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Expression of concern: Ligand discrimination of myoglobin in solution: an iron L-edge X-ray absorption study of the active centre

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Expression of concern for 'Ligand discrimination of myoglobin in solution: an iron L-edge X-ray absorption study of the active centre' by Kathrin M. Lange *et al.*, *Chem. Commun.*, 2013, **49**, 4163–4165.

rsc.li/chemcomm

The Royal Society of Chemistry has been contacted by the authors of this *Chemical Communications* paper to inform us that this paper was investigated by the Ombudsman of the Helmholtz-Zentrum Berlin (HZB) as a consequence of an independent inquiry commission set up by HZB. They informed us that it cannot be fully excluded that the presented data is misleading due to an honest error.

The authors have provided the following statement on the re-investigation of their data:

"We recently reinvestigated our experimental results of this work in the light of a later published K-edge X-ray absorption study of carboxymyoglobin (MbCO), nitrosylmyoglobin (MbNO), oxymyoglobin (MbO₂), cyanomyoglobin (MbCN), aquomet myoglobin (metMb) and unligated myoglobin (deoxyMb) in physiological media.¹ Whereas in our L-edge study no significant energetic shifts of the L-edges are observed for the different myoglobin species, although one would expect these for iron species with different oxidation states, the K-edge data shows in the pre-edge region, which is correlated to the formally electric dipole forbidden Fe 3d ← 1s transitions, features that arise at different energies. Even though the pre-edge features of the K-edge do not necessarily need to mirror the L-edge results, since they might arise besides electric quadrupole transitions partially from 4p mixing into the final state, whereas the L-edge transition probes directly the d-orbitals, we reviewed all the raw data and lab book notations that were the basis of our publication one more time. The aim was to clarify whether X-ray induced sample damage and deposition of fragmented iron complexes on the membrane could have affected our experiment, leading to spectra that do not exclusively arise from the species in solution. We would like to share with you our experimental observations of that time in detail:

During the measurements of all the myoglobin species, we observed in the first scans a high background signal that was decreasing with time. In parallel, the signal at the iron L-edge was increasing. Following our lab book notations, we interpreted this observation at this time initially as arising from possible sample deposition on the membrane, which would lead to a reduced background from the solvent and an increased signal from Fe. We therefore moved the positioning motor of the cell to irradiate the membrane at a different position once we obtained a decent Fe-signal. On the new sample position, we directly obtained a strong Fe-signal. Also, we observed that the Fe signal disappeared when flushing the cell with water only. Thus, we concluded at this time that the observed decrease of background and the increase of iron signal is rather correlated to an initial diffusion process of the sample into pockets of water resting in the embayment of the cell where the membrane is located.

In conclusion, even though we discarded at this time the interpretation of our experimental observations as sample deposition on the membrane, with a view to the later published K-edge study we cannot fully exclude this possibility. We would like to share this notice with the scientific community."

The Royal Society of Chemistry has consulted with an independent expert who has reviewed the matter and who has informed us that in their opinion "there is absolutely no doubt, besides the bifurcation of arguments that certain data in this article needs to be reinvestigated and the measurements corrected for posterity."

In line with Committee on Publication Ethics guidelines, *Chemical Communications* is publishing this expression of concern in order to alert readers that we are presently unable to confirm the accuracy of the data reported in this paper.



An expression of concern will continue to be associated with the article until we receive conclusive evidence regarding the reliability of the reported data.

Richard Kelly

27th August 2019

Executive Editor, *Chemical Communications*.

References

- 1 F. A. Lima, T. J. Penfold, R. M. van der Veen, M. Reinhard, R. Abela, I. Tavernelli, U. Rothlisberger, M. Benfatto, C. J. Milne and M. Chergui, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1617–1631.

