

LONG-TERM PRESERVATION OF ORGANIC COMPOUNDS UNDER THE EXTREME ACIDIC CONDITIONS OF RÍO TINTO SUGGESTS THAT THE ACIDIC MARS DEPOSITS ARE A HOT TARGET FOR MARS ASTROBIOLOGY. T. Huang¹, D. C. Fernández-Remolar². ¹Planetary Science Institute, China University of Geosciences, Wuhan 430074, China (huanglotte@cug.edu.cn). ²Univ Grenoble Alpes, CEA, CNRS, IBS, Metalloproteins Unit, F-38000 Grenoble, France.

Introduction:

The geological evolution of the Río-Tinto acidic system over the last 30 Ma has been recorded as different gossan and fluvial ferruginous deposits. This includes three different sets of Quaternary terraces, recording an acidic activity between 2.1 Ma and ~ 2 Ka [1]. The acidic Río Tinto system has largely been studied as a first-class terrestrial analog of the ancient acidic paleoenvironments of Mars that have been recorded as ferric sulfates and oxides in regions like Meridiani Planum [2]. In this regard, Río Tinto can provide key information about the living forms that could have thrived, and their preservation pathways under such extreme conditions.

Despite the extreme acidity (pH ~ 1.5 to 3), the microbial life in Río Tinto is quite diverse [3, 4]. Previous research has found the potential preservation of biomarkers preserved in the old terrace from aspects of morphology and component. Organic compounds (esters, alkanes, lipids, and amines) were detected as evidence of preservation of traces of biomolecules under acid conditions [5, 6]. A portion of lipids is contributed by acidophiles whose remains were preserved in iron sulfates and iron oxides [7]. However, the diversity and preservation state of the biological compounds and their relation with mineral matrix remain uncertain, which characterization is essential to understand its preservation pathways and persistence over the long temporal scales of the Mars geological record.

In order to evaluate the potential preservation of the acidic systems of Mars, we collected samples from the 2.1-Ma old Río Tinto terrace and searched for organic compounds in terms of its diversity and its relation with the mineral matrix.

Analytic Methods:

For the molecular analysis of the Río Tinto old terrace, a polished section of the sample was prepared. It was subsequently analyzed by a ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) instrument (ToF-SIMS IV, ION-TOF, Münster, Germany), which provided the mapping of the positive and negative ions in relation to the mineral matrix. Such a technique did also show the distribution of the positive and negative ions coming from the minerals composing the original sedimentary materials.

The identification of the organic compounds was done using both the ion distribution in the sample and

the fragmentation pattern of positive and negative ions by using mMass 5.5.0 [8], ChemSpider molecular database (<http://www.chemspider.com/>) [9] and the ChemCalc online tool [10].

Results:

The ToF-SIMS analysis has identified different families of positive and negative ions to ~ 950 Da in the 2.1-Ma terrace sediments of Río Tinto. Attending to the fragmentation pattern (Fig 1) and mapping (Fig 2) of positive and negative ions, in the sample, different lipids including terpenoids, esters, hopanoids, steroids, and fatty acids were detected. Indeed, the occurrence of a high abundance of cholesterol derivatives associated to large microbial filamentous structures obtained by the mapping capabilities of the ToF-SIMS that is consistent with the large eukaryotic biomass found in the modern system including fungi and algae. Furthermore, there is the occurrence of secondary compounds that appear in the mineral matrix following other morphologies different from filament networks. They include different lipidic compounds that likely includes terpenoid, fungal (e.g. ergosterol) and/or plant-derived steroids. While the occurrence of fatty acids, short and long chained n-alkanes, hopanes, and fragmented esters could come from bacterial degradation, its association to the larger filamentous networks suggests that they are well-preserved fragments of biomolecules originated by eukaryotic living forms. Furthermore, alkylenes might be related to different biological degradation paths related to bacterial decarboxylation of fatty acids and bacterial wax.

However, the most outstanding result is the detection of very large ions (higher than 650, and up to 950 Da) associated to some different structures like the filamentous suggesting that the integrity of biomolecules is very high. In this regard, such well-preserved compounds meet the distribution pattern of different sulfate ions, which evidences a direct relation between early mineralization and preservation.

Implications:

ToF-SIMS analysis has provided the distribution of positive and negative fragments of different organic compounds in a polished sample of the 2.1-Ma old terrace. As a result, this method provides a direct association between microstructure and mineral composition. This is essential to support the syngenicity and preservation of the biological traces in relation with the

mineralization process. Therefore, under fast and early mineralization, it is evidenced that the preservation of biomolecules is possible even in the harsher conditions of low-pH environments [6].

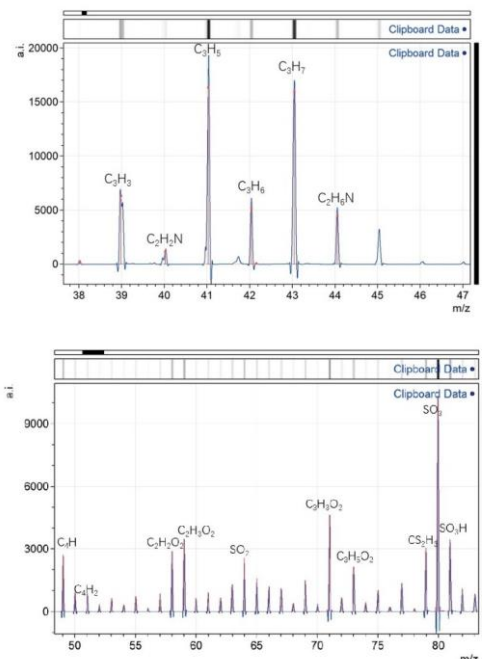


Fig 1. Spectrum showing ions obtained by the ToF-SIMS analysis of the old terrace sample. Where a.i. is the average intensity, and m/z mass-to-charge ratio.

Due to the similarity between Meridiani Planum and the Río Tinto on minerals [1, 11], if life ever existed in Meridiani Planum, the diagenesis process run under extremely acidic, though highly mineralizing, conditions would have probably preserved traces of life following the primary biological morphology and templated by the mineral composition. In this regard, ToF-SIMS could play an essential role in detecting organic compounds in old rocks of extraterrestrial origin.

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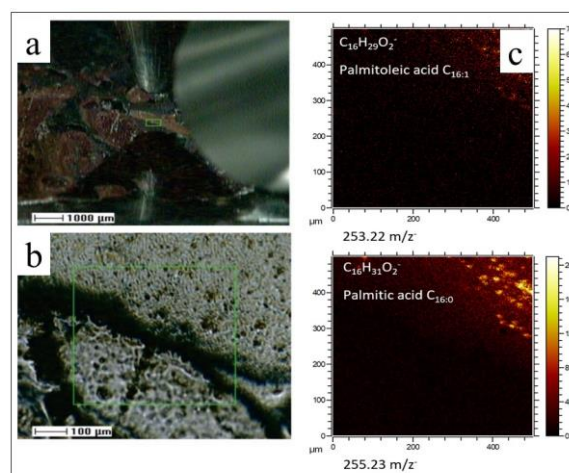


Fig 2. (a) ToF-SIMS camera image showing the data-collection of one area in the sample, (b) SEM image of the testing range (the green box corresponds to the analyzed area), (c) mapping of possible fatty acids in the sample.