

RPC 2020



Virtual Research Presentation Conference

A New Magnetic Electron Detection Technique for Astrobiology

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Program: Innovative Spontaneous Concepts

Assigned Presentation #RPC-097

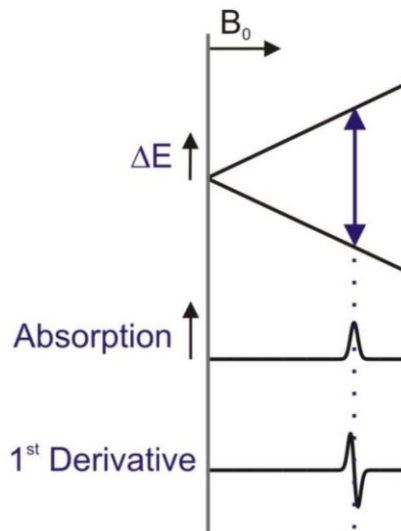


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Tutorial Introduction

Electron Paramagnetic Resonance (EPR) is a spectroscopic tool used to detect organic and inorganic materials containing unpaired electrons. Many minerals and organic radicals relevant to geologic settings are visible through this method. We set out to explore if EPR could be a viable technique in order to detect if minerals are interacting with organics. We tested Mars relevant metals specifically, Mn^{2+} , Fe^{2+} , and Fe^{3+} with 4 different organics to determine if the organics had any impact on the EPR spectra.





Problem Description

- a) **Context (Why this problem and why now):** Searching for biosignatures on other worlds is a growing field in planetary science and adapting new instruments to test this is important for future missions. As organics and any living matter in planetary samples will coexist within minerals or solutions containing dissolved metals, it is imperative to determine the feasibility of techniques capable of deconvoluting signals from metals, organics, and potential biosignatures within a lab setting prior to using the instrument in flight.
- b) **SOA:** EPR is frequently utilized to characterize inorganic and radical compounds in the field of chemistry. Within the last 10 years, EPR has been a growing technique in the field of astrobiology and biosignatures¹⁻⁵. For example, manganese minerals (which have been found on Mars⁶) have been shown to generate unique EPR signals due to biological reactions².
- c) **Relevance to NASA and JPL:** JPL has access to these instrument with one instrument at JPL and two at Caltech. This makes JPL uniquely situated to become a leader in this area of astrobiology.
 - a) We are collaborating with the EPR facility at Caltech with staff scientist Dr. Paul Oyala, the first JPL group to do so.
 - b) EPR could be a powerful technique for identifying organic-induced magnetic effects in planetary analog samples or samples returned from other worlds, and EPR has even been proposed to be used in flight⁵.
 - c) Incorporating this new EPR astrobiology expertise into our work at JPL could help enable technologies for future missions to Mars or the ocean worlds, and could also assess the value of EPR to Mars Sample Return concepts.

Methodology

a) All experiments were kept anoxic and ran inside of a glovebox.

Isolated solutions contained: 1 mM metal both with and without additives:

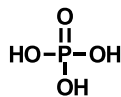
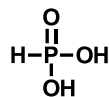
Metal

Mn²⁺

Fe²⁺

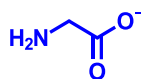
Fe³⁺

P Species

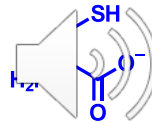


Phosphite

Phosphate



Glycine

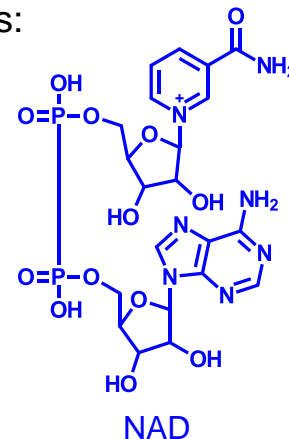


Cysteine



Benzoquinone

Organics



EPR samples were frozen in a liquid N₂ dewar prior to analysis

Samples were ran at 5 K with pulse and parallel EPR.

b) **Innovation, advancement:** This experimental study used advanced EPR technology to characterize organometallic interactions in planetary relevant samples

- Typically EPR studies done on biological samples with focus on metalloenzymes
- Caltech's Pulse EPR is a newer instrument (Sep. 2016) capable of detecting minor magnetic interactions

Results

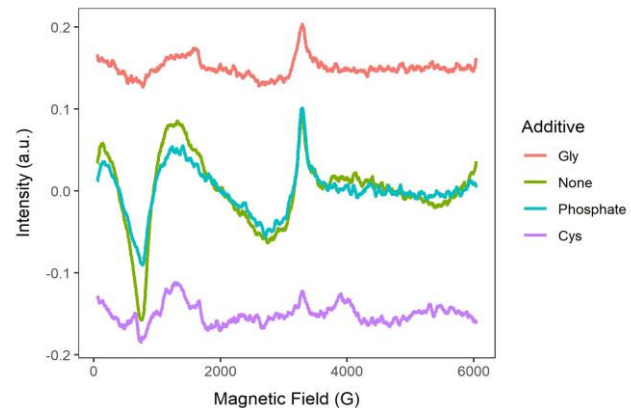
General Observations

- Typically additives formed EPR silent complexes with the metals including:
 - P species with Fe^{3+}
 - Amino acids with Mn^{2+} and Fe^{2+} ; however, new signals were detected for gly in Fe^{2+} samples
 - NAD with Mn^{2+}
- Benzoquinone generated several new EPR peaks for both Fe^{2+} and Fe^{3+} samples

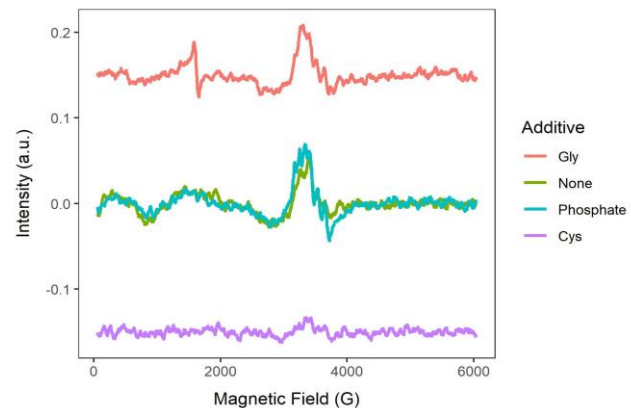


parallel

EPR Spectra of Samples Containing Ferrous (Fe^{2+}) Iron



perpendicular





Results

- a) **Accomplishments versus goals:** We accomplished all of the experiments we set out to test. Specifically, we tested how the EPR spectrum of three metals (Mn^{2+} , Fe^{2+} , Fe^{3+}) were impacted by organics (glycine, cysteine, benzoquinone, and NAD) or P species (phosphite or phosphate).
- b) **Significance:** Some organics did have a notable impact on the spectra while others were EPR silent. The phosphorous compounds did not change the spectra visibly. Spectra tended to be improved when liquid samples were used and at lower temperatures.
 - a) EPR of prebiotic and natural complex samples are grossly understudied. Here we laid the foundation for characterizing the components of mineralogical samples using EPR
- c) **Next steps include:**
 - a) expanding the organics and minerals tested
 - b) test under “mission relevant” conditions – synthesize a well characterized mineral with organics doped into it and dissolve with acid to to determine what is visible via EPR
 - c) Determine methods to remove organics, liberating metals for detection by EPR



Publications and References

- [1] Skrzypczak-Bonduelle, A. *et al. Appl Magn Reson* **2008**, 33: 371–97.
- [2] Kim, S. S. *et al. Astrobiology* **2011**, 11: 775–86.
- [3] Bourbin, M. *et al. Astrobiology* **2013**, 13: 151–162.
- [4] Ilya, A. *et al. Astrobiology* **2010**, 10: 425–36.
- [5] Tsay, F.-D. *et al. NASA ARC, Exobiology and Future Mars Missions* 1995 p 56-58 (SEE N89-26334 20-51).
- [6] Lanza, N. *et al. GRL* **2016**, 43: 7398–7407.