

ticular, it was unclear whether “S₄” existed as a discrete chemical intermediate, or whether it might simply represent a transition state containing S₃ with an oxidized tyrosine (S₃Y_Z^{ox}). The latter would imply an intimate role for Y_Z^{ox} in water oxidation, perhaps through hydrogen-atom transfer (9). In contrast, if S₄ exists as a discrete intermediate, then a range of mechanisms for the terminal reaction preceding oxygen formation are possible. A subtle delay in oxygen release relative to Y_Z^{ox} reduction (10, 11) hinted that S₄ might exist as a discrete intermediate rather than simply being a transition state between S₃ and S₀. This conclusion was strengthened by a recent experiment showing that if one increases the partial pressure of oxygen on photosystem II, water oxidation is blocked at S₃. This suggests that increasing oxygen concentration shifts the equilibrium from S₄ + oxygen to S₃ (12).

Haumann *et al.* (1) used a conceptually straightforward but experimentally challenging “pump-probe” time-resolved x-ray spectroscopy experiment to obtain direct structural evidence for an S₄ state. To appreciate the difficulty of this approach, it is important to remember that even “simple” static x-ray absorption spectroscopy of photosystem II is challenging because of the intrinsically low Mn concentration. The present measurements would have been impossible without the high-brightness third-generation synchrotron sources that provide higher x-ray flux. Kinetic traces (1) show clearly that the S₁→S₂ and S₂→S₃ steps have very similar transient behavior, although the latter is somewhat slower. This finding is important because of the continuing controversy over whether Mn has been oxidized during the S₂→S₃ transition (13). The Haumann *et al.* data provide further support for the growing consensus that Mn is oxidized during both the S₁→S₂ and S₂→S₃ transitions. In contrast, the kinetic transient for the S₃→S₀ transition is distinct, with a 250-μs lag phase followed by a slow 1.1-ms transient phase. The latter phase is of opposite sign, representing Mn reduction to the S₀ state, and corresponds to the observed rate of oxygen release and reduction of Y_Z^{ox}. The former, more rapid phase provides direct evidence for the existence of a discrete S₄ intermediate state.

The lag phase indicates that the S₃ and S₄ states have similar x-ray absorption spectra and rules out several possible mechanisms for oxygen evolution. There has been widespread speculation that water oxidation might use a manganyl (Mn=O) species as the oxidant (9). This possibility was recently ruled out for S₃ (14). The present work by Haumann *et al.* extends this exclu-

sion to S₄ because neither the S₃ nor S₄ state shows an intense transition on the low-energy side of the x-ray absorption “edge” (this is the abrupt increase in x-ray absorption cross section that occurs when the x-ray energy matches the binding energy of the Mn 1s electron). Such “pre-edge” transitions are the spectroscopic signature of manganyl species (14). Alternatively, the high-pressure oxygen studies (12) were interpreted in terms of an S₂ state with an associated H₂O₂ molecule for “S₄.” This too is now excluded, because the Mn would be reduced in this state, relative to the previous S₃ state.

Haumann *et al.* (1) favor a model in which “S₄” contains S₃Y_Z^{ox}. That is, the fourth oxidizing equivalent in the water oxidation cycle resides on the tyrosine cofactor. On the basis of the positive reaction entropy and the equilibrium isotope effect for S₄ formation, they suggest that the 250-μs lag phase represents the lifetime for proton release from an intermediate chemical species bound to the oxygen-evolving complex. Tests of this and more detailed mechanistic studies will await future experiments. For now, the availability of the intense x-ray beams available at third-generation synchrotron sources has permitted the detec-

tion of a new intermediate in the water oxidation reaction. With this demonstration of feasibility, a wide range of other applications of microsecond time-resolved x-ray absorption spectroscopy to chemically and biologically important reactions can now be imagined.

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PLANETARY SCIENCE

What Do We Need to Know to Land on the Moon Again?

Maria T. Zuber and Ian Garrick-Bethell

In July 1969, the Apollo 11 lunar excursion module *Eagle* descended toward the Sea of Tranquility with Neil Armstrong in command. At 300 m above the lunar surface, short on fuel and looking for a smooth area on which to land, Armstrong “did not like what he saw. A crater as big as a football field was just ahead, surrounded by a field of boulders, some as big as Volkswagens” (1). Despite the obstacles, *Eagle* touched down safely, delivering the first human beings to the surface of the Moon in one of humankind’s greatest technological achievements. As the United States and other nations actively plan to return to the Moon, a renewed discussion of the scientific knowledge of the lunar surface that is needed for future landings is appropriate.

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Of the dramatic and successful Apollo 11 landing, one thing can be said with certainty: We won’t do it like that again. Starting with the Ranger 7 spacecraft and continuing with the Lunar Orbiters, images were used to characterize potential lunar landing sites by accumulating statistics of small-scale surface slopes and roughness. Most landings occurred in the maria, relatively smooth volcanic plains marred by small craters surrounded by rougher ejecta blankets and blocks. Two Apollo missions, 14 and 16, landed in non-mare (highland) regions, thanks to the skill of astronauts in manually piloting the lunar modules to locations safe enough for landing. But in today’s risk-averse climate, the Apollo-era knowledge of the lunar surface—and, arguably, even our present knowledge—would not meet expectations with respect to safety. Future landings on the Moon, whether human or robotic, will demand a greater scientific knowledge of the lunar surface. In the selection of a landing site, two factors are relevant: landing safety and

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