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Calcium's influence on oxygen formation

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Abstract

Calcium is a necessary component of the catalyst that forms oxygen from water in photosynthesis. A study suggests that part of calcium's job is to enable the release of oxygen from this catalyst.

The mechanism of oxygen production in photosynthesis remains unresolved, despite many studies. The presence of a calcium ion in the inorganic active site of the complex that produces oxygen is particularly puzzling, because the reaction is a redox process involving the transfer of multiple electrons, whereas calcium is redox inactive (it cannot transfer electrons under biological conditions). Writing in *Nature Chemistry*, Bang *et al.*¹ provide insight into calcium's possible role. They report that, under oxidative conditions, oxygen molecules can be released from iron peroxide complexes — which can be thought of as simplified models of the active site — in the presence of calcium ions, but not in the presence of other metal ions that are better Lewis acids (electron-pair acceptors) than calcium.

Oxygenic photosynthesis, the process by which plants convert carbon dioxide to organic matter using solar energy, has generated the majority of oxygen (O₂ molecules) in the atmosphere, enabling life on Earth as we know it. The oxygen forms when water is oxidized, a complex chemical reaction involving the transfer of four electrons and four protons (H⁺ ions; Fig. 1a). The reaction is catalysed by the oxygen-evolving complex (OEC) — an inorganic cluster of four manganese ions and one calcium ion bridged by oxide ligands², buried in the photosynthetic protein complex known as Photosystem II (PSII). The mechanism of water oxidation is debated, particularly the role of calcium and the site in which the oxygen–oxygen (O–O) bond of the dioxygen molecule forms. Further insight might allow the rational design of effective catalysts for artificial photosynthesis³.

Chemists often target the synthesis of small molecular complexes that display structural motifs similar to enzyme active sites, for use as models that can be systematically investigated. This approach has been challenging for the OEC because the cluster is structurally complex and contains two types of metal. For their models, Bang *et al.* targeted complexes that contain one redox-active metal (iron) and one redox-inactive metal.

The authors focused on a step of water-oxidation chemistry that occurs after O–O bond formation, hypothesizing that it relates to the role of calcium in the OEC: the formation of oxygen from a peroxide moiety (O₂²⁻). They added solutions of redox-inactive metal ions to a redox-active iron peroxide species, Fe–(O₂²⁻), and obtained complexes containing the Fe–(O₂²⁻)–M motif (Fe is iron; M can be ions of calcium, strontium, zinc, lutetium, yttrium, or

scandium). This series of compounds conceptually mimics a putative peroxide complex from the OEC, and allowed them to systematically compare the effects of the redox-inactive metals on the properties of these compounds (Fig. 1b, c). The models are structurally different from the OEC because they have one iron rather than four manganese ions. However, they distill the effect of redox-inactive metals on the peroxide moiety into a simple combination of two metal ions that is easier to interrogate than the OEC.

Using electrochemical analysis, Bang *et al.* showed that the redox-inactive metals have a significant effect on electron transfer to and from the complexes. The propensity of the complexes to be chemically reduced (that is, to accept an electron) increases with the Lewis acidity of the M ion. Conversely, the ease with which the complexes are oxidized (an electron is removed) shows the opposite trend: the researchers observed an oxidation event in the presence of calcium or strontium ions, or in the absence of a redox-inactive metal, but not when the M ion was a stronger Lewis acid (zinc, lutetium, yttrium or scandium). Similar effects have been invoked previously to unravel the role of calcium ions in the OEC, in studies of complexes containing oxo (O^{2-}) or hydroxo (HO^-) motifs instead of peroxide moieties⁴⁻¹¹, but this is the first detailed study of a series of peroxide species in this context.

So what does this mean for oxygen release from the complex? In agreement with the electrochemical results, Bang and colleagues observed that the complexes incorporating zinc, lutetium, yttrium or scandium ions did not react with a chemical oxidant (ceric ammonium nitrate), so that no oxygen was produced. By contrast, treatment with the same oxidant led to oxygen release from the calcium and strontium complexes, and from Fe- (O_2^{2-}) that was not bound to a redox-inactive metal ion.

The effects of calcium and strontium ions are of particular interest because they are biologically relevant: calcium is the native component of the OEC, and strontium is the only metal that can replace calcium and still generate a functional catalyst. Notably, the authors' calcium and strontium complexes not only have similar electrochemical properties, but they also allow oxygen evolution from peroxide. The parallels between the biological and synthetic systems suggest that the study's conclusions may extend to the OEC — although the more complicated structure of the OEC and the different metals within it will affect the interactions with and the chemical reactivity of the peroxide moiety.

Do the findings reveal the mechanism of water oxidation? Not completely, but they cast light on the terminal step of the process. The observation that the iron peroxide compound can be oxidized to generate oxygen molecules in the absence of any redox-inactive metal implies that the role of calcium ions in PSII cannot be only to promote oxygen release. As the authors assert, the crucial point is that the calcium ion does not hinder oxygen release, whereas metals that are stronger Lewis acids could.

Because Bang and colleagues' metal complexes contain a preformed peroxide ligand, they do not tell us anything about the most elusive step in the water oxidation reaction: the formation of the O–O bond. This remains a challenging but key target for future studies. Their work nonetheless provides an insightful contribution to the ongoing debate about the role of calcium ions in PSII.

References

1. Bang S, et al. *Nature Chem.* 2014; XXX:XXX–XXX.
2. Umena Y, Kawakami K, Shen JR, Kamiya N. *Nature.* 2011; 473:55–60. [PubMed: 21499260]
3. Lewis NS, Nocera DG. *Proc Natl Acad Sci USA.* 2006; 103:15729–15735. [PubMed: 17043226]
4. Fukuzumi S, et al. *Nature Chem.* 2010; 2:756–759. [PubMed: 20729896]
5. Lee YM, et al. *Chem Sci.* 2013; 4:3917–3923. [PubMed: 25426288]
6. Li FF, Van Heuvelen KM, Meier KK, Munck E, Que L. *J Am Chem Soc.* 2013; 135:10198–10201. [PubMed: 23802702]
7. Yoon H, et al. *J Am Chem Soc.* 2013; 135:9186–9194. [PubMed: 23742163]
8. Park YJ, et al. *Chem Sci.* 2013; 4:717–726. [PubMed: 24058726]
9. Kanady JS, Tsui EY, Day MW, Agapie T. *Science.* 2011; 333:733–736. [PubMed: 21817047]
10. Tsui EY, Tran R, Yano J, Agapie T. *Nature Chem.* 2013; 5:293–299. [PubMed: 23511417]
11. Herbert DE, Lionetti D, Rittle J, Agapie T. *J Am Chem Soc.* 2013; 135:19075–19078. [PubMed: 24304416]

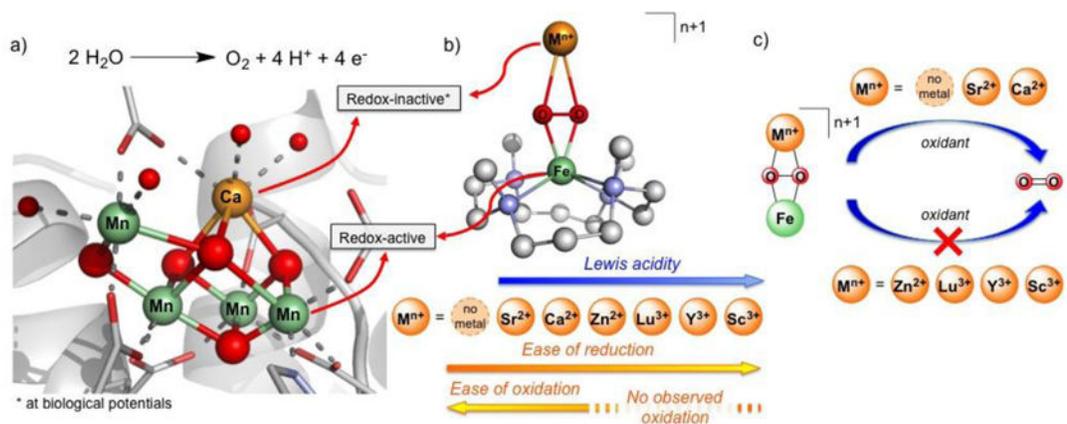


Figure 1. Oxygen release from iron peroxide complexes

a, In the oxygen-evolving complex (OEC) of the photosynthetic apparatus, water is oxidized to produce oxygen — a reaction involving the transfer of four electrons (e^-) and four protons (H^+). The OEC's structure contains four redox-active manganese ions and one calcium ion,² which is redox-inactive under biological conditions. Oxygen atoms are shown in red., Bang *et al.*¹ prepared complexes that model the OEC in the final step of water oxidation. In these complexes, a redox-active iron atom (green) is bound to a TMC ligand (shown in grey and blue) and a peroxide moiety (red), which binds a redox-inactive metal (M) ion. The ease with which the complexes can be reduced correlates with the Lewis acidity of the metals. Only the complexes that contained strontium ions (Sr^{2+}) or calcium ions (Ca^{2+}), or which lacked a redox-inactive metal, could be oxidized. **c**, When treated with an oxidant, only the oxidizable complexes reacted to produce oxygen.