked with red dots and ellipses), plotted over a MGS Mars Orbiter Laser Altimeter altitude reference map. In yellow are

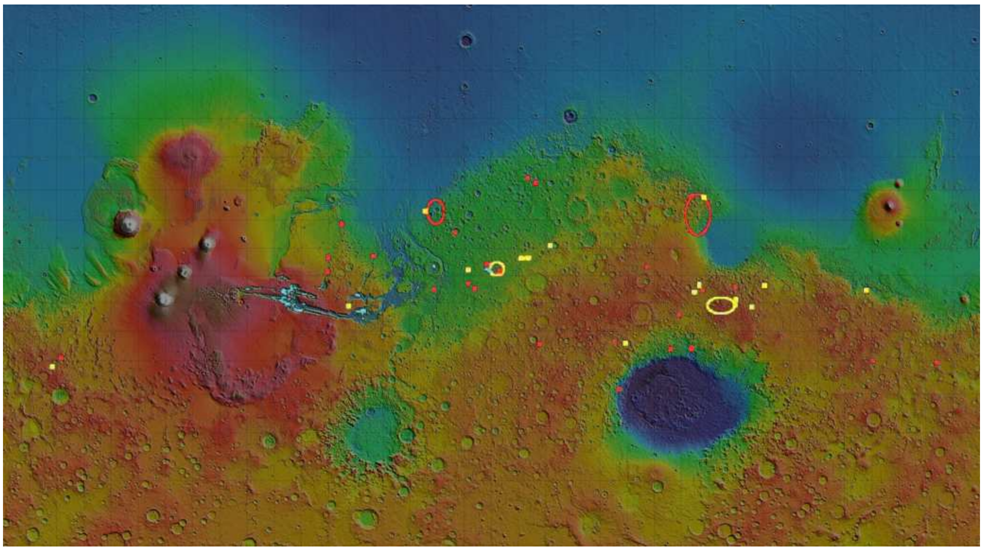

Fig. 4. Global map of phyllosilicate deposits on Mars (red dots and ellipses) after Bibring et al.,2006.

reported the sites where other hydrated minerals are present; in these cases the lack of a marked spectral feature (such as that due to metal-OH vibration) does not allow the exact identification.

As discussed in the previous section, the level of degradation may be much lower if fossils are found surrounded by clay minerals that evidently are able to retain some of their biotic features for longer times. In the light of this result, in agreement with previous findings (Butterfield, 1990; Fraser et al., 1996; Farmer and Des Marais, 1999; Orr et al., 1998), the phyllosilicate regions discovered on Mars may represent very interesting environments that can provide conditions favorable to preserving evidence of biomarkers, and hence can be regarded as good candidates as locations for their detection (Bishop et al., 2009).

Acknowledgements. A. Varola and L. Ruggiero are warmly thanked for very useful discussions and for providing some fossil samples. This research has been partially supported by Italian Space Agency (ASI) and the Italian Ministry of University and Research (MUR).

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