Research pinpoints role of 'helper' atoms in oxygen release

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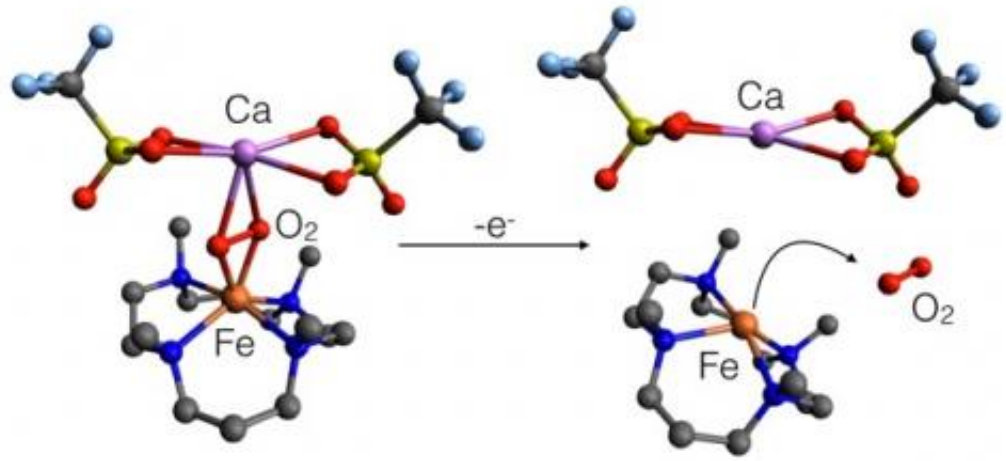

This illustration shows a model molecular complex that mimics the final step in the cycle of photosynthesis: oxygen release. Only ions of calcium (Ca2+) and strontium (Sr2+) are able to release oxygen molecules (O2), while other elements failed to do so. A study detailing this oxygen-releasing process provides important insights into why nature chose calcium ions to assist the oxygen-releasing steps in photosynthesis. Credit: Riti Sarangi/SLAC

(Phys.org) —Experiments at the Department of Energy's SLAC National Accelerator Laboratory solve a long-standing mystery in the role calcium atoms serve in a chemical reaction that releases oxygen into the air we breathe. The results offer new clues about atomic-scale processes that drive the life-sustaining cycle of photosynthesis and could help forge a foundation for producing cleaner energy sources by synthesizing nature's handiwork.

The research is detailed in a paper published Sept. 14 in *Nature Chemistry*. X-ray experiments at SLAC's Stanford Synchrotron Radiation Lightsource (SSRL), a DOE Office of Science User Facility, played a key role in the study, led by Wonwoo Nam at Ewha Womans University in Korea in a joint collaboration with Riti Sarangi, an SSRL staff scientist.

"For the first time, we show how calcium can actually tune this oxygen-releasing reaction in subtle but precise ways," said Sarangi, who carried out the X-ray work and supporting computer simulations and calculations. "The study helps us resolve the question, 'Why does nature choose calcium?'"

Photosynthesis is one of many important biological processes that rely on proteins with metal-containing centers, such as iron or manganese. The chemistry carried out in such centers is integral to their function. Scientists have known that the presence of calcium is necessary for the oxygen-releasing stages of photosynthesis, but they didn't know how or why.

The SSRL experiment used a technique known as X-ray absorption spectroscopy to explore the chemical and structural details of sample systems that mimic of the oxygen-releasing steps in photosynthesis. The basic oxygen-releasing system contained calcium and was centered around an iron atom.

Researchers found that charged atoms, or ions, of calcium and another element, strontium, bind to the oxygen atoms in a way that precisely tunes the chemical reaction at the iron center. This, in turn, facilitates the bond formation between two oxygen atoms. The study also revealed that calcium and strontium do not obstruct the release of these bound oxygen atoms into the air as an oxygen molecule—the final step in this reaction.

"We saw that unless you use calcium or strontium, this sample system will not release oxygen," Sarangi said. "Calcium and strontium bind at just the right strength to facilitate the oxygen release. Anything that binds too strongly would impede that step."

While the sample system studied is not biological, the chemistry at work is considered a very good analogue for the oxygen-releasing steps carried out in photosynthesis, she said, and could assist in constructing artificial systems that replicate these steps. The next step will be to study more complex samples that perform more closely to the actual chemistry in photosynthesis.

More information: S. Bang, et al., *Nature Chemistry*, 14 September 2014. DOI: 10.1038/nchem.2055

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