



The photosynthetic oxygen evolution does not exclude the important role and contribution of bicarbonate photolysis

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Abstract Photosynthesis is the most important biochemical reaction on Earth. It has co-evolved and developed with the Earth, driving the biogeochemical cycle of all elements on the planet and serving as the only chemical process in nature that can convert light energy into chemical energy. Some heavy oxygen isotopic (^{18}O) labeling experiments have “conclusively” demonstrated that the oxygen released by photosynthesis comes only from water and are written into textbooks. However, it is not difficult to find that bicarbonate has never been excluded from the direct substrate of photosynthesis from beginning to end during the history of photosynthesis research. No convincing mechanism can be used to explain photosynthetic oxygen evolution solely from water photolysis. The bicarbonate effect, the Dole effect, the thermodynamic convenience of bicarbonate photolysis, the crystal structure characteristics of photosystem II, and the reinterpretation of heavy oxygen isotopic labeling (^{18}O) experiments all indicate that the photosynthetic oxygen evolution does not exclude the important role and contribution of bicarbonate photolysis. The recently proposed view that bicarbonate photolysis is the premise of water photolysis, bicarbonate photolysis and water photolysis work together with a 1:1 (mol/mol) stoichiometric relationship, and the stoichiometric relationship between oxygen and carbon dioxide released during photosynthetic

oxygen evolution is also 1:1, has excellent applicability and objectivity, which can logically and reasonably explain the precise coordination between light and dark reactions during photosynthesis, the bicarbonate effect, the Dole effect, the Kok cycle and the neutrality of water and carbon in nature. This is of great significance for constructing the bionic artificial photosynthetic reactors and scientifically answering the question of the source of elemental stoichiometric relationships in nature.

Keywords Bicarbonate effect · Dole effect · Kok cycle · Heavy oxygen isotope · Artificial photosynthetic reactor

1 Introduction

Photosynthesis is the only chemical process on Earth that converts light energy into chemical energy. Along with the evolution and development of the Earth, it drives the biogeochemical cycle of all the elements on the planet. The widely accepted view is that the photosynthetic oxygen evolution comes from water, not from inorganic carbon. However, from the photosynthesis discovery, photosynthetic oxygen evolution experiments and the structural characteristics of the photosystem II in the oxygen-evolving center, it can be seen that the photosynthetic oxygen evolution can never exclude the important role and contribution of bicarbonate photolysis. From the thermodynamic convenience of bicarbonate photolysis, the overall equation of photosynthesis, the earth's own water/carbon balance and the Dole effect, bicarbonate photolysis dominates the photosynthetic oxygen evolution, and bicarbonate photolysis and water photolysis play a role in photosynthetic oxygen evolution with a 1:1 (mol/mol) stoichiometric relationship (Wu 2023).

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2 Photosynthetic inorganic carbon assimilation does not preclude bicarbonate assimilation

Although it is widely accepted that the oxygen evolution during photosynthesis comes from water rather than inorganic carbon (Shevela et al. 2023), However, from the history of photosynthesis research, it is not difficult to find that people have never excluded bicarbonate from the direct substrate of photosynthesis. In Van Helmont's experiment, not only rain or distilled water itself could nourish the willow tree, but also the bicarbonate dissolved in it. In the experiments of Ingen-Housz and Senebier, leaves submerged in solutions could absorb not only carbon dioxide but also but also bicarbonates dissolved in water. Similarly, in de Saussure's experiments, the additional weight gained by plants could come from water or bicarbonate dissolved therein (Govindjee et al. 2006; Wu and Rao 2023). Not only aquatic plants such as algae can directly utilize bicarbonate (Yamano et al. 2015; Xie and Wu 2017), but also terrestrial plants have numerous evidences that they can directly use root-derived bicarbonate (Gao and Zhou 2001; Wu and Xing 2012; Rao and Wu 2017).

3 Photosynthetic oxygen evolution does not exclude bicarbonate photolysis

Although the experiment using heavy oxygen isotopic (^{18}O) labeling by Ruben et al. (1941) “conclusively” proved that the oxygen release during photosynthesis came solely from water (Ruben et al. 1941) and was written into textbooks. However, there is still a lack of convincing explanation for the precise mechanism of solely water photolysis to account for the oxygen evolution during photosystem II. Especially, “whether the photosynthetic oxygen-evolving center in the $\text{S}_3 \rightarrow \text{S}_4 \rightarrow \text{S}_0$ transition state of the Kok cycle is bound to water or not” lacks theoretical (large energy barrier problem) and experimental basis (S_4 state is not directly observed) (Guo et al. 2023; Song and Wang 2023; Song et al. 2023). Moreover, more and more experimental evidence also proves that the Hill reaction increases the amount of oxygen release several times or even more than ten times under the stimulation of bicarbonate (bicarbonate effect). The standard free energy of bicarbonate photolysis ($\text{H}^+ + \text{HCO}_3^- \rightarrow 1/2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ + \text{CO}_2$) (24.8 kcal/mol) significantly less than that of water photolysis ($\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{e}^- + 2\text{H}^+$) (37.3 kcal/mol) (Dismukes et al. 2001). These have raised serious doubts about that the photosynthetic oxygen evolution comes solely from water (Warburg and Krippahl 1958; Stemler and Radmer 1975; Govindjee et al. 2006; Wu 2021a).

Photosynthetic oxygen evolution is the physiological response of plants under specific physiological conditions. These experiments of heavy oxygen isotopic (^{18}O) labeling to conclusively prove oxygen released solely from water (Ruben et al. 1941; Stemler and Radmer 1975; Radmer and Ollinger 1980; Clausen et al. 2005; Hillier et al. 2006), the hydroxylamine treatment experiments (Shevela et al. 2008; Ulas et al. 2008), the analysis of Fourier transform infrared difference spectroscopy (Aoyama et al. 2008), and the resolution of crystal structures in photosystem II (Loll et al. 2005; Umena et al. 2011; Bhowmick et al. 2023) have been conducted under non-actual physiological conditions, their results cannot rule out the possibility of oxygen released from bicarbonate photolysis under actual physiological conditions.

Chloroplasts possess diverse carbonic anhydrases isoenzymes, thylakoid carbonic anhydrase has the characteristics of photosystem II, photosystem II exhibits carbonic anhydrase activity, and dehydration and hydration of thylakoid carbonic anhydrase depends on pH. The above characteristics of photosystem II and thylakoid carbonic anhydrase make oxygen of OH, COOH, O–O, C=O and other groups exchange rapidly with that of water in the photosynthetic oxygen-evolving system. The oxygen of labeled bicarbonate from heavy oxygen isotopic (^{18}O) labeling experiments conducted by Ruben et al. (1941) and Stemler and Radmer (1975) is almost completely exchanged with that of other groups, so the isotope composition of oxygen released are consistent with that of water (Wu 2021a). Even so, it is remain uncertain whether it came solely from water or from bicarbonate because ^{18}O of bicarbonate had be exchanged almost entirely with ^{16}O of water in these experiments.

The degree to which bicarbonate binds to the photosynthetic oxygen-evolving center depends on physiological conditions (Bearden and Malkin 1973; Stemler and Murphy 1983; Bowden et al. 1991; Moubarak-Milad and Stemler 1994; Lu and Stemler 2007; Kozlov et al. 2010; Tikhonov et al. 2018; Shevela et al. 2020). The ^{18}O -labeled experiments of saturated flash illuminating dark-adapted chloroplasts demonstrated that the released oxygen was not related to exogenous added bicarbonates (Radmer and Ollinger 1980; Clausen et al. 2005; Hillier et al. 2006), but it cannot be ruled out that the oxygen in these experiments came from bicarbonates, because exogenous added bicarbonates are difficult to reach the photosystem II oxygen-evolving center under saturated flash illumination (Wu 2023). Therefore, the oxygen release of photosystem II is independent of exogenous bicarbonate, but the bound-bicarbonate photolysis of photosystem II is not excluded, which can be supported by the fact that the photosynthetic oxygen evolution of photosystem II under a short-time saturated flash is less than that under the continuous

illumination by a factor of 10 (Radmer and Ollinger 1980), and the binding of bicarbonate to photosystem II is controlled by pH and redox potential (Stemler and Murphy 1983; Kozlov et al. 2010).

Fourier transform infrared difference spectroscopy analysis shows the similarity between the $\text{H}^{12}\text{CO}_3^-$ -minus- $\text{H}^{13}\text{CO}_3^-$ -double difference spectra of photosystem II oxygen-evolving center and that of photosystem II non-heme iron under first flash illumination. However, it cannot be ruled out that bicarbonate of the photosystem II oxygen-evolving center, which treated by a lower pH (pH 6.0) prior to infrared spectral determination, may have been dissociated by weak acids (Aoyama et al. 2008). The absence of CO_2 release from the photosystem II oxygen-evolving center by hydroxylamine destruction does not exclude the binding of bicarbonate to the photosystem II oxygen-evolving center under physiological conditions, as the binding of bicarbonate to the photosystem II oxygen-evolving center may have been liberated by a weak acid environment (pH 6.0) prior to hydroxylamine treatment in their experiments (Shevela et al. 2008; Ulas et al. 2008).

Similarly, Loll et al. (2005), Umena et al. (2011) and Bhowmick et al. (2023) did not observe the binding of bicarbonate to the oxygen-evolving center of photosystem II crystals grown at pH lower than 7.0, which does not rule out the binding of bicarbonate to the oxygen-evolving center of photosystem II under physiological conditions. The binding probability of bicarbonate to the oxygen-evolving center of photosystem II crystals grown at lower pH is significantly lower than that grown at pH 7.5 (Ferreira et al. 2004). The binding of bicarbonate to the oxygen-evolving center is most likely not observed in photosystem II crystals grown at pH below 7.0, while this binding can be observed in the crystal structure of photosystem II grown at pH 7.5 with a high probability (Ferreira et al. 2004). The binding of the oxygen-evolving center of photosystem II and bicarbonate may depend on the physiological environment of crystal growth such as pH and redox potential, and plant physiological environment may determine the photosynthetic function.

If water photolysis of plants is the sole source of atmospheric O_2 , and the concentration of O_2 in the atmosphere remains essentially unchanged on geological scales, and seawater constitutes the vast majority of Earth's water, then the content of ^{18}O in atmospheric O_2 should be consistent with that in seawater. However, paradoxically, the ^{18}O content of O_2 in the atmosphere is significantly higher than that of water in ocean and lower than that of CO_2 dissolved in seawater. The enrichment of ^{18}O in atmospheric O_2 is nearly 24‰ higher than that in seawater (currently 23.5‰), and this enrichment of ^{18}O is known as the Dole effect (Dole 1935; Dole and Jenks 1944).

Many scientists have attempted to analyze the causes of the Dole effect by studying the fractionation of oxygen isotopes in the nature, but ultimately failed to identify the main contributor to the Dole effect other than photosynthetic oxygen evolution. The transportation of photosynthetic oxygen released by plants hardly undergoes isotopic fractionation (Guy et al. 1993). The global ^{18}O enrichment of water in leaves relative to seawater is only 4.4‰ (Farquhar et al. 1993). Even considering global canopy transpiration, the reduction of the Dole effect induced by terrestrial vegetation is very small (0.3‰–0.4‰) (Bender et al. 1994); the ratio of global terrestrial and oceanic primary production remains between 1.8 and 1.0, which does not affect the Dole effect in the mid-Holocene (Beerling 1999). The isotopic fractionation caused by respiration and diffusion in soil is also small, with the $\delta^{18}\text{O}$ content of soil O_2 ranging from -1.6‰ to 0.06‰ . Even considering global soil respiration, it would only reduce the Dole effect by 1–1.5 ‰ (Angert and Luz 2001; Angert et al. 2001, 2003). The photochemical reaction between stratospheric CO_2 and O_2 causes isotopic exchange, reducing the $\delta^{18}\text{O}$ of atmospheric O_2 by only 0.4 ‰ (Bender et al. 1994). Overall, when scientists consider all factors (chemical, physical, and biological) on a global scale, the ^{18}O enrichment of atmospheric O_2 relative to that of seawater (Dole effect) remains at 21–24 ‰ (Bender et al. 1994; Hoffmann et al. 2004; Mader et al. 2017). Therefore, we can't help but question whether the photosynthetic oxygen released by plants only comes from water (Metzner 1975; Wu 2023).

4 Bicarbonate photolysis and water photolysis has a 1:1 (mol/mol) stoichiometric relationship

Any evidence that water is the sole substrate for photosynthetic oxygen evolution is becoming increasingly indefensible in the face of new knowledge and discoveries. Since it cannot be ruled out that bicarbonate photolysis occurs in photosynthetic oxygen evolution, does it mean that bicarbonate photolysis and water photolysis coexist in the process of photosynthetic oxygen evolution? What is the stoichiometric relationship between bicarbonate photolysis and water photolysis?

Although the fact that photosynthetic oxygen release is several times higher under stimulation by bicarbonate indicates that bicarbonate photolysis dominates and plays an absolute superior role in photosynthetic oxygen evolution (Warburg and Krippahl 1958; Stemler and Radmer 1975). However, the fact that a very small amount of oxygen in $\text{HC}^{18}\text{O}_3^-$ labeling experiments comes from labeled $\text{HC}^{18}\text{O}_3^-$ seems to indicate that bicarbonate photolysis accounts for a small share, and the role of

Table 1 $\delta^{18}\text{O}$ and ^{18}O content of different components in the atmosphere and seawater (data from Metzner 1975) (maximum oxygen exchange coefficient between carbon dioxide and bicarbonate is 1.012, data from Reid and Urey (1943))

	$\delta^{18}\text{O}$	^{18}O content
Water in seawater	0‰	0.1995
Atmospheric O_2	22.06‰	0.2039
	23.56‰	0.2042
Atmospheric O_2 (average)	23.06‰ (Calculated value)	0.2041
HCO_3^- in seawater (maximum exchange)	54.14‰	0.2103
HCO_3^- in seawater (moderate exchange)	47.62‰	0.2090
HCO_3^- in seawater (no exchange)	41.60‰	0.2078

bicarbonate photolysis in photosynthetic oxygen release is minimal or even negligible (Hillier et al. 2006). To correctly understand the process and mechanism of photosynthetic oxygen evolution, we need to discover the natural laws from these two contradictory “appearances” and eliminate the false while preserving the true, and understand them from the surface to the essence.

The standard free energy of bicarbonate photolysis to release oxygen (24.8 kcal/mol) is significantly lower than that of water photolysis to release oxygen (37.3 kcal/mol), indicating that bicarbonate photolysis has a thermodynamic advantage (Dismukes et al. 2001). In the overall equation of photosynthesis, $\text{CO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{chlorophyll}} (\text{H}_2\text{O} + \text{H}^+ + \text{HCO}_3^-) + \text{light} \rightarrow \text{C}(\text{H}_2\text{O}) + \text{O}_2$, it can be seen that if bicarbonate photolysis produces CO_2 , which then enters the dark reaction (carbon dioxide concentrating mechanisms (CCMs) in photosystem II) (Wu 2021b), maintaining the balance of the chemical reactions requires a stoichiometric relationship of 1:1 mol/mol between bicarbonate photolysis and water photolysis. Additionally, from the perspective of the Earth's own water and carbon balance, the stoichiometric relationship between bicarbonate photolysis and water photolysis is also 1:1 mol/mol (Wu and Wu 2022; Wu 2023).

In addition, the chemical stoichiometry of bicarbonate photolysis and water photolysis can be obtained from the oxygen isotopic composition from the atmospheric O_2 , water and bicarbonate dissolved in seawater. Table 1 shows the $\delta^{18}\text{O}$ and ^{18}O content of different components in the atmosphere and seawater (data from Metzner 1975). If the oxygen in the atmosphere comes only from water, the $\delta^{18}\text{O}$ and ^{18}O content of water in the ocean should be close to those in the atmosphere. However, in fact, the difference between $\delta^{18}\text{O}$ of water in the ocean and that in the atmosphere is 21‰ to 24‰, which is called the Dole effect (Mader et al. 2017). If the oxygen in the atmosphere comes from both water and bicarbonate dissolved in water, we can calculate the proportion of bicarbonate photolysis to total photosynthetic oxygen evolution with different degrees of oxygen isotope exchange between carbon dioxide and bicarbonate ion (maximum exchange, medium exchange, and 0 exchange) according to the data in Table 1, which are

42.59%, 48.42% and 55.42%, respectively. When the degree of oxygen isotope exchange between carbon dioxide and bicarbonate reaches 42%, the stoichiometric relationship between bicarbonate photolysis and water photolysis is 1:1 (mol/mol).

If we calculate the enrichment of ^{18}O in atmospheric O_2 based on the assumption that bicarbonate photolysis and water photolysis account for half of the photosynthetic oxygen production, the results are 0.2036 (no exchange), 0.2043 (moderate exchange), and 0.2049 (maximum exchange), respectively. When the degree of oxygen isotope exchange between CO_2 and HCO_3^- is moderate, the calculated value (0.2043) is very close to the observed average value (0.2041).

5 Conclusion and outlook

From the history of photosynthesis discovery, the mechanism of known photosynthetic oxygen evolution, the thermodynamic characteristics of bicarbonate photolysis and water photolysis, the general equation of photosynthesis, the water and carbon balance in nature, and the verification calculation based on the oxygen isotopic composition of O_2 in the atmosphere, water in seawater, and bicarbonate dissolved in seawater, it can be concluded that plants can assimilate bicarbonate, bicarbonate photolysis is the prerequisite for water photolysis, and bicarbonate photolysis and water photolysis work together in a 1:1 (mol/mol) stoichiometric relationship. The stoichiometric relationship between oxygen and carbon dioxide released during photosynthetic oxygen evolution is also 1:1.

In the future, we can use the dual-element bidirectional isotope tracer (culture) technology to obtain evidence and stoichiometric relationship between bicarbonate photolysis and water photolysis, confirm the occurrence of bicarbonate photolysis events by investigating the crystal structure of photosystem II in a simulated physiological dynamic environment, and further verify the stoichiometric relationship between bicarbonate photolysis and water photolysis in photosynthetic oxygen release by measuring the tri-oxygen isotopic composition of water in ocean,

bicarbonate dissolved in seawater and atmospheric oxygen in the biosphere, challenging the traditional view of oxygen evolved only from water splitting. The regulation of photosynthesis by inorganic carbon is extended to the photo-reaction stage, which provides a theoretical basis for revising the chapter on photosynthesis in textbooks and helping people reconsider the mechanism of photosynthesis.

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Declarations

Conflict of interest The author declares no conflict of interest.

References

- Angert A, Luz B (2001) Fractionation of oxygen isotopes by root respiration: Implications for the isotopic composition of atmospheric O_2 . *Geochim Cosmochim Acta* 65(11):1695–1701
- Angert A, Luz B, Yakir D (2001) Fractionation of oxygen isotopes by respiration and diffusion in soils and its implications for the isotopic composition of atmospheric O_2 . *Global Biogeochem Cycl* 15(4):871–880
- Angert A, Barkan E, Barnett B, Brugnoli E, Davidson EA, Fessenden J, Maneepong S, Panapitukkul N, Randerson JT, Savage K, Yakir D, Luz B (2003) Contribution of soil respiration in tropical, temperate, and boreal forests to the ^{18}O enrichment of atmospheric O_2 . *Global Biogeochem Cycl* 17(3):1089
- Aoyama C, Suzuki H, Sugiura M, Noguchi T (2008) Flash-induced FTIR difference spectroscopy shows no evidence for the structural coupling of bicarbonate to the oxygen-evolving Mn cluster in photosystem II. *Biochemistry* 47(9):2760–2765
- Bearden AJ, Malkin R (1973) Oxidation-reduction potential dependence of low-temperature photoreactions of chloroplast photosystem II. *BBA Bioenergetics* 325(2):266–275
- Beerling DJ (1999) The influence of vegetation activity on the Dole effect and its implications for changes in biospheric productivity in the mid-Holocene. *Proc Roy Soc Lond B* 266(1419):627–632
- Bender M, Sowers T, Labeyrie L (1994) The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core. *Global Biogeochem Cycl* 8(3):363–376
- Bhowmick A, Hussein R, Bogacz I, Simon PS, Ibrahim M, Chatterjee R, Doyle MD, Cheah MH, Fransson T, Chernev P, Kim I-S, Makita H, Dasgupta M, Kaminsky CJ, Zhang M, Gätcke J, Haupt S, Nangca II, Keable SM, Aydin AO, Tono K, Owada S, Gee LB, Fuller FD, Batyuk A, Alonso-Mori R, Holton JM, Paley DW, Moriarty NW, Mamedov F, Adams PD, Brewster AS, Dobbek H, Sauter NK, Bergmann U, Zouni A, Messinger J, Kern J, Yano J, Yachandra VK (2023) Structural evidence for intermediates during O_2 formation in photosystem II. *Nature* 617:629–636
- Bowden SJ, Hallahan BJ, Ruffle SV, Evans MCW, Nugent JHA (1991) Preparation and characterization of photosystem II core particles with and without bound bicarbonate. *BBA Bioenergetics* 1060(1):89–96
- Clausen J, Beckmann K, Junge W, Messinger J (2005) Evidence that bicarbonate is not the substrate in photosynthetic oxygen evolution. *Plant Physiol* 139(3):1444–1450
- Dismukes GC, Klimov VV, Baranov SV, Kozlov YN, DasGupta J, Tyrishkin A (2001) The origin of atmospheric oxygen on earth: the innovation of oxygenic photosynthesis. *Proc Natl Acad Sci USA* 98(5):2170–2175
- Dole M (1935) The relative atomic weight of oxygen in water and in air. *J Am Chem Soc* 57:2731–2731
- Dole M, Jenks G (1944) Isotopic composition of photosynthetic oxygen. *Science* 100:409–409
- Farquhar GD, Lloyd J, Taylor JA, Flanagan LB, Syvertsen JP, Hubick KT, Wong SC, Ehleringer JR (1993) Vegetation effects on the isotope composition of oxygen in atmospheric CO_2 . *Nature* 363:439–443
- Ferreira KN, Iverson TM, Maghlaoui K, Barber J, Iwata S (2004) Architecture of the photosynthetic oxygen-evolving center. *Science* 303(5665):1831–1838
- Gao K, Zou D (2001) Photosynthetic bicarbonate utilization by a terrestrial cyanobacterium, *Nostoc flagelliforme* (Cyanophyceae). *J Phycol* 37(5):768–771
- Govindjee G, Beatty JT, Gest H, Allen JF (2006) Discoveries in photosynthesis. Springer, Dordrecht, pp 63–105
- Guo Y, Messinger J, Kloo L, Sun L (2023) Alternative mechanism for O_2 formation in natural photosynthesis via nucleophilic oxo-oxo coupling. *J Am Chem Soc* 145:4129–4141
- Guy RD, Fogel ML, Berry JA (1993) Photosynthetic fractionation of the stable isotopes of oxygen and carbon. *Plant Physiol* 101:37–47
- Hillier W, McConnell I, Badger MR, Boussac A, Klimov VV, Dismukes GC, Wydrzynski T (2006) Quantitative assessment of intrinsic carbonic anhydrase activity and the capacity for bicarbonate oxidation in photosystem II. *Biochemistry* 45:2094–2102
- Hoffmann G, Cuntz M, Weber C, Ciais P, Friedlingstein P, Heimann M, Jouzel J, Kaduk J, Maier-Reimer E, Seibt U, Six K (2004) A model of the Earth's dole effect. *Global Biogeochem Cycl* 18(1):1008
- Kozlov YN, Tikhonov KG, Zastrizhnaya OM, Klimov VV (2010) pH dependence of the composition and stability of Mn^{III} -bicarbonate complexes and its implication for redox interaction of Mn^{II} with photosystem II. *J Photochem Photobiol B* 101(3):362–366
- Loll B, Kern J, Saenger W, Zouni A, Biesiadka J (2005) Towards complete cofactor arrangement in the 30 Å resolution structure of photosystem II. *Nature* 438:1040–1044
- Lu YK, Stemler AJ (2007) Differing responses of the two forms of photosystem II carbonic anhydrase to chloride, cations, and pH. *BBA Bioenergetics* 1767:633–638
- Mader M, Schmidt C, van Geldern R, Barth JA (2017) Dissolved oxygen in water and its stable isotope effects: a review. *Chem Geol* 473:10–21
- Metzner H (1975) Water decomposition in photosynthesis? A critical reconsideration. *J Theor Biol* 51(1):201–231
- Moubarak-Milad M, Stemler A (1994) Oxidation-reduction potential dependence of photosystem II carbonic anhydrase in maize thylakoids. *Biochemistry* 33(14):4432–4438
- Radmer R, Ollinger O (1980) Isotopic composition of photosynthetic O_2 flash yields in the presence of $H_2^{18}O$ and $HC^{18}O_3^-$. *FEBS Lett* 110(1):57–61
- Rao S, Wu YY (2017) Root-derived bicarbonate assimilation in response to variable water deficit in *Camptotheca acuminata* seedlings. *Photosynth Res* 134:59–70
- Reid AF, Urey HC (1943) The use of the exchange between carbon dioxide, carbonic acid, bicarbonate ion, and water for isotopic concentration. *J Chem Phys* 11(9):403–412
- Ruben S, Randall M, Kamen M, Hyde JL (1941) Heavy oxygen (O^{18}) as a tracer in the study of photosynthesis. *J Am Chem Soc* 63(3):877–879

- Shevela D, Su JH, Klimov V, Messinger J (2008) Hydrogencarbonate is not a tightly bound constituent of the water-oxidizing complex in photosystem II. *BB -Bioenergetics* 177(6):532–539
- Shevela D, Do HN, Fantuzzi A, Rutherford AW, Messinger J (2020) Bicarbonate-mediated CO₂ formation on both sides of photosystem II. *Biochemistry* 59(26):2442–2449
- Shevela D, Kern JF, Govindjee G, Messinger J (2023) Solar energy conversion by photosystem II: principles and structures. *Photosynth Res* 156:279–307
- Song X, Wang B (2023) O–O bond formation and oxygen release in photosystem II are enhanced by spin-exchange and synergetic coordination interactions. *J Chem Theory Comput* 19(9):2684–2696
- Song Y, Li X, Siegbahn PEM (2023) Is there a different mechanism for water oxidation in higher plants? *J Phys Chem B* 127(30):6643–6647
- Stemler A, Murphy J (1983) Determination of the binding constant of H¹⁴CO₃[–] to the photosystem II complex in maize chloroplasts: effects of inhibitors and light. *Photochem Photobiol* 38:701–707
- Stemler A, Radmer R (1975) Source of photosynthetic oxygen in bicarbonate-stimulated Hill reaction. *Science* 190(4213):457–458
- Tikhonov K, Shevela D, Klimov VV, Messinger J (2018) Quantification of bound bicarbonate in photosystem II. *Photosynthetica* 56(1):210–216
- Ulas G, Olack G, Brudvig GW (2008) Evidence against bicarbonate bound in the O₂-evolving complex of photosystem II. *Biochemistry* 47(10):3073–3075
- Umena Y, Kawakami K, Shen JR, Kamiya N (2011) Crystal structure of oxygen evolving photosystem II at a resolution of 1.9 Å. *Nature* 473:55–60
- Warburg O, Krippahl G (1958) Hill-reaktionen. *Z Naturforsch B* 13(8):509–514
- Wu Y (2021a) Is bicarbonate directly used as substrate to participate in photosynthetic oxygen evolution. *Acta Geochim* 40(4):650–658
- Wu Y (2021b) Bicarbonate use and carbon dioxide concentrating mechanisms in photosynthetic organisms. *Acta Geochim* 40(5):846–853
- Wu Y (2023) Combined effect of bicarbonate and water in photosynthetic oxygen evolution and carbon neutrality. *Acta Geochim* 42:77–88
- Wu YY, Rao S (2023) Root-derived bicarbonate assimilation in plants. Springer, Dordrecht, pp 1–13
- Wu Y, Wu Y (2022) The increase in the karstification-photosynthesis coupled carbon sink and its implication for carbon neutrality. *Agronomy* 12(9):2147
- Wu YY, Xing DK (2012) Effect of bicarbonate treatment on photosynthetic assimilation of inorganic carbon in two plant species of *Moraceae*. *Photosynthetica* 50:587–594
- Xie T, Wu Y (2017) The biokarst system and its carbon sinks in response to pH changes: a simulation experiment with microalgae. *Geochem Geophys Geosyst* 18(3):827–843
- Yamano T, Sato E, Iguchi H, Fukuda Y, Fukuzawa H (2015) Characterization of cooperative bicarbonate uptake into chloroplast stroma in the green alga *Chlamydomonas reinhardtii*. *Proc Natl Acad Sci USA* 112(23):7315–7320

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