TRIBUTE

Warwick Hillier: a tribute

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Abstract Warwick Hillier (October 18, 1967–January 10, 2014) made seminal contributions to our understanding of photosynthetic water oxidation employing membrane inlet mass spectrometry and FTIR spectroscopy. This article offers a collection of historical perspectives on the scientific impact of Warwick Hillier’s work and tributes to the personal impact his life and ideas had on his collaborators and colleagues.

Keywords Bicarbonate · FTIR · Isotopes · Mass spectrometry · Oxygenic photosynthesis · Photosystem II

Abbreviations
ANU Australian National University
FTIR Fourier transform infrared spectroscopy
MSU Michigan State University
OEC Oxygen evolving complex of PSII, also known as WOC
PsbO Manganese stabilizing protein of PSII
PSII-WOC Photosystem II water oxidizing complex
RSB Research School of Biology

Fig. 1 Warwick Hillier, September 2007

Warwick Hillier (Fig. 1) was born on October 18, 1967 and died on January 10, 2014. He is survived by his wife Sari, son Henry Oscar and daughter Stella Amelia. As a child, family vacations were invariably spent camping, an activity that gave Warwick a great appreciation for nature, both its living and non-living forms. This gift from his parents later became a dominant influence in his adult life, expressed in both his hobbies and his profession. His mother—who was trained as a midwife and nurse—imparted Warwick with a great awareness of the gift of life which was revealed in his sensitivity to others. As a child and teenager, Warwick learned from his father how to take things apart, put them back together and to modify them to suit his needs. Together they built a beautiful treehouse from driftwood found on the beach. This lofty treehouse had a fold down table, working
telephone to the garage, a trap door and a flying fox (zipline) which would hurtle you across the back yard at an alarming speed. It was the perfect escape and command center for future discoveries. This skill was refined as a teenager as he became a builder of telescopes and an avid star gazer. Among the telescopes that he built, one featured a 20-inch mirror that he ground himself. Warwick’s fascination with stars and the light they radiate extended to how photosynthetic life utilized this energy source. This avocation eventually led him to university training and became his main interest and area of his greatest professional contributions. Warwick was a graduate of the Australian National University (ANU; BSc (Honors), 1991; MSc, 1994; PhD, 1999) (Fig. 2). He was a perpetual tinkerer who shared his passion for astronomy and the building of instruments with his scientific collaborators. He developed close working relationships and friendships with others who, like him, enjoyed building unique instruments.

Beyond his scientific impact, outlined below, those who knew him well describe him as an exceptional human being (see personal recollections at end). The sentiments expressed by his students and colleagues emphasized his warm personal character, unpretentious self-image, eager sharing of experience, generous giving of time, and playful mischievousness. Warwick’s strong sense of humanity was made evident following his PhD training while at Michigan State University (MSU, 1999–2003). When his postdoctoral mentor, Gerald (Jerry) T. Babcock, was diagnosed with lung cancer and died soon thereafter, everyone expected Warwick would move on to complete his postdoctoral training elsewhere. Instead, Warwick stayed on for another 36 months to guide several pre-doctoral candidates in the Babcock laboratory to complete their PhD theses.

His fun loving mischievousness infiltrated both his scientific interests in photosynthetic water splitting and astronomy and his personal life. When Sari’s and Warwick’s first child arrived, Henry Oscar Hillier, none of us could believe that the initials were a mere coincidence (HOH or H 2O !). But he never admitted otherwise. Later when their second child arrived, Stella(r), there could be no denying it. We all knew what playfulness he was up to. Sharon, Warwick’s sister, noted that his enthusiasm for astronomy and all aspects of science defined him as a father. He encouraged Henry and Stella to do photography and got them into stargazing—including keeping them home from school to observe the transit of Venus in Australia (on June 6, 2012). Warwick’s colleagues from the ANU honored him by naming a star in the constellation of Telescopium (star 607417 in the Sydney Southern Star Catalogue) after him.

Hillier’s scientific impact

Warwick dedicated his scientific career to understanding photosynthesis—the fundamental process whereby green plants and all phototrophs capture sunlight and convert it into chemical energy that sustains all life on Earth. Specifically, he was interested in the mechanism by which photosystem II (PSII) oxidizes water for delivering the electrons and protons required for the conversion of carbon dioxide into carbohydrates, and in the process releases oxygen forming the atmosphere essential for aerobic respiration.


Warwick was Thomas (Tom) J. Wydrzynski’s first Master’s student. He joined Tom’s group in 1990 shortly after Tom had started his new position at the Research School of Biological Sciences at the ANU in Canberra, Australia. He helped Tom to set up his lab and worked during his Master’s thesis among others on light-induced peroxide formation by salt-washed PSII preparations and on the effects of high concentrations of ethylene glycol on PSII (Hillier et al. 1992; Hillier and Wydrzynski 1993; Wydrzynski et al. 1996; Hillier et al. 1997). In 1993 Johannes Messinger joined Tom’s lab as a postdoc and established with the help of Murray Badger the instrumentation and the protocol for the measurement and analysis of the binding affinity of the two water molecules (substrate water) that are bound to the Mn4CaO5 cluster in PSII (Messinger et al. 1995a). In 1993 Johannes Messinger joined Tom’s lab as a postdoc and established with the help of Murray Badger the instrumentation and the protocol for the measurement and analysis of the binding affinity of the two water molecules (substrate water) that are bound to the Mn4CaO5 cluster in PSII in order to be oxidized to molecular oxygen (Messinger et al. 1995a). In these experiments, which significantly improved previous attempts (Radmer and Ollinger 1986; Bader et al. 1993), the binding affinity of the two substrate waters to the...
Mn$_4$CaO$_5$ cluster is probed by measuring the rate of exchange with bulk water after short-time incubations of PSII with H$_2^{18}$O. The isotopic composition of the oxygen generated after a series of different incubation times is then assayed by isotope-ratio membrane inlet mass spectrometry (Fig. 3) (Konermann et al. 2008; Beckmann et al. 2009; Cox and Messinger 2013). Warwick was immediately fascinated by these experiments and decided to make them the subject of his PhD thesis. Thus, he took over the instrumentation from Johannes after he left for London in 1995 (Fig. 4), and further reduced the time required for complete mixing of the PSII sample with H$_2^{18}$O (from 30 to 10 ms). This additional improvement was critical to allow resolving the exchange kinetics of the fast exchanging (more loosely bound) substrate water in the S$_3$ state (Messinger et al. 1995b; Hillier et al. 1998a). He then extended the experiments to the S$_2$, S$_1$, and S$_0$ states (Messinger et al. 1995b; Hillier et al. 1998b; Hillier and Wydrzynski 2000), which he studied not only under one experimental condition, but also at several temperatures and pH values. This was a formidable achievement considering that the determination of each exchange kinetic requires the collection of 20–30 individual measurements that take about 1 h each and completely stable instrumentation over this period. Curious as he was, he studied the water exchange not only in spinach thylakoids, but also in various other PSII preparations from spinach, Thermosynechococcus elongatus and Synechocystis sp. PCC6803 (Hillier et al. 2001). To gain even deeper insight, he also determined the substrate water exchange rates after removing or substituting the Ca$^{2+}$ or Cl$^-$ cofactors. Many of the results he obtained during his PhD thesis (Hillier 1999) were published only several years later.

After completion of his PhD (1999), he took a post-doctoral position at Michigan State University with Jerry Babcock to learn Fourier transform infrared (FTIR) spectroscopy (see below). In 2003 he returned to ANU and rejoined the Photobioenergetics group at the RSBS as a postdoc funded by the Human Frontier Science Program. He continued the substrate water exchange experiments and obtained a permanent position in RSBS (now Research School of Biology, RSB) in May 2007. In order to localize the substrate water binding sites on the Mn$_4$CaO$_5$ cluster he started, in collaboration with Richard (Rick) Debus (Singh et al. 2008; Hillier et al. 2008; Service et al. 2011) and others (Sugiura et al. 2009) to map the effects of PSII point mutations on the substrate water exchange rates. Warwick and Tom Wydrzynski have summarized their seminal work on substrate water binding in several excellent reviews (Hillier and Wydrzynski 2001, 2004; Hillier and Messinger 2005; Hillier and Wydrzynski 2008) (see also Cox and Messinger 2013). The importance of Warwick’s substrate water-exchange measurements for the understanding of the mechanism of water oxidation in PSII lies in the fact that this technique is the only one that directly reports on the properties of the substrate water molecules in the different oxidation states of PSII. In 2007 Warwick shared the Robin Hill Award, given at the 14th International Photosynthesis Congress, for his seminal work on the mechanism of water oxidation (Fig. 5). In 2009, he won an Australian Future Fellowship for research in this area and at the time of his
death was a Laboratory Leader in the Division of Plant Sciences in the RSB (Fig. 6).

In search of the fingerprints of water oxidation by infrared spectroscopy (1999–2014)

Warwick sought to obtain more detailed information about the chemical bonds and atomic vibrations of the substrate water molecules and the atoms they interacted with in the water oxidizing complex (WOC) and so turned to vibrational spectroscopy for answers. After completing his PhD dissertation in 1999 in Wydrzynski’s laboratory, Warwick joined Jerry Babcock’s laboratory at MSU as a postdoctoral fellow (Fig. 7). At this time the Babcock’s laboratory was beginning to apply FTIR difference spectroscopy to study the structural changes that accompany the S state transitions in PSII. Jerry, graduate student Matt Gardner, and postdoctoral fellows Hsiu-An (Andy) Chu, and John O’Brien were developing FTIR instrumentation capable of measuring spectra between 1,000 and 350 cm$^{-1}$ (Chu et al. 1999). Jerry was particularly interested in this region because metal–ligand vibrations appear here and the Mn-ligand and Mn-substrate modes of the Mn$_4$CaO$_5$ cluster of PSII were expected to be found between 200 and 900 cm$^{-1}$. The technical obstacles to measuring FTIR spectra in this spectral region are formidable, including strong absorption from water, few materials for optical windows and low detector sensitivity.

Warwick helped develop the group’s “third generation” spectrometer, pushing the lower frequency limit from 550 cm$^{-1}$ down to 350 cm$^{-1}$ (Chu et al. 2000a, b). Also, before 2000, only the $S_2$-minus-$S_1$ FTIR difference spectrum of PSII had been reported (Noguchi et al. 1992, 1995a, b; Zhang et al. 1998; Chu et al. 1999). Warwick’s specific task was to extend the application of FTIR difference spectroscopy to the study of ALL of the S state transitions in the mid-frequency region (2,000–1,000 cm$^{-1}$), where vibrations from amino acid side chains and the polypeptide backbone appear. He assisted with the first report of a $S_3$-minus-$S_2$ FTIR difference spectrum in this region (Chu et al. 2000c), then developed the methodology for recording all of the $S_n$-minus-$S_{n-1}$ FTIR difference spectra in this region in spinach PSII core complexes (Hillier and Babcock 2001). This was a landmark publication that was published alongside an equally significant publication from Takumi Noguchi and Miwa Sugiura, who developed the methodology independently and simultaneously for PSII core complexes from T. elongatus (Noguchi and Sugiura 2001). For this work, Warwick designed the sample compartment and cryostat for a new spectrometer that Babcock’s laboratory had.
recently acquired, configured the FTIR spectrometer and Nd:YAG laser system, and developed software that would allow actinic laser illumination and data collection to occur automatically. Warwick loved to tinker and developed numerous “bits” and jigs for helping prepare samples for FTIR measurement.

After Jerry Babcock passed away in December 2000, Warwick remained at MSU for three years to help guide students (Fig. 8). During this time, he built a sample cell for generating electrochemically induced FTIR difference spectra, then employed it, in combination with global $^{15}$N labeling and $^{15}$N-labeling of histidine, to assign heme and histidine peaks in an electrochemically induced FTIR difference spectrum of cytochrome c oxidase (Schmidt et al. 2004). Also during this time, Warwick began collaboration with Rick Debus, who had just acquired a new FTIR spectrometer at The University of California (UC) Riverside (Fig. 9). During a visit by Rick to MSU in 2002, Warwick taught Rick how to prepare samples for FTIR analysis and to record spectra. Soon after, Warwick traveled to UC Riverside to help set up Rick’s new spectrometer, configuring it with a new laser system and writing software that would allow actinic laser illumination and data collection to occur automatically. For the next eleven years, Warwick would become an almost annual visitor to Rick’s laboratory where he would update the spectrometer’s configuration and software and discuss new types of experiments. When Rick acquired a newer spectrometer in 2007, Warwick configured it, wrote its software, and designed its cryostat and sample compartment. For most of the decade between 2003 and 2013, the collaboration focused on the ligands of the Mn$_{4}$CaO$_{5}$ cluster. The first product of this collaboration provided evidence that the C-terminal carboxylate group of the D1 polypeptide at Ala-344 ligates a Mn ion in the Mn$_{4}$CaO$_{5}$ cluster (Chu et al. 2004; Strickler et al. 2005). Subsequent publications (Debus et al. 2005; Strickler et al. 2006, 2007; Service et al. 2011, 2013) provided the unexpected result that the individual mutation of four of the Mn$_{4}$CaO$_{5}$ cluster’s six carboxylate ligands produces no significant changes in the $S_{n+1}$-minus-$S_{n}$ FTIR difference spectra. Not only do mutations of D1-Asp170, D1-Glu189, D1-Glu333, and D1-Asp342 fail to eliminate carboxylate vibrational modes, they fail to produce significant changes in the response of the protein’s polypeptide backbone to the oxidations of the Mn$_{4}$CaO$_{5}$ cluster during the individual S state transitions. The realization that the wealth of features in the $S_{n+1}$-minus-$S_{n}$ FTIR difference spectra must reflect changes in the Mn$_{4}$CaO$_{5}$ cluster’s second coordination and beyond, led the collaboration into studies of the hydrogen-bonding networks surrounding the Mn$_{4}$CaO$_{5}$ cluster (Service et al. 2010, 2014) and the water reactions that accompany the S state transitions. The latter include the region between 3,600 and 2,000 cm$^{-1}$ where the vibrational modes of hydrogen bonded OH groups and delocalized protons in highly polarizable hydrogen bonds appear (Service et al. 2013; Debus 2014). Most of the mutants examined during this collaboration were also examined by Warwick for their effects on the exchange of substrate water molecules (Singh et al. 2008; Hillier et al. 2008; Service et al. 2011). One of Warwick’s goals was to configure FTIR spectrometers for technically daunting time-resolved measurements. Towards that goal, Warwick developed sample compartments fitted with computer-controlled sample wheels that would increase sample throughput many-fold. He was still working on this goal at the time of his passing.

Fig. 8 Gerald T. Babcock group at MSU, ~2001 (from left to right). Back row: Denis Proshlyakov, Bryan Schmidt, Neil Law, Steve Seibold, Warwick Hillier; Front row: Hsiu-An Chu, Vada O’Donnell, Jose Cerda, and Shannon Haymond

Fig. 9 FTIR mini-summit in Tokagawa Garden, Nagoya, Japan, 2010. Front to back: Takumi Noguchi, Warwick Hillier, Rick Debus. Photo provided by Takumi Noguchi

Warwick researched the biogenesis of oxygenic photosynthesis, the process by which it came to exist following accretion of the Earth at the beginning of life. His iconic images of cyanobacterial stromatolites from Shark Bay, Australia (http://www.photosynthesisresearch.org/resources/Theme/images/Warwick%20st4250L.jpg), and “champagne bubbles” video of oxygen gas fizzing from blades of underwater grass at Ewens Pond, Australia, are examples of his outstanding amateur photography skills that have inspired us all and been sought after by textbook writers.

During his postdoctoral research at MSU, Warwick visited Charles (Chuck) Dismukes’ laboratory at Princeton University to present his research on substrate water exchange and FTIR of intermediates during photoassembly (biosynthesis) of the PSII-WOC. Discussions on interpretation of these data led to the literature on the chemical speciation of water as substrate for O2 evolution. Earlier mass spectrometric work by Ruben et al. (1941) using 18O enriched water had demonstrated that under equilibrium conditions water, not CO2 alone, is the ultimate source of O2. Because water can rapidly and reversibly hydrolyze CO2 to give ionized forms of carbonic acid (H2CO3, HCO3− and CO32−) in excess water, it was unclear whether these species needed to be considered as potential candidates for the active form of substrate water molecules. Hartmut Metzner’s group had provided time-resolved mass spectrometric evidence implicating bicarbonate as a possible directly oxidizable electron donor to PSII (Metzner 1978; Metzner et al. 1979). This work has been mostly overlooked, having appeared mainly in conference proceedings. The rapid mixing mass spectrometry system developed at the ANU looked to be the best tool for answering this question and Warwick was eager for the challenge. These experiments began after Warwick finished his work at MSU and returned to the ANU to take a postdoctoral position funded by the Human Frontier Science Program. There was already strong evidence demonstrating that bicarbonate influenced the steady-state rate of water oxidation by intact plant PSIIIs and that at least two effects where involved, the so-called acceptor and donor sites (Stemler et al. 1974). Govindjee’s group at the University of Illinois Urbana-Champaign originated this terminology based on work done by Govindjee’s then PhD students, first Alan Stemler and later Tom Wydrzynski (Shevela et al. 2012). They established clear evidence for bicarbonate binding to the acceptor side at the non-heme iron and showed that removal resulted in slowing of electron transfer Q⊂Qb → QAQB−. A postulated functional consequence for regulation is appealing. First Govindjee’s group, and later Metzner’s (Metzner 1978; Metzner et al. 1979), Stemler’s (Stemler 2002) and Klimov’s group (Klimov et al. 1995) provided evidence for bicarbonate stimulation of PSII activity on the donor side of PSII. The donor side effects of bicarbonate have been far more species dependent and difficult to pin down. One of the hypotheses was that bicarbonate might serve as the substrate for O2 evolution as it is energetically easier to dissociate CO2 from bicarbonate to give hydroxide than it is to dissociate a proton from water. This hypothesis implied that the contemporary oxygenic reaction center could have evolved from a bicarbonate oxidizing prokaryotic reaction center (Dismukes et al. 2001).

Warwick reckoned that the rapid mixing isotope ratio MS instrument that he helped to develop at the ANU could answer this question by using 13C/18O-labeled bicarbonate to measure both the potential flux of oxygen from bicarbonate into O2, while monitoring the self-exchange reaction of labeled bicarbonate with unlabeled water. He used an inhibitor of carbonic anhydrase to slow the latter reaction. The measurements were made with both plant and cyanobacterial sources of PSII prepared from spinach and T. elongatus in order to examine the earlier evolving prokaryotes, and from Arthrospira maxima which grows naturally in alkaline soda lakes at high (bi)carbonate levels. Warwick’s data showed that bicarbonate is not the substrate for O2 production in any of these contemporary oxygenic photoautotrophs when assayed under single turnover conditions (Hillier et al. 2006). Clausen had independently reached similar conclusions on plant PSII by showing the absence of an effect from high CO2 pressure on the UV absorbance changes of manganese (Clausen et al. 2005). Warwick’s work provided strong evidence and stimulated subsequent studies which have been interpreted in favor of bicarbonate acting as mobile proton acceptor for water oxidation (Carrieri et al. 2007; Koroidov et al. 2014).

Personal accounts

Tom Wydrzynski, ANU (PhD Mentor)

It is with great sadness in my heart that I write these few words for my beloved mate and friend, Warwick Hillier. We met when I joined the RSBS in October, 1990. A few days later, he joined me as my first master student (see Fig. 2).

Warwick revealed himself to be a true scientist and naturalist in the genre of Alexander von Humboldt. He displayed a curiosity in many different areas—he cared for the small wonders of nature as well as the vastness of the universe. So keen was his interest in astronomy, that he even built his own telescope.
The first time Warwick came to the USA with me was in 1993. It was summer here and we set out to make a cross-country trip to San Francisco, California from St. Louis, Missouri. As we were driving through Missouri, we happened upon the world’s largest fireworks stand. Since it was around the Fourth of July (America’s Independence Day), we bought some fireworks to “shoot off” later. As we were camping just outside of Flagstaff, Arizona, we heard fireworks being shot off, so we decided to “shoot off” the ones we had purchased. The very first firecracker we shot off caught fire about 50 feet away from our campsite. Warwick quickly ran over to put out the flames, and then we realized how easily we could have burnt the San Francisco mountains!

On our second trip to the USA a year later, Warwick and I decided to visit Mike Siebert (Fig. 10) at National Renewal Energy Laboratory (NREL) in Denver, Colorado. While we were driving across the loneliest road in the USA, the engine in the Jeep failed. We continued driving, inch by inch, to the next town where we spent the night. The next morning the service man told us the engine was damaged because there were filings in the motor. He said it was possible that we could make it to Denver but we had to cross a ridge of mountains. Warwick was ready to meet the next challenge with me, so we decided to try it. About 20 min into our drive, the engine quit again. As we made a U-turn to head back to town to buy a refurbished engine, we got stuck in the snow. At this point, it was decided I would hitch a ride back to town and Warwick would stay with the Jeep. I picked up a ride and, as we were turning into the gas station, I was surprised to see Warwick drive past us in the Jeep! He had managed to get the Jeep out of the rut and driving again! End of story, we rented a car and made it to Denver on time.

After Warwick graduated with his PhD, he did a post-doc at the Department of Chemistry at MSU where he developed a keen sense of doing FTIR spectroscopy. At one time I asked him why he was doing a post-doc and he replied that he wanted to become the world’s expert in FTIR spectroscopy. Warwick developed many new techniques in FTIR spectroscopy, which are covered by Rick Debus (also see the main text). After his post-doc, Warwick returned to the ANU. During this time, he continued mass spectrometry experiments which led to information that has been critical for understanding the oxygen evolution mechanism.

I will always remember Warwick. He was my colleague and best friend in the truest sense of the word. I will miss him dearly.

Hsiu-An Chu, Institute of Plant and Microbial Biology, Academia Sinica, Taiwan

It was my privilege to work with Warwick during 1999–2001 in the late Professor Jerry Babcock’s Lab at MSU (see Fig. 8). At that time, Warwick was a young post-doc but already famous for his work with Tom Wydrzynski on measuring water exchange rates of the oxygen-evolving complex (OEC) in PSII. He was extremely talented and creative. He built a very useful FTIR instrumental setup to measure structural changes of the OEC during the entire S state cycle. His innovation was published as the back-to-back Biochemistry papers in 2001 independently with Professor Takumi Noguchi’s work. It was a significant breakthrough in our research field. In addition, we accomplished several publications on FTIR studies of the OEC with Jerry and other colleagues. Warwick also built a setup to measure electrochemically induced FTIR difference spectra of cytochrome c oxidase. Furthermore, through collaborations with Rick Debus at UC Riverside, Warwick contributed many insightful FTIR papers in understanding mechanism of photosynthetic water oxidation. Moreover, he had made numerous other important scientific innovations and inspired many people around him. His death is a great loss to our research community. He will be greatly missed by all of us.

Rick Debus, UC Riverside

Warwick was my friend and closest scientific colleague. Most of what I know about FTIR spectroscopy, I learned from Warwick, including how to collect FTIR data (Fig. 11). I always looked forward to discussing research with Warwick via Skype (sometimes for an hour at a time) and treasured his nearly annual visits to my laboratory, usually for several days before or after a Gordon Conference. During these trips he would update my equipment and reconfigure it for additional experiments that we then proceeded to try. He was always remarkably calm, even
when critical components failed. One highlight of these visits was a night or two of stargazing. We have a local astronomy club, so I was able to take Warwick to star parties in the desert or mountains or to the club’s dark site east of Riverside near Joshua Tree National Park. Observing the northern sky was a particular treat for Warwick. Shortly before one of Warwick’s visits, I acquired an integrating video camera for viewing particularly dim deep sky objects. It was Warwick’s tinkering with the camera that first allowed us to see objects with clarity and colors rivaling those of published astrophotos. The night of our last outing together, clouds rolled in about 11 PM and I retreated to the warmth of the club’s nearby clubhouse. When I returned 30 min later, I was greeted by a seated and smiling Warwick. “Look what I did!” he exclaimed proudly. I looked up and saw that the clouds had disappeared. We continued to observe galaxies and nebulae past dawn. I greatly valued our conversations about data and interpretations and about science and other things. I will miss him greatly.

Barry Osmond, ANU

To most of us, his coworkers, Warwick was such an unassuming, low-key guy who achieved great things. Those closer to him clearly admired his warm and sympathetic support in all aspects of life. His can-do attitude came to the fore a few years back as we helped Tom Wydrzynski move from his lovely hillside home to an apartment in the city. At a particularly critical moment of the move Warwick arrived in his trusty Brumby (vintage Subaru mini-pickup) to take on an amazing last load of gear that enabled Tom to settle immediately at his new address.

Kastoori Hingorani (PhD student 2008–2013)

Warwick was my PhD mentor for the five years that I was at ANU (Fig. 12). It was a pleasure for me to work with him and learn from him. Warwick stepped up to the role of my PhD supervisor seamlessly, when my primary supervisor Tom Wydrzynski had to take an early retirement. He was my supervisor, friend and an inspiration from then on. I will ever be so grateful to Warwick for leading by example as an excellent scientist and an exceptional human being. His calm and gentle demeanor and that kind smile on his face has touched many hearts. While a great loss to his family, friends and the scientific community, we have his teachings to live up to and the wonderful memories to keep. There are numerous valuable lessons he taught to those around him (unknowingly), simply through his actions and carefully selected words. For example, he inspired his students to never stop questioning, and to keep an eye out for the ‘black swan.’ He taught us to believe in ourselves, and that there is nothing that we cannot learn to do. In Warwick’s lab, a molecular biologist could be found troubleshooting a complex multipart spectrometer, disassembling, changing parts and reassembling, using a user’s manual and minimal guidance. In other words, with his mentoring ‘we learnt—how to learn, anything.’ Lastly I would like to share what he told me once when I was writing my thesis —“Stress, is a wasted emotion.” I don’t recall ever seeing him stressed.
Tom Faunce, ANU

I came to know my colleague Warwick through his joint editing of the Royal Society Molecular Solar Fuels volume (Wydrzynski and Hillier 2012) in which I contributed Chapter 18 ‘Future Directions on Solar Fuels.’ Warwick was very encouraging on the idea of globalizing artificial photosynthesis and gave a presentation at the Lord Howe Island conference on that theme I had organized. He was also a joint author on our Energy and Environmental Science paper (Faunce et al. 2013) making the case for a global project on artificial photosynthesis. He once had made this suggestion in an e-mail to me that I still strive to keep in mind: “I make a comment that if you are planting a seed then the idea might be more important than the individual.” But this is style perhaps that I am not accustomed to and it stumps me at times. Our family interacted closely with him throughout his final illness. He wrote a diary and left videos to celebrate the milestones to come in the lives of his children. He accepted and kept trying to share.

Robert (Rob) Burnap, Oklahoma State University

My earliest recollections of Warwick date to my six week visit to Tom Wydryzynski’s lab at ANU in 1996 to study the effects of the extrinsic proteins on water exchange. The extrinsic proteins of PSII are known to control the accessibility of ions to the manganese cluster and we were testing the effects of genetic removal of PsbO protein in the cyanobacterium Synechocystis. At the time, Warwick was working on his PhD under Tom’s supervision and he was asked to guide me in the lab and to work out how to apply the water exchange techniques to cyanobacterial preparations. The technique had been worked out for spinach thylakoids and core preparations while Johannes Messinger had been in the lab, but it was unclear how to best apply the techniques to the cyanobacterial preparations including those from site-directed mutants. Warwick was wonderful to work with—enthusiastic and an irrepressible problem solver. He was also very sharp and open minded when experiments began producing exactly the opposite results as we initially had anticipated. We had hypothesized that the genetic removal of PsbO would increase the exchange rates due to increased accessibility of the substrate water to the Mn cluster. What we observed was the opposite—water exchange was diminished. At the moment the calculations were completed, Warwick cheerfully announced something to the effect “So Science can work just as they tell us it is supposed to—Rob, I believe we have just rejected your hypothesis.” Of course it didn’t end at that, since the result told us that the exchange rates reflected chemical binding characteristics at the Mn cluster as opposed to diffusion to and from the catalytic site (Hillier et al. 2001).

Ronald (Ron) Pace, ANU

He was, in local Australian usage, simply a really nice bloke, really nice, as well as a first rate scientist. The substrate water exchange work, with Johannes and Tom, was ground-breaking. We refer to it constantly; that is at least an outstanding scientific legacy. See sketch of Warwick Hillier (Fig. 13).

Acknowledgments We sincerely thank all colleagues, Sari Hillier, and the Hillier family for contributing recollections and photographs, and Govindjee for the invitation to prepare this tribute and for his editing the final draft.

References


Fig. 13 Sketch of Warwick Hillier by Ron Pace


Debus RJ (2014) Evidence from FTIR difference spectroscopy that D1-Asp61 influences the water reactions of the oxygen-evolving Mn4CaO6 cluster of photosystem II. Biochemistry 53:2941–2955

Debus RJ, Strickler MA, Walker LM, Hillier W (2005) No evidence from FTIR difference spectroscopy that aspartate-170 of the D1 polypeptide ligates a manganese ion that undergoes oxidation during the S2 to S1, S1 to S2, or S2 to S3 transitions in photosystem II. Biochemistry 44:1367–1374


Hillier W, Wydrzynski T (1993) Increases in peroxide formation by the photosystem II oxygen evolving reactions upon removal of the extrinsic 16, 22, and 33 kDa proteins are reversed by CaCl2 addition. Photosynth Res 38:417–423


Strickler MA, Hillier W, Debus RJ (2006) No evidence from FTIR difference spectroscopy that glutamate-189 of the D1 polypeptide ligates a Mn ion that undergoes oxidation during the S0 to S1, S1 to S2, or S2 to S3 transitions in photosystem II. Biochemistry 45:8801–8811

Strickler MA, Walker LM, Hillier W, Britt RD, Debus RJ (2007) No evidence from FTIR difference spectroscopy that aspartate-342 of the D1 polypeptide ligates a Mn ion that undergoes oxidation during the S0 to S1, S1 to S2, or S2 to S3 transitions in photosystem II. Biochemistry 46:3151–3160


