

ORGANIC MATTER PRESERVATION IN CLAYS UNDER MARS-LIKE CONDITIONS

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Abstract

The Mars Science Laboratory (MSL) mission, which scientific objective is determining the habitability of Mars, has evidenced the relationship between clays and organic compounds. We investigated whether the exposure to different environmental conditions (acid vs. alkaline fluids) can compromise the capacity of smectites to protect organic compounds (i.e., glycine) under Mars-like conditions. We chose nontronite as mineral matrix because it was already proven to be a good organic preserver on Mars [1, 2]. For comparison, we used pyrite, a photoactive mineral unstable at current subaerial Mars conditions.

1. Introduction

The present-day surface of Mars is characterized by an oxidizing regolith that receives a high flux of UV radiation, including most of the UV-C range (190–280 nm), capable of degrading organic molecules through photochemical processes [3]. Under this inhospitable environment, biosignature preservation is only possible inside a mineral matrix able to protect from the oxidizing Martian conditions [4]. Clay Minerals present low permeability, high cation exchange capacity (CEC) and high specific surface area (SSp), becoming excellent reservoirs to hold and protect organic compounds during geological time scales [5]. Among them, smectites are of particular interest on Mars due to their widespread distribution, and their expandable 2:1 sheet structure capable to incorporate small organic molecules into their interlayer region.

The geological setting of Gale Crater contains several ancient fluvial lacustrine environments with potential past habitability. Analysis performed with the Sample Analysis at Mars (SAM) instrument suite, on board the Curiosity rover, identified the presence of chloride- and sulphur-rich organic compounds in drill samples collected from: (i) the Sheepbed member [6]; and (ii) Pahrump Hills [7], respectively. The mineralogy of these sedimentary units records multiple episodes of aqueous alteration processes under different geochemical environments, and includes evidence of both smectites and organic compounds.

Here, we investigated whether the exposure to different weathering fluids (i.e., alkaline and acid) could affect the structural and sorption capacities of nontronite, testing their capacity to preserve organics

under Mars-like conditions (P atm ~ 7 mbar and high fluxes of UV). For comparison, we also tested the preservation capacity of pyrite, a photoactive mineral unstable at current subaerial Mars conditions.

2. Methods

2.1 Samples preparation

Nontronite (NaU-1) was purified by centrifugation to obtain a fraction <2 μ m size. Two different samples of NaU-1 were exposed during 2 hours to 2.5% HCl and 2N NaOH respectively, washed in HPLC water and dried. Pyrite was obtained from Lanzarote (Spain), grounded and subsequently washed in ethanol, HCl and deoxygenated water. Treated clays and pyrite sample were exposed to a glycine suspension during 24 hours and dried afterwards, obtaining a mixture of 0.001 mol gly/g mineral.

2.2 Simulation chamber

Simulation experiments were performed in the Planetary Atmospheres and Surfaces Chamber (PASC) [8]. Pellets of organic-mineral mixtures were exposed to 80 h of UV flux conditions (deuterium UV lamp ~ 2.3 W/m²) under a simulated Martian atmosphere (99% CO₂ and 0.6% H₂O at a pressure of 7mbar). A Raman spectrometer (532nm) was recently added, allowing *in situ* characterization of the samples under study.

2.3 Analytical techniques

Nontronite was characterized after exposure to acid and alkaline conditions by XRD and FTIR. Pellets of organic-mineral mixtures were also characterized by mineralogical and chemical analyses (Raman, FTIR, XPS, SEM) before and after exposition to UV radiation under Mars-like conditions

3. Results and discussion

NIR spectra of both treated clays showed slightly differences between them. The acid-treated spectrum revealed a decrease in the overtones and combination bands of the OH group. This intensity diminution reflects a partial dissolution of octahedral cations.

XRD patterns show an amorphization of the basal peak d (001) in the acid-treated clay that migrated to higher distances (from 12.6 Å to 14.5 Å) (Fig. 1a).

This shift might indicate a change in the hydration state. After reaction with a suspension of glycine, the swelling capacity of the acid-treated nontronite was lower than the alkaline-treated (Fig. 1b).

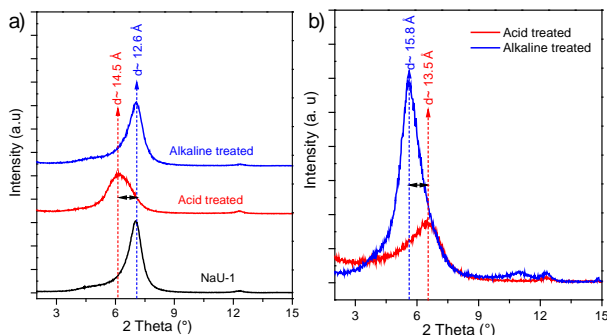


Figure 1. a) From bottom to top, XRD patterns of an oriented aggregate (OA) of the NaU-1 purified clay, acid-treated and alkaline-treated. b) XRD patterns of OA of the acid- and alkaline-treated clay samples after glycine incorporation.

DRIFT spectra of organic-clay pellets (data not shown) revealed that glycine was adsorbed in the zwitterion form ($^+\text{NH}_3\text{CH}_2\text{COO}^-$). After UV exposition, the most remarkable changes were a decrease of the bands at 1033 cm^{-1} ($\nu\text{CN} + \nu\text{CC}$) in both clay samples. However, the acid-treated sample also showed a sharp decrease in the $\delta_{\text{as}}\text{NH}_3$ vibration (1615 cm^{-1}), and in the symmetrical and asymmetrical $\nu(\text{COO}^-)$ at 1415 cm^{-1} and 1590 cm^{-1} , respectively, suggesting further organic degradation.

XPS analysis showed that the mineral matrix in organic-clay samples did not suffer damage after UV exposition. Then, the information of C1s and N1s allowed us to determine how glycine changes after exposition to Mars-like conditions (Fig. 2). C1s spectra showed a higher diminution of the C-N contribution in the acid treated sample. Regarding the N1s orbital, the acid-treated sample showed a remarkable reduction of the NH_3^+ contribution in favour of the formation of NH_2 . The decrease of the $\text{NH}_3^+/\text{NH}_2$ ratio could be attributed to the generation of amino moieties by the chemical degradation of glycine [9].

In situ and *ex situ* Raman spectra (data not show) also revealed a higher degradation of acid-treated clays. We analysed the intensity decrease of the Raman peaks at 888 cm^{-1} ($\nu\text{CC} + \nu\text{CN}$) and at 2968 and 3003 cm^{-1} , ($\nu_{\text{s}}\text{CH}$ and $\nu_{\text{as}}\text{CH}$) and corroborated that the acid treated clay show a higher diminution of these peaks.

The results of organic-pyrite samples are more difficult to interpret because this mineral is unstable under UV radiation, masking the organic degradation of glycine. For Raman *ex-situ* spectra, we labelled the surface of pellets in order to analyse the same area with the microRaman. Interestingly, the mark

imprinted in the surface of the pyrite-glycine sample disappeared after exposition to Mars-like conditions. In this case, the carbon loss was higher than that in the clay samples (2% vs >1%). We hypothesize that the upper layer of the pyrite pellet could have been removed due to the UV exposition.

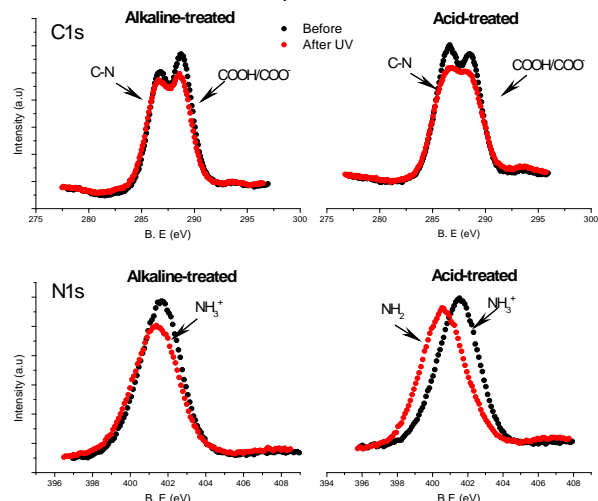


Figure 2. XPS spectra of the organic-clay samples comparing glycine species (C1s and N1s) before and after UV exposition.

4. Conclusions

Nontronite aptly preserves organic matter under Mars-like conditions, but when the clay is exposed to weathering fluids its preservation capacity can vary. Here, we show that alkaline-treated Nontronite provides a better radiation shielding effect under Mars-like conditions. On the other hand, pyrite seems to catalyse organic degradation under UV Martian conditions. These results may help guiding the search and detection of biosignatures on Mars with the upcoming missions.

5. References

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