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Spectroscopic Techniques on the Study of Biosignatures: Degradation of the Heme Group under Environmental Stress

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This study aims to examine preservation and degradation processes of biologically important molecules by spectroscopic techniques. The biomolecule model adopted as biosignature is the class of the porphyrins in their native as well degraded form (particularly the heme group), as this is an ubiquitous molecule on life as we know, and very resilient to degradation on the environment. The analysis of the degradation of heme group is mainly made by the study of the central metal ion behavior, through XANES, and neighboring chemical groups, by molecular spectroscopy techniques - Raman and Infrared. Our initial goal is to better understand the alterations suffered by the central metal ion after being exposed to simulated environmental stress, especially in which conditions the ion substitution happens. This may provide a diagnostic tool to infer the paleoenvironment from a measured substitution rate on fossil porphyrins. Simulations of extreme conditions (such as of the surface of Mars and extreme terrestrial environments), with varying pressure, temperature and incidence of electromagnetic radiation in different energy ranges are being performed in order to improve our understanding of the behavior of the molecules and to test their endurance. An interesting characteristic of porphyrins is the diversity of metal ions that can bind at its center, as in the heme (Fe) and chlorophyll (Mg), which can be replaced by geochemical processes. An example is the change of Fe by V in the heme group. The initial experiments were performed in aqueous media, in which the heme is not soluble, but some vanadium salts are, such as vanadium(III) chloride - VCl3, which is soluble in hydrochloric acid, in which heme is not. Using X-ray Absorption Spectroscopy - XAS (in particular XANES), it was possible to assess the substitution grade, the oxidation state and chemical neighborhood of the central metal ion of heme in the native or degraded forms, as well as in contact with the vanadium solution. Within this scope, synchrotron based XAS is a powerful tool for the characterization of the results of the simulations, as well as for direct measurement of environmental samples containing preserved porphyrin groups. Practically without any need of special sample preparation or environmental simulations, in the first case due to the high brightness of the source and the second energy range and because of flow that can subjecting the sample.