

Comment on mr-2022-10

Anonymous Referee #1

Referee comment on "Insight into the structure of black coatings of ancient Egyptian mummies by advanced electron magnetic resonance of vanadyl complexes" by Charles E. Dutoit et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2022-10-RC1>, 2022

This paper extends earlier CW EPR work (Dutoit, 2020) on vanadyl complexes in black matter found on Egyptian mummies to high-resolution pulse EPR experiments aimed at measuring hyperfine couplings to ligand nitrogens and matrix protons. From these data, conclusions about the size of bitumen particles and about the chemical variety of vanadyl compounds are drawn.

The spectroscopy is well executed, the data analysis and interpretation is reasonable, the writing is excellent, and the conclusions are supported by the presented evidence.

The following comments should be addressed:

1.
Line 134: It is very rare for organic radicals to have g values less than 2.002. Here, the authors give 1.9994. What is the uncertainty in this number? How was the magnetic field calibrated? Is the line asymmetric?
2.
It should be discussed why for the VO-nP species, not all hyperfine lines are visible. Presumably this is due to a distribution of hyperfine couplings resulting from ligation geometries that are less rigid than in porphyrins?
3.
In the experimental section, include the RF power used in the CW ENDOR experiments

4.

Figure 4c uses on the horizontal axis the weight-percentage VO-P content of the samples. Describe how this was determined. Also, add horizontal error bar to Figure 4c.

5.

The X/Y ratio model assumes a Gaussian lineshape (see SI page 7, line 83). What is the assumed linewidth, and how is it justified. Also, why is the assumption of a Gaussian lineshape valid?

6.

Do the spectral features for A-parallel and A-perpendicular occur at the same frequency offset in all samples?

7.

From the experimental data and the model fit in Figure 4c, it is concluded that the

8.

Line 231: The statement that the A-parallel ^1H ENDOR peak broadens and weakens as more bioorganic matter is mixed with bitumen needs some supporting evidence. Were reference spectra recorded for this? It is obvious that disorder in the hyperfine coupling will broaden and weaken the peak, but from where is it known that the mixing of bitumen with other substances will lead to this?

9.

Line 238: It is implied that protons more than 5-6 nm from the electron have zero electron-proton dipolar interactions. This is not correct. The interactions are small, but not zero. Also, it seems that

10.

Line 265: It is stated that VO-nP complexes are localized to the interfaces between bitumen aggregates and natural substances. Could it also be that VO-P from bitumen has been solubilized as VO-nP during processing and has migrated into the non-bitumen phase? How can this be excluded?

11.

In Eq.(3), it is not clear what A^2 in the second term represents. Does the 2 indicate squaring, or something else?

12.

Line 388: Regarding the orientation of the ^{14}N quadrupole tensor, what do DFT

calculations predict?

13.

By assigning different ^{14}N peaks in the HYSCORE spectra to different VO-P species, it is implicitly assumed that all four nitrogens in a porphyrin complex have the same coupling parameters. Is this assumption valid?

Other notes:

- Line 69: It is unclear what a "hindered" hyperfine interaction is. Maybe "unresolved" hyperfine interaction is the intended meaning.
- Line 75: "than in" -> "as in"
- Figure S6: "chlorophyle" -> "chlorophyll"
- In general, // should be replaced by || to indicate "parallel"
- Line 104: Pulse EPR was probably done on an E580, not a E500 spectrometer
- Figure 3d: the three colors for the three wavepackets indicating the three microwave pulses should be the same; different colors visually imply different frequencies
- Line 185: In CW ENDOR, the RF field doesn't have to be saturating.
- Lines 388: What is meant by "hindered"? "hidden"?