

Magn. Reson. Discuss., referee comment RC2
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Comment on mr-2022-10

Anonymous Referee #2

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-RC2>, 2022

This work presents an unusual application of EPR spectroscopy and related hyperfine techniques to the study of ancient egyptian mummies. The Authors apply ENDOR and HYSORE spectroscopies to characterize the local environment of vanadyl porphirin complexes contained in the bitumen present in the embalming mixture. Based on different ^{14}N hyperfine couplings, different types of vanadyl porphirin complexes are identified, which appear to be related to the origin of the mummy. The work is well written and the experiments carefully performed and I think they represent a new and original application of hyperfine techniques. I have a few comments that should be addressed before publication.

- The different VO species are assigned based on small differences in the dq-dq correlation peaks shown in Figure 6. However, the spectra were recorded using a single tau value ($\tau=200$ ns), which raises some doubts on the effect of blind spots. At least another tau value, possibly with a shorter length (96-100 ns) should be used to firmly assign the dq-dq cross peaks to different VO species and not, for example to the result of a distribution of hf values (strain). A simulation analysis showing the effect of different tau values on the dq-dq cross-peaks assuming the presence of the four VO different species or the effect of strain may be used as a possible alternative to substantiate the Authors assignment.
- It would be interesting to compare the data from these unusual samples with those of related vanadyl phthalocyanine and porphyrin molecular complexes (see for example H. Moons, Z. Phys. Chem. 2017, 231, 887; K. Fukui, J. Phys. Chem. 1993, 97, 11858 and reference therein). In these systems the full ^{14}N hyperfine and nuclear quadrupole tensors are derived. These values may be used as starting point for the simulation of the HYSORE experiments
- It would be useful to show at least as supplementary material, the simulation of the HYSORE experiments taken at the two magnetic field settings superimposed to the experimental data. This allows to better judge on the quality of the simulation.
- The negative g-shift ($g=1.9994$) of the signal assigned to carbon organic radicals of asphaltene should be commented. Do the Authors have a structure in mind for these radical species?

Minor points

- In Table 2 it would be useful to include the assignment to the different VO-P complexes
- The value of the magnetic field setting at which the HYSCORE and ENDOR spectra have been recorded should be given in the Figures caption