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HISTORICAL NOTE

In photosynthesis, oxygen comes from water: from a 1787 book for women by Monsieur De Fourcroy

Pierre Joliot[1] · **Antony R. Crofts**[2] · **Lars Olof Björn**[3] · **Christine T. Yerkes**[4] · **Govindjee**[5]

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Abstract It is now well established that the source of oxygen in photosynthesis is water. The earliest suggestion previously known to us had come from René Bernard Wurmser (1930). Here, we highlight an earlier report by Monsieur De Fourcroy (1787), who had already discussed the broad outlines of such a hypothesis in a book on Chemistry written for women. We present here a free translation of a passage from this book, with the original text in French as an Appendix.

Keywords Antoine Lavoisier · Joseph Priestley · Otto Warburg · Richard Willstätter · René Wurmser

Contrary to the ideas of two Nobel laureates Richard Willstätter (1872–1942) and later Otto Heinrich Warburg (1883–1970), René Wurmser (1930) suggested that the source of oxygen in photosynthesis was water; he proposed that the primary photochemical reaction of photosynthesis must be coupled to the "photolysis" of water and that the assimilation of CO_2 takes place in the stroma region of chlotoplasts (see Joliot (1996) for Wurmser's obituary).

The concept of water as the source of oxygen, was most elegantly obvious in the equations of Cornelis Bernardus van Niel (1941), and became accepted with the ^{18}O experiments of Ruben et al. (1941). (See Rabinowich (1945) for early history; and Govindjee and Krogmann (2004) for a Timeline of discoveries in photosynthesis.) However, we note here that in 1787, Monsieur De Fourcroy (Antoine François de Fourçroy (1755–1809)) had already suggested that oxygen in photosynthesis came from water, in a book on Chemistry written for women; this appears to be the first such record.[1] We further note that De Fourcroy[2] was a contemporary of Antoine Lavoisier[3] (1743–1794), who is credited with being the father of modern chemistry. De Fourcroy was a distinguished scientist in his own right, and a great popularizer of science to the general public, but more importantly in the present context, a close associate of Lavoisier (also see Smeaton 1962; and Wisniak 2005). Undoubtedly, the hypothesis Fourcroy presented, which

✉ Govindjee
gov@illinois.edu

1 Institut de Biologie Physico-Chimique, 13 Rue Pierre et Marie Curie, 75005 Paris, France

2 Department of Biochemistry and Center of Biophysics and Quantitative Biology, University of Illinois at Urbana-Champaign, Champaign, IL 61801, USA

3 Department of Molecular Cell Biology, Lund University, 22100 Lund, Sweden

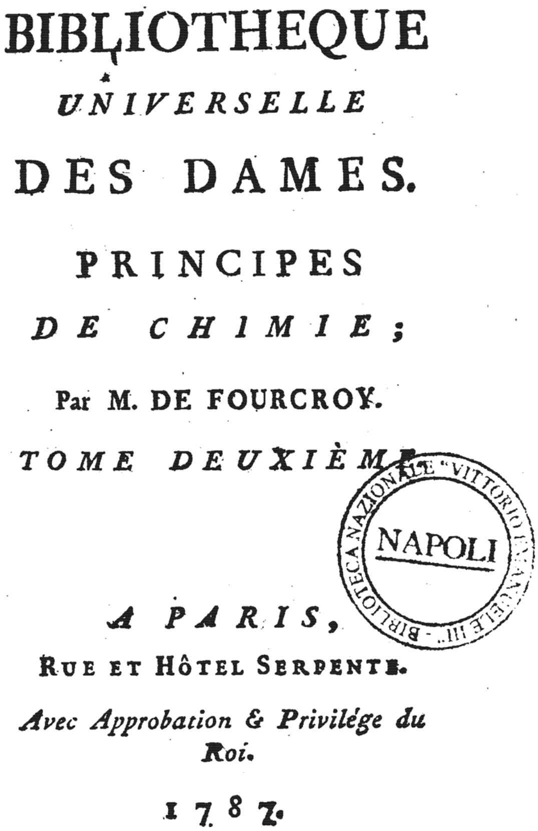
4 School of Chemical Sciences, University of Illinois at Urbana-Champaign, Champaign, IL, USA

5 Department of Plant Biology, Department of Biochemistry and Center of Biohysics & Quantitative Biology, University of Illinois at Urbana-Champaign, Champaign, IL 61801, USA

[1] A copy of this book was given to Anne and Pierre Joliot by René Wurmser. The first time Wurmser showed this book to Pierre, he explained to him that he did not want to fight for the recognition of something that had been proposed almost 2 centuries earlier!

[2] de Fourcroy was born in a family of lesser nobility. He was a student of Antoine Lavoisier and had collaborated in the "*Chemistry revolution*". During the Revolution and the beginning of the Empire, he became Fourcroy and was appointed as the first director of education. At the end of his life, he became the Comte de Fourcroy (Comte d'empire, nominated by Napoleon) and therefore got a noble name.

[3] https://en.wikipedia.org/wiki/Antoine_Lavoisier; for information on some others mentioned in this article, see https://en.wikipedia.org/wiki/C._B._van_Niel; https://en.wikipedia.org/wiki/Eugene_Rabinowitch; https://en.wikipedia.org/wiki/Sam_Ruben; https://en.wikipedia.org/wiki/Martin_Kamen



BIBLIOTHEQUE
UNIVERSELLE
DES DAMES.
PRINCIPES
DE CHIMIE;
Par M. DE FOURCROY.
TOME DEUXIÈME.
A PARIS,
RUE ET HÔTEL SERPENTE.
Avec Approbation & Privilége du Roi.
1787.

Fig. 1 Front cover of M. De Fourcroy's (1787) book, scanned and made available by Google. (A copy of the book is held by the University of Illinois Library at Champaign-Utbana, Illinois, USA.)

Fig. 2 A portrait of Antoine François de Fourcroy. (*Source* http://www.sil.si.edu/digitalcollections/hst/scientific-identity/fullsize/SIL14-F004-02a.jpg)

quite explicitly has oxygen generated by decomposition of water driven by light, with the reducing power also generated and used to drive synthesis of plant materials, owes a great deal to Lavoisier's work from this period.

We present below a free translation from a few passages (pp. 145–150; the original French is in the Appendix) from De Fourcroy (1787); the text within square brackets has been added by the authors of this "historical note". Figure 1 shows the front cover of this book, and Fig. 2 is a portrait of Antoine François de Fourcroy (from the World Wide Web).

"The illustrious [Joseph] Priestley[4] [1733–1804] was the first to observe that air becomes healthier when a strawberry plant under a bell-jar is exposed to light. M(onsieur) [Jan] Ingen-Housz[5] [1730–1799] put tree leaves in water under a bell-jar, and discovered that when this container was illuminated by the rays of the sun, it was filled, little by little, with an "elastic fluid"; the upper leaf surface was covered with bubbles that rose above the water. The production of this elastic fluid is even faster when the sunlight is stronger. **It is purest "vital air" [oxygen] that is given off by the leaves.** [bolded by the authors] These same leaves brought into shade only give an impure elastic fluid; without water no air production was observed at the leaf surface; without light, these effects do not work properly; without one or the other of these agents, the vegetation perishes. If water acts alone on the leaves without sunlight they become white, weak, and their channels are swelled with stale and watery juices. **There is, therefore, a need for simultaneous action of water and of light on plants** [bolded by the authors of this historical note],—a reciprocal effect,—a reaction that only modern understanding can explain. As the vital air is released from moistened leaves, and the plant is exposed to sunlight, the vegetation becomes colored, the oily material forms, all of which indicates that it is the decomposition of atmospheric water which produces this effect. Sunlight and a certain degree of warmth favor this decomposition; the leaves absorb hydrogen from the water through their vessels while the light combines with oxygen and converts it to vital air. So, when spring seems to revive Nature, the sun rising above the horizon is the cause of all major effects that so delight our eyes. It works on the vegetation, and by a double benefit, it produces various oily combinations in the plant, and renews the atmosphere by making torrents of vital air. Tree leaves are used for this operation, and water, with the help of sunlight, is the essential agent."

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[4] https://en.wikipedia.org/wiki/Joseph_Priestley.

[5] https://en.wikipedia.org/wiki/Jan_Ingenhousz.

GIAN (Global Initiative on Academic Network, Ministry of Human Resources, Govt. of India*)* to lecture on "Photosynthesis" in the Spring of 2016 at JNU. We thank Robert Blankenship for helpful comments. De Fourcroy is his academic sixth generation great grandfather! Rajni Govindjee and George C. Papageorgiou also read our letter. George wrote to one of us (G): You truly have something "très extraordinaire" in your hands, and "L' air vital très pur" of de Fourcroy is certainly oxygen. You are about to provide a very important background on the history of photosynthesis research.

Appendix: The following text, in French, is reproduced from De Fourcroy (1787)

"L'illustre Priestley vit le premier l'air devenir plus salubre par l'action d'un fraisier renfermé sous une cloche, & exposé à la lumière. M. Ingen-housz mit des 'feuilles d'arbres dans l'eau sous une cloche, & découvrit que ce vaisseau frappé par les rayons du soleil, se remplissoit peu à peu d'un fluide élastique: la surface supérieure des feuilles se couvre de bulles qui montent: au-dessus de l'eau; cette production de fluide élastique est d'autant plus prompte, que le soleil dard mieux ses rayons: c'est de l'air vital très-pur qui se dégage; ces feuilles portées à l'ombre ne donnent plus qu'un fluide élastique impur: sans eau, la production d'air n'a pas lieu à la surface des feuilles; sans lumière, elle ne s'opère pas davantage; & sans l'un & l'autre de ces agens, les végétaux périssent. Si l'eau agit sur eux sans soleil, ils croissent blancs, faibles, & leurs canaux sont gorgés de sucs fades & aqueux. *Il y a donc dans l'influence nécessaire & simultanée de l'eau & de la lumière sur les plantes* un effet réciproque, une réaction que les connaissances modernes peuvent seules expliquer. A mesure que l'air vital est dégagé des feuilles humectées & exposées à la lumière du soleil, les végétaux se colorent, la matière huileuse se forme, tout indique que c'est la décompofition de l'eau atmosphérique qui produit cet effet; la lumière solaire & un certain degré de chaleur favorisent cette décomposition, les feuilles absorbent l'hydrogène de l'eau par leurs vaisscaux, tandis que la lumière s'unit à l'oxigène & le met dans l'état d'air vital. L'hydrogène porté par les vaisseaux des feuilles dans tout le tissu du végétal, s'y fixe & y forme le composé huileux; ainsi, lorsque le printemps semble ranimer la Nature, le soleil élevé sur l'horison est la cause de tous les grands effets qui charment alors nos yeux; il opère la végétation, & par un double bienfait, il produit les diverses combinaisons huileuses dans les végétaux, & il renouvelle l'atmosphère en y faisant verset des torrens d'air vital; les feuilles des arbres servent à cette opération, & l'eau aidée de la lumière solaire en est l'agent."

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