Are iron porphyrins stable enough to withstand ion bombardment?

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Abstract:
Porphyrin-type cofactors, especially hemes (iron porphyrins) occur in virtually all terrestrial organisms and are involved in basic metabolic processes. Therefore, hemes are regarded as evolutionary very old biomolecules. Furthermore, it has been speculated that molecules similar to heme could have also evolved on other planets or moons (Suo et al. 2007). Because of their aromaticity, porphyrins are generally very stable and can be easily detected with various analytical methods. These were among the reasons why porphyrins were presumed to be ideal biosignatures (Suo et al. 2007). However, abiotic syntheses for (metallo)porphyrins are now known (e.g., Fox and Strasdeit 2013; Pleyer et al., manuscript submitted). Consequently, these molecules may well be "false positive" biosignatures (Fox and Strasdeit 2017). Nevertheless, porphyrins are very interesting and important molecules in the search for extraterrestrial life. If porphyrins were found somewhere beyond Earth, this place would be worth a closer look. In such a case, however, a thorough examination of the geological context and a set of different analytical methods would be indispensable to minimize the risk of a false interpretation.
On Mars and some icy moons (e.g., Enceladus), which could potentially host life, porphyrins would be exposed to harsh conditions, such as extreme temperatures and radiation. Early experiments with γ-radiation showed that metalloporphyrins were not completely destroyed by doses of around 440 kGy (Dunning and Moore 1959). These results prompted us to study the effects of simulated cosmic radiation on metalloporphyrins. In a first series of experiments, chlorido(octaethyl-porphyrinato)iron(III), a simple model for heme and heme ancestors, was irradiated with helium (150 MeV n^{-1}; LET: 2.2 keV μm^{-1}) and iron ions (500 MeV n^{-1}; LET: 200 keV μm^{-1}). The doses were up to 1.5 kGy. The irradiation experiments were performed at the Heavy Ion Medical Accelerator at the National Institute of Radiological Sciences (NIRS) in Chiba, Japan. The study focused on the simulation of the behavior of iron porphyrins ejected by the "plumes" at the south pole region of Enceladus. Among the constituents of Enceladus' plumes are salts, mainly sodium chloride and sodium bicarbonate (Postberg et al. 2009). Therefore, chlorido(octaethylporphyrinato)iron(III) was embedded in a sodium chloride/sodium bicarbonate (4:1 mol/mol) matrix. To determine the radiation-induced decomposition, the remaining amount of metalloporphyrin was quantified by UV-visible and infrared spectroscopy. The experimental procedure will be described, and the results and their potential usefulness for future space missions will be discussed.

References

Dunning, H. N. and Moore, J. W. (1959) Decomposition of metal-porphyrin complexes by gamma irradiation. *Ind. Eng. Chem.* **51**, 161–164.
Fox, S. and Strasdeit, H. (2017) Inhabited or uninhabited? Pitfalls in the interpretation of possible chemical signatures of extraterrestrial life. *Front. Microbiol.* **8**, 1622.
Fox, S. and Strasdeit, H. (2013) A possible prebiotic origin on volcanic islands of oligopyrrole-type photopigments and electron transfer cofactors. *Astrobiology* **13**, 578–595.
Postberg, F., Kempf, S., Schmidt, J., Brilliantov, N., Beinsen, A., Abel, B., Buck, U. and Srama, R. (2009)Sodium salts in E-Ring ice grains from an ocean below the surface of Enceladus. *Nature* **459**, 1098–1101.
Suo, Z., Avci, R, Schweitzer, M. H. and Deliorman, M. (2007) Porphyrin as an ideal biomarker in the search for extraterrestrial life. *Astrobiology* **7**, 605–615.