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TRIBUTE

Vyacheslav (Slava) Klimov (1945–2017): A scientist par excellence, a great human being, a friend, and a Renaissance man

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Abstract Vyacheslav Vasilevich (V.V.) Klimov (or Slava, as most of us called him) was born on January 12, 1945 and passed away on May 9, 2017. He began his scientific career at the Bach Institute of Biochemistry of the USSR Academy of Sciences (Akademy Nauk (AN) SSSR), Moscow, Russia, and then, he was associated with the Institute of Photosynthesis, Pushchino, Moscow Region, for about 50 years. He worked in the field of biochemistry and biophysics of photosynthesis. He is known for his studies on the molecular organization of photosystem II (PSII). He was an eminent scientist in the field of photobiology, a well-respected professor, and, above all, an outstanding researcher. Further, he was one of the founding members of the Institute of Photosynthesis in Pushchino, Russia. To most, Slava Klimov was a great human being. He was one of the pioneers of research on the understanding of the mechanism of light energy conversion and of water oxidation in photosynthesis. Slava had many collaborations all over the world, and he is (and will be) very much missed by the scientific community and friends in Russia as well as around the World. We present here a brief biography and some comments on his research in photosynthesis. We remember him as a friendly and enthusiastic person who had an unflagging curiosity and energy to conduct outstanding research in many aspects of photosynthesis, especially that related to PSII.

Keywords Biochemistry and biophysics of photosynthesis · Pheophytin · P680 · Bicarbonate · Carbonic anhydrase · Photosystem II

This manuscript was edited by William W. Adams III for language, and then edited and approved for publication, by Barbara Demmig-Adams, in Photosynthesis Research. She added "This tribute celebrates the contributions of Vyacheslav Vasilevich Klimov, an outstanding scientist who was also a generous mentor and dear friend to many. He embodied the synergy between the passion for life itself and for the pursuit of knowledge to make the world a better place".

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Fig. 1 A 2015 portrait of Vyacheslav Vasilevich Klimov, V.V. Klimov to many, but Slava to his friends. *Source* Family Archives, provided by Larisa Klimova

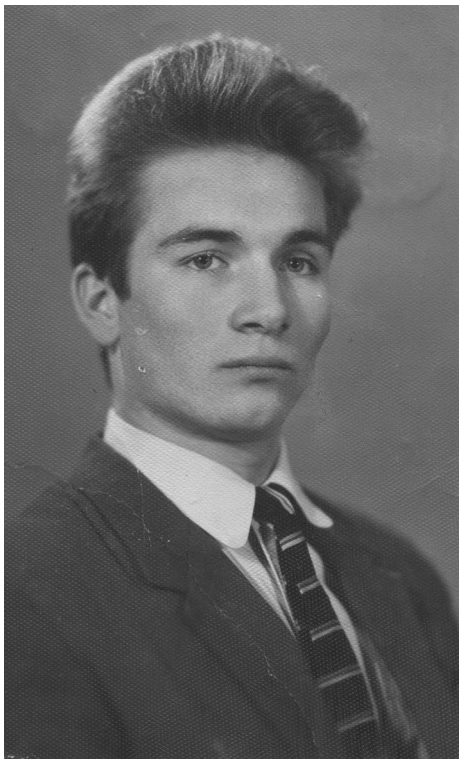

Fig. 2 Slava Klimov as a first year student at Moscow State University, 1964. Provided by Larisa Klimova

Early life and education

Vyacheslav (Slava) Vasilyevich Klimov (see Fig. 1 for a 2015 portrait) was born on January 12, 1945 in the village of Karavainka, Stalingrad (later Volgograd) in the Union of Soviet Socialist Republics (USSR). His parents were teachers: his father (Vasiliy Alexandrovich Klimov) was a history teacher and his mother (Elizaveta Ivanovna Klimova) a primary school teacher. See Supplementary Material for a photograph of Slava's parents.

In 1963, after graduating from Gorno-Balykley secondary school, also in the Volgograd region, Slava Klimov entered the Department of Biology and Soil Science of Mikhail V. Lomonosov Moscow State University (see Fig. 2). In 1968, after graduating cum laude, he did post-graduate work on "Photoinduced Changes of Chlorophyll a Fluorescence Yield during Photosynthesis" in the same Department. This research was done under the mentorship of Academician (Prof.) Alexander A. Krasnovsky, a world-recognized leader in photobiochemistry, and (Prof.) Navasard V. Karapetyan (see, e.g., Karapetyan and Govindjee 2014; Yurina et al. 2017). Later, after Slava Klimov obtained the Candidate degree (equivalent to a Ph.D.), he joined research group (s) led by A.A. Krasnovsky and Vladimir (Vlad) A. Shuvalov and worked first as a junior, and later as a senior, research investigator at the Institute of Photosynthesis of AN SSSR in Pushchino, Moscow Region. Then, in 1982, Slava Klimov was appointed as the head of the research laboratory for "Photosynthetic Water Oxidation and Oxygen Evolution" at the Institute of Basic Biological Problems (formerly Institute of Photosynthesis), Russian Academy of Science, RAS, where he worked until the last days of his life.

In 1986, Slava Klimov obtained his Doctor of Science degree (specialization: Biochemistry) from the A. (Alexsey) N. (Nikolaevich) Bach Institute of Biochemistry, RAS, for his work on "Light Reactions of Electron Transfer in

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Photosystem II of Plants and Algae". Slava Klimov was not only a brilliant scientist in the field of photosynthesis, but he was equally involved in educating young scientists. He became Professor of Biochemistry, teaching initially at the Pushchino State University and then at the Pushchino Branch of Moscow State University (MSU). In 1991, he became one of the laureates of the USSR State Prize for Science, awarded to the school of Academician Krasnovsky (A.A. Krasnovsky; Yu.E. Erokhin; V.B. Evstigneev [posthumously]; N.V. Karapetyan; A.V. Klevanik; V.V. Klimov; and V.A.Shuvalov) for studies on the *Photobiochemistry of Chlorophylls*. In addition, Slava Klimov was named to the prestigious Soros Professorship several times.

Research

As mentioned above, Slava Klimov's research centered on the molecular mechanism of light energy conversion and water oxidation during photosynthesis. He formulated and experimentally proved fundamentally new ideas about the mechanism of light energy conversion in oxygen-evolving photosystem II (Klimov and Krasnovsky 1981) that were widely accepted and included in contemporary reviews, monographs, and university courses on photosynthesis and advanced plant physiology. During his scientific career, Slava Klimov pioneered, along with his coworkers, the investigation of pheophytin participation in primary charge separation at the reaction center of PSII (see Klevanik et al. 1977; Klimov et al. 1977, 1978, 1979a, b, 1980a, b, c, 1986). Furthermore, he and his collaborators (including some of the authors here: SIA, SKZ, VAS) revealed the quantitative composition and heterogeneity of the manganese cluster of WOC, the water oxidizing complex (Klimov et al. 1982, 1985, 1990; Allakhverdiev et al. 1983).

Under Slava Klimov's guidance, the concept of water photooxidation through a two-electron mechanism with the production of peroxide as an intermediary product was experimentally justified (Ananyev et al. 1992; Klimov et al. 1993b). In addition, the role of bicarbonate as a significant component for the formation and functioning of the WOC was revealed (Klimov et al. 1995a, b, 1997a, b; Wincencjusz et al. 1996; Allakhverdiev et al. 1997a; Hulsebosch et al. 1998; Yruela et al. 1998). Slava Klimov, together with others, put forward and experimentally proved the hypothesis for the crucial role of Mn-bicarbonate complexes in the evolutionary origin of oxygenic photosynthesis (Klimov et al. 1995a, b; Dismukes et al. 2001). For discoveries on the unique role of bicarbonate bound to non-heme-iron involved in electron transport (between Q_A and Q_B) and protonation in the laboratory of one of us (G), see Shevela et al. (2012).

Furthermore, Slava was involved in the discovery of a new class of photosynthesis inhibitors (see Allakhverdiev et al. 1989a, b, 1997b; Klimov et al. 1992, 1993a, 1995c, for details). In contrast to the known inhibitors, the action of this class of chemicals was shown to be based on the formation of a short electron cycle around the PSII reaction center. Being a powerful tool for the investigation of charge separation and recombination in PSII, such inhibitors can also be considered as potential eco-friendly herbicides since they inhibit reactions specific to plants (but not animals). In the laboratory headed by Slava Klimov, PSII associated carbonic anhydrase, important for both WOC functioning and stability, was also revealed (Villarejo et al. 2002; Shutova et al. 2008; Shitov et al. 2009, 2011; Karacan et al. 2012, 2014, 2016; also see Rodionova et al. 2017). Further, upon the removal of a Mn-cluster from the WOC, an increase in photoinhibition was described by Klimov et al. (1990).

On the chlorophyll (Chl) a fluorescence front, a new hypothesis for the origin of PSII variable Chl a fluorescence, as a recombination luminescence, was put forward (Klimov et al. 1978; Allakhverdiev et al. 1994a), and the redox potential values of the PSII primary electron donor and acceptors were first determined in his lab (Klimov et al. 1979a, b; Allakhverdiev et al. 2010, 2011). Slava Klimov had collaborations at many universities and research centers in The Netherlands, USA, United Kingdom, Canada, Japan, Sweden, and Spain. His colleagues and friends remember him as a kind-hearted, cheerful person, a wise leader, and trusted comrade ready to help in any situation. We note that he had worked with a large number of scientists including Robert Carpentier (Canada), Norio Murata (Japan), Hans van Gorkom (The Netherlands), late Arnold Hoff (The Netherlands), late Gernot Renger (Germany), and Rafael Picorel (Spain). A list of most of Slava's publications is provided in the Supplementary Material.

We will begin the next section on Reminiscences from others, but first from his wife Larisa Klimova. In order to retain the originality of these reminiscences, we decided not to condense them even though there is some duplication; they are personal tributes.

Reminiscences

Larisa Klimova [translated from Russian to English by Ivan Proskuryakov; e-mails: pros@issp.serpukhov.su, ii-pros@yandex.ru, kla942@mail.ru]

Slava was born on January 12, 1945 in a village in the Volgograd (at that time the Stalingrad) region into a family of country teachers. In 1963, he graduated from school with honors ("gold medal") and entered the M.V. Lomonosov Moscow State University, from where he graduated in 1968, also with honors. After that he dedicated all his life to his beloved activity, i.e., to science and the study

Fig. 3 Larisa Klimova and Slava Klimov exchanging rings at their wedding in 1969. *Source* Larisa Klimova

of photosynthesis. Despite the fact that he was a world-renowned scientist, in everyday life he remained a very modest, open-hearted, charming person. He dearly loved life in all its manifestations. He had friends all over Russia and outside it, whom he always treated with deep respect and affection. Slava took great care of his family, loved his kids, and was a marvelous grandfather. It is important to emphasize that he was a very honest and decent person. He visited many countries around the globe, working in many of them, while remaining a great patriot of his homeland—Russia. It is a tragedy that when such a person, full of life, energy, and lots of plans for the future suddenly passes away. I hope, however, that the memories of Slava will continue to live among all his numerous students and colleagues, whom he helped in multiple ways. I strongly believe that his many research publications will be a treasure for future generations. I want to thank all his coworkers for the wonderful memory of Slava.

On a personal note: Slava and I met while studying at the Biology faculty of Moscow University and we were married in 1969. We lived together for 47 years. We have two children, a daughter Elena and a son Alexei, and four grandchildren. Figure 3 shows the two of us exchanging rings at our wedding, and Fig. 4 shows us with Elena and Alexei in 1987. We all miss Slava dearly.

Suleyman Allakhverdiev

It is obvious that the contribution of the laboratory headed by Slava Klimov had a great impact on the investigation of photosynthetic water oxidation and the mechanism of light energy conversion. Among Slava Klimov's students, there were 18 Candidates of Science (Ph.D.) and 2 Doctors of Science (Dr. Sci.), *and I was his first Ph.D. student*; Slava was not only my teacher, but a good friend. On October 2,

Fig. 4 A 1987 photograph of Klimov's family. Left to right: Elena (daughter), Larisa Klimova, Slava Klimov and Alexei (son). Photo provided by Larisa Klimova

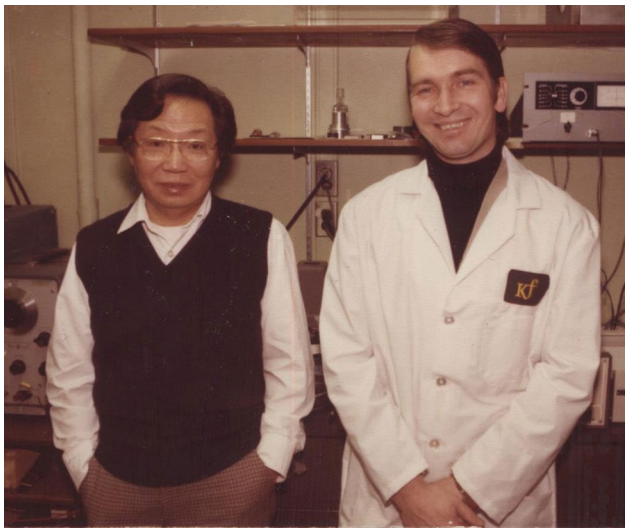

Fig. 5 A 1980 photograph of Slava Klimov and Bacon Ke at the Charles F. Kettering Research Lab, Yellow Springs, Ohio. *Source* Klimov's laboratory

1977, I came from Baku (Azerbaijan) to Pushchino (Moscow Region, USSR) for my Ph.D. thesis, and I joined the same group led by A.A. Krasnovsky and Vladimir A. Shuvalov. I worked on the investigation of pheophytin in photosynthetic reaction centers (RCs) under Slava Klimov and Academician A.A. Krasnovsky as my supervisors. At that time two papers on pheophytin were published (Klevanik et al. 1977; Klimov et al. 1977). But this work was criticized by other researchers, who stated that it was an artifact. These were really very exciting times! Together, we tried to show that the participation of pheophytin in reaction centers of PSII is not an artifact. At that time, we published several papers in Russian, and then Slava visited Bacon Ke's Lab in USA (see Fig. 5 for a photograph of Slava with Ke; see Klimov et al. 1980b, c for details of their research together) where he performed additional experiments. The experimental evidence for pheophytin participation, and the energetics and kinetics of electron transport in PSII in the presence of pheophytin, was summarized in my Ph.D. thesis. In 1984, I defended my thesis (in Physics and Mathematics [Biophysics]): "Photoreduction of Pheophytin in Reaction Centers of Photosystem II in Higher Plants and Algae" at the Institute of Biophysics, USSR Academy of Sciences, Pushchino, Moscow region, Russia. Then, in 2002, I obtained my Doctor of Science degree (highest/top degree in science) in Plant Physiology and Photobiochemistry from the Institute of Plant Physiology, RAS, Moscow, on "Functional Organization and Inactivation of Photosystem II".

During 1977–1986, together with Slava, Sasha Klevanik, Vlad Shuvalov, and Professor Likhtenshtein's group (at the branch of the Institute of Chemical Physics of the USSR Academy of Sciences in Chernogolovka, Moscow Region), we determined the number of manganese (Mn) atoms acting in the WOC of PSII. It had been shown that the WOC on the PSII donor side contains four atoms of Mn. Reconstitution of the Mn-cluster after a complete removal of Mn from PSII preparations had been shown using Mn(II) as well as various artificial Mn-organic complexes (binuclear and/or tetranuclear). We studied the magnetic interaction of Mn with $Pheo^-$ and $P680^+$, and evaluated the distance between the main components of PSII. The immersion depths of the main components of PSII RC in thylakoid membranes were also analyzed (Klimov et al. 1982, 1985, 1990; Allakhverdiev et al. 1983, 1986, 1989a, b, 1994b; Kulikov et al. 1983).

The effect of enhancement of PSII photoinhibition, upon the removal of Mn-cluster from the WOC, had been described by Klimov et al. (1990). In our joint work with Ivan Setlik's group in Třeboň, we showed that under anaerobic and reducing conditions, photoinhibition occurs on the acceptor side of PSII at the level of Q_A and Q_B, whereas under aerobic conditions, it occurs on the acceptor and/or the donor side of PSII; at the same time, separation and stabilization of charges in PSII RC remain unchanged (Allakhverdiev et al. 1987, 1993; Klimov et al. 1990; Setlik et al. 1990).

From 1988 to 1995, together with Slava, we spent more time on the bicarbonate effect on the electron donor side of PSII. Whereas previously bicarbonate was considered only as an important component for electron transfer between the plastoquinone electron acceptors, Q_A and Q_B, while bound to the non-heme Fe (Shevela et al. 2012), we found that removal of bicarbonate affects the PSII donor side reactions (see Klimov et al. 1995a, b, 1997a, b). Bicarbonate availability for the PSII donor side is especially significant for reactivation of the Mn-containing WOC after its removal by different treatments. It was suggested that bicarbonate may serve as a ligand to Mn, convert the aqua-ions of Mn^{2+} (non-oxidized by PSII) into an easily oxidizable form $Mn(HCO_3)^+$, or act as a structural component important for the formation of a functionally active Mn cluster, or function in proton transfer (from water to the lumen). We didn't risk publishing our results until 1995, and then investigations in The Netherlands (in the research groups of Arnold Hoff and Hans van Gorkom), in Spain (in the research group of Rafael Picorel), and in Sweden (in the research group of Göran Samuelsson) contributed to the shaping of our studies (see Klimov et al. 1995a, b, 1997a, b; Wincencjusz et al. 1996; Allakhverdiev et al. 1997a; Hulsebosch et al. 1998; Yruela et al. 1998; Shutova et al. 2008).

Once again, I would like to emphasize that, for me, Slava was a teacher, a senior colleague, but also a good friend, serving as an adviser in both science and life in general. It is true to say that he was my very close friend and a dear teacher. I very much miss Slava Klimov for his stimulating attitude.

Tatyana Savchenko (savchenko_t@rambler.ru)

We, the members of *Klimov's lab*[1], were deeply shocked and saddened to hear about the sudden death of Professor Klimov. He was always at the work place, in his office—ready to discuss science, to advise, and to help. He spent most of his time in the laboratory, even on the day of his death. During the holidays, he was always seen working in his office. I met Prof. Klimov for the first time in Baku, Azerbaijan, many years ago when he visited the Institute of Botany. At that time, I was preparing to defend my Ph.D. thesis on salt-induced carbonic anhydrase from *Dunaliella salina*. Klimov, of course, was interested in everything concerning this enzyme. More than 10 years later after working in several great labs around the world, I knew, for sure, that I wanted to work in Klimov's lab for high quality research and in a wonderful work environment. During our tenure together, we published three papers (Savchenko et al. 2014, 2017; Tikhonov et al. 2017a, b). Vyacheslav Klimov instilled high standards of research in all of us, and this knowledge as well as his memory will always be with us.

James (Jim) Barber

When I heard from Suleyman Allakhverdiev that Slava Klimov had passed away, I could not help shouting "Oh No". Slava was a close friend; he had worked in my lab at Imperial College several times. In fact, I was awarded a grant from the Royal Society of London to support our collaboration and to cover his travel and stay expenses in London. He always came with a colleague from his Institute in Pushchino, and several times with Vladimir (Vlad) Shuvalov. Slava was a "country boy", and on the weekends he would come to our country cottage in West Sussex and help me with my chores. He was exceptionally brilliant at splitting logs with an axe and experienced at growing vegetables. When I was in Pushchino, Russia, in 2016, he and I spent some time together at the conference party discussing the best way to grow cucumbers, at which he was very successful compared with my efforts. One year he sent me some seeds of the type he had used, but without his magic, I failed miserably. In addition, he was a world-renowned dedicated experimental scientist and it was he, who, with colleagues, discovered in 1977 that pheophytin is the primary electron acceptor of photosystem II (Klevanik et al. 1977; Klimov et al. 1977, 1978, 1979a, b, 1980a, b, c, 1986). This brought him into the limelight of the day and since then he has been in the top league of scientists unraveling the details of the electron pathway of oxygenic photosynthesis.

For many years Klimov, in addition to Alan Stemler (in USA), reported that bicarbonate could stimulate the rate of oxygen production by acting on the electron donor side of the PSII reaction center, presenting very convincing data on the topic (see Klimov et al. 1995a, b, 1997a, b; Wincencjusz et al. 1996; Allakhverdiev et al. 1997a; Hulsebosch et al. 1998; Yruela et al. 1998; cf. Stemler et al. 1974; Stemler 1982, 1997, 1998, 2002). This claim had been treated as controversial especially because there is a well-accepted role for bicarbonate on the electron acceptor side of PSII, pioneered by Govindjee and his coworkers (see Govindjee and van Rensen 1978; Shevela et al. 2012). However, PSII had evolved when there was a very high level of CO_2 in the atmosphere and it is hard to ignore Klimov's claim, which he vigorously defended until his untimely death. Fortunately others, e.g., Chuck Dismukes, is a great supporter of Klimov's findings (see Dismukes et al. 2001; also see below for his Reminiscences) and the work he started will continue until the picture is totally solved.

I would like to note that I had a great time doing research with Slava on several important aspects of PSII. Instead of describing them, I simply refer the readers to Bianchetti et al. (1998), Boichenko et al. (1993), and Klimov et al. (1995c).

I have met Slava's wife (Larisa) and son (Alexei) although not his daughter (Elena), but to all of them I send my most sincere condolence. He was a special friend and will be greatly missed as a human being and an excellent and creative scientist. I end my reminiscence by showing two photographs: Fig. 6 shows him walking in a Forest and Fig. 7 shows him playing pool, when he visited our cottage.

Charles (Chuck) Dismukes

I first met Slava Klimov in 1982 while visiting Douglas Winget's laboratory at the University of Cincinnati in Ohio. Independently, we were drawn there by the exciting report in 1980, by Mark Spector and his advisor Professor Douglas Winget, of the first isolation of the manganese enzyme responsible for the catalysis of water oxidation in photosynthesis (Spector and Winget 1980). Both Slava and I (together with my first graduate student, Daniel Abramowicz) spent several days working with Mark (even attending his MS thesis defense) with the intention of learning how to isolate this important enzyme. There was great interest in this enzyme by others as well; Spector and Winget had sent their "sample" to Govindjee, and a paper was published (Govindjee et al. 1980). The Spector-Winget report was later discredited by Daniel and myself, working at Princeton University; we found evidence that Spector's results were incorrect and

[1] The current members of the ex-Klimov team (including technical personnel), in alphabetical order, are: Galina Abramova; Suleyman Allakhverdiev; Tatyana Antropova; Andrew Khorobrykh; Mikhail Khristin; Zoya Maevskaya; Alexey Pigolev; Tatyana Savchenko; Alexander Shitov; Nadezhda Shutilova; Tatyana Smolova; Vasily Terentyev; Konstantin Tikhonov; Denis Yanykin; Olga Zastrizhnaya; and Sergey Zharmukhamedov.

Fig. 6 A 1995 photograph in the forest near Jim and Lyn Barber's cottage. Left to right: Olaf Kruse (then a post-doc with Jim Barber), Lynn Barber (with her dog Eric), and Slava Klimov. Photo by Jim Barber

Fig. 7 Slava Klimov playing pool, in 1994, at Jim and Lyn Barber's cottage in the UK. Photo by Jim Barber

that serious errors must have been made. Slava was also unsuccessful in reproducing Spector's results upon return to Pushchino, and Govindjee's Lab could not reproduce the preparation either, with experiments working *only* when the sample came from Spector. However, our experience led Daniel and I to discover that manganese can associate with two other proteins from spinach, the beta-subunit of the coupling factor (the ATP synthase) and the 33 kDa-manganese stabilizing protein of PSII (psbO gene product; see:

Fig. 8 Left to right: Charles Dismukes and Slava Klimov, 1984; celebrating Slava's visit to Princeton. Photo provided by Charles Dismukes

Abramowicz and Dismukes 1984a, b). The Spector-Winget report was later found to be fraudulent. One hypothesis is that Spector was simply using and sending "intact thylakoids", not the "enzyme". It was later revealed that Spector had fabricated even his Ph.D. research at Cornell University, Ithaca, NY, under Efram Racker, leading to a public scandal and rejection of his thesis. (Also see: "My Favorite Fraud" by Steven Wiley at http://www.the-scientist.com/?articles.view/articleNo/26694/title/My-Favorite-Fraud/.)

Having survived getting trapped in Spector's deception earlier in our careers, Slava and I gained mutual respect and became frequent collaborators and great friends. We interacted on several joint projects, grants, and conferences and exchanged visits at our home institutions. Slava's knowledge of photosynthesis, especially of oxygenic photosynthesis, was extremely comprehensive; his energy seemed tireless, and his easy-to-get-along leadership role was revealed through his collaborations worldwide! In 1984, Slava spent a few months working with me in Princeton, USA (see Fig. 8). In 1990, he hosted me in Pushchino, Russia (see Fig. 9). Together with our coworkers, we examined the role of inorganic cofactors of the photosynthetic WOC of PSII. This included studies on chloride dependence of the S2 state multiline EPR signal from PSII-WOC of spinach (Damoder et al. 1986), the role of bicarbonate in accelerating the rate of photo-assembly of the inorganic cofactors making up the PSII-WOC of spinach (Baranov et al. 2000, 2004), the strong influence of bicarbonate chelation on the thermodynamic stability of $Mn^{2+/3+}$ (as measured by redox potentiometry; Kozlov et al. 2004), the lack of electron donation to PSII from bicarbonate as a "surrogate" in place of water (Hillier et al. 2006), a model and hypothesis based on biogeochemical evidence for the role of bicarbonate in the evolution of the Mn cluster of oxygenic photosynthesis

Fig. 9 A group photograph taken at the reception of a Photosynthesis Conference in Pushchino, Russia, 1990. Standing (left to right): Govindjee and Slava Klimov. Sitting (left to right): Robert Blankenship, Leslie (Les) Dutton, Vladimir (Vlad) Shuvalov, Charles (Chuck) Dismukes, and Marina Samueleva. Photo provided by Charles Dismukes

(Dismukes et al. 2001), and direct experimental evidence demonstrating bicarbonate-dependent Mn photooxidation by an anoxygenic photoreaction center (Khorobrykh et al. 2013). All this research has led to the current accepted picture of the direct participation of dissolved inorganic carbon in the photo-assembly of the WOC, its function in optimal catalytic turnover of the holo-enzyme, and its role in the evolution of anoxygenic to oxygenic photosynthesis. This, of course, is, in addition to the well-known unique role of bicarbonate on electron and proton transport on the electron acceptor side of PSII, the Q_B site, as discovered by Govindjee and his coworkers (see, e.g., Govindjee and van Rensen 1978; Shevela et al. 2012).

Outside the laboratory, Slava was great fun to be with too. He was the first to initiate recreational sports during group gatherings in Pushchino. If there was no ball to be kicked or batted, he could be found on the dance floor moving with the music with or without a partner (see his photograph in the Supplementary Material). He was an avid chess player and a mischievous practical joker (his joke on the late Horst Witt is memorable). Slava led a life full of rich experiences, sharing freely his intellect, engaging others around the globe to both learn and teach, all done while sharing his zest for life, playful spirit and innocent mischief. Goodbye admired scientist, colleague, and dear friend. My admiration for Slava and his group is expressed in a poem that I gave to them upon my departure from Pushchino in June 1990:

> As a stranger I came to all but one to the land of Lenin's great theory.
> Seeking answers to questions of nature's puzzle on how did the green flora evolve?
> But a fortnight was given to master her plan, which took millions of years to design.
> Our struggle was brief but within it I reached another answer as tall.
> New colleagues I found to join in this quest whose spirit was truer than all.
> Willing hands and quick minds they eagerly gave, although we struggled without gain.
> Yet knowledge arose of a different sort I suppose, shared passions for insight we save.

Göran (Slim) Samuelsson

Around 2000, Dr. Tatiana Shutova, a former Ph.D. student of Slava Klimov, came to my laboratory as a guest researcher/post doc fellow. We started research on the PsbO protein and I became immediately impressed by Tatiana's deep knowledge on PsbO and other PSII proteins, a knowledge that she obviously had obtained under Slava's supervision.

After about 1 year in Umeå, she was able to start a second Ph.D. in my laboratory. I managed to convince her to do research on carbonic anhydrase (CA), which we had earlier identified in *Chlamydomonas reinhardtii*, Cah3, in addition to the PsbO work. At that time, Arsenio Villarejo, a postdoc from Spain, was also working with us and together Tatiana and Arsenio made some really interesting observations on a *Chlamydomonas* mutant lacking Cah3. In isolated thylakoids and BBY (Berthold Babcock Yocum) particles they could show that PSII electron transport and oxygen evolution in the CA-less mutant was dependent on the concentration of bicarbonate in the medium (Villarejo et al. 2002) but that this was not the case in the wild type. When we obtained the first thrilling results, we immediately decided to invite Slava to Umeå to share our excitement with him and to design other experiments to prove or disprove our hypothesis. Slava was one of the pioneers together with Alan Stemler (who had done his Ph.D. under Govindjee's mentorship; see Stemler et al. 1974; Stemler 1982, 1997, 1998, 2002; Lu and Stemler 2002; Lu et al. 2005) to claim that bicarbonate played a role on the donor side of PSII, in addition to that on the acceptor side of PSII, pioneered in Govindjee's Lab (see, e.g., Govindjee and van Rensen 1978; Shevela et al. 2012), and therefore I felt that it would be nice to have him involved in our work. Slava immediately accepted and came to Umeå within 2 weeks from receiving the invitation. From that time we became good friends and applied for a joint project that was funded, leading to the exchange of students and post docs and senior scientists between the labs. I visited Pushchino two times and Slava visited us in Umeå several times. My major memory of Slava from his time in my lab is of his enormous excitement about research and especially everything that had to do with photosystem II, combined with the feeling of joviality that he spread around himself. His many ideas about new and better experiments would sometimes stress us, but his nice personal character never made it unpleasant to work with him.

We often spent evenings together following the Russian tradition with nice conversations, vodka, and lots of food. I remember that he liked pizza and our working days often ended, together with the rest of the group, over a pizza from the local pizzeria. On one occasion in my home I had prepared a soup from funnel chanterelles. No one, before or after that day, has ever shown such an appreciation for my cooking as Slava did that night. I think he had at least three bowls of this exotic soup.

My most personal memory is of the time I invited him to come to my summerhouse (in mid-winter) in the middle of the woods in Sweden. We went ice fishing on a snowy, cold December day. Slava was very interested in fishing. As I recall, we did not get a lot of fish, but in the evening I cooked something for us; he "happened" to have a bottle of Russian vodka in his bag that we shared over dinner. After dinner, he "happened" to find a bottle of Armenian Cognac that we also shared. I had made a fire in the wood stove and it was warm and nice inside in contrast to the dark and cold evening outside. Then Slava suddenly suggested that we should sing. He would sing Russian folksongs for me and I was supposed to sing Swedish songs. It turned out that he really could sing, but not me I must say. However I will always remember that night when we, Slava and I, were singing songs to each other.

Thus, despite differences in political systems, religion, and background, we can all be friends if we only take the time to get to know each other. In our case, Vodka and singing helped. I end my reminiscence with a photograph of Slava with Andrew Khorobrykh, Tatiana Shutova and Pavel Shutov (Fig. 10; additional photographs may be obtained by writing to me).

Jian-Ren Shen

It was really a sad news to hear that Prof. Slava Klimov passed away suddenly in May 2017. I met and talked with him many times at international conferences, and knew his great work along with his colleagues on the discovery of pheophytin in photosystem II, when I was a graduate student. I followed his numerous studies on the structure and function of photosystem II since then. He was a great person, and I have a wonderful memory of meeting him when I was in Pushchino to attend the "Photosynthesis Research for Sustainability" conference in 2014. His passing away is a great loss to the photosynthesis community, and I will miss him much.

Dmitriy (Dima) Shevela (Umeå University, Sweden; dmitry.shevela@umu.se) and Johannes Messinger (Umeå/Uppsala University; johannes.messinger@umu.se)

Dima Shevela

I have known Vyacheslav (Slava) Klimov since November 2002, when I was a post-graduate student in his laboratory (Institute of Basic Biological Problems, Pushchino, Russia). It was he who introduced me to the fascinating world of Photosystem II (PSII), and involved me into the "bicarbonate"

Fig. 10 Slava Klimov relaxing after a pizza party in 2002 in Umeå, Sweden. From left to right Andrew Khorobrykh, Slava Klimov, Tatiana Shutova and Pavel Shutov. Photo provided by Göran (Slim) Samuelsson

project, which went beyond my Ph.D. days, and continues until now… In 2005, I went to Johannes Messinger's group (then at the Max-Planck-Institut für Bioanorganische Chemie, Mülheim an der Ruhr, Germany) on a Deutscher Akademischer Austausch Dienst (DAAD) fellowship to continue my studies on the effect of bicarbonate during the reduction of the Mn_4CaO_5 cluster (Shevela et al. 2006, 2007). At the end of this 7-month research visit, I decided to continue my Ph.D. work in Messinger's laboratory. Slava Klimov accepted my decision (although it was, likely, not so easy for him) and agreed to become my co-supervisor together with Johannes Messinger. Although the "bicarbonate" project became one of several other projects since then, we continued our collaboration with Slava.

Dima Shevela and Johannes Messinger

During 2006–2008, our main focus within the "bicarbonate" project was to probe if bicarbonate is a ligand of the Mn_4CaO_5 cluster, a favorite idea of Slava at the time (Klimov and Baranov 2001; Ferreira et al. 2004). Our experiments clearly indicated that bicarbonate is *not* a tightly bound ligand to the Mn_4CaO_5 cluster. Although these results contradicted Slava's initial ideas about bicarbonate as a constituent of the oxygen-evolving complex (OEC), he readily accepted our data and conclusions (Shevela et al. 2008a, b). On the other hand, it had been clear, at that time, from the data and concepts of Govindjee and co-workers that bicarbonate was bound, and functioned, on the electron acceptor side of PSII, close to the Q_B site (see, e.g., Xiong et al. 1998; Van Rensen et al. 1999). The open-minded attitude of Slava clearly characterized him as a true and objective scientist who considered experimental data over the hypothesis. As Dmitry's (Dima's) co-supervisor, Slava participated at his Ph.D. defense at Technische Universität Berlin in March 2008. During his visit at this time, we discussed additional experiments that we could do together. However, our next joint collaboration became feasible much later (in 2013–2014) when Slava and Konstantin Tikhonov (a member of Slava's group in Pushchino) visited us in Umeå (Sweden) for joint experiments. Together, we developed a new approach to quantify the amount of bound bicarbonate per PSII under air-saturating conditions. With this new approach, Slava was hoping to get confirmation of his idea about multiple binding sites (at least two) of bicarbonate within PSII (Pobeguts et al. 2010). However, using different sample types and preparations, the new approach always gave us very close to one bicarbonate per PSII, while in earlier experiments, including our own, numbers from 0.3 to 1.3 (Govindjee et al. 1991, 1997; Shevela et al. 2008b) were found. Nevertheless, Slava accepted these results as well and was positive about preparing a paper on these results. Sadly, the news that Slava suddenly passed away came just before finishing this joint paper (Tikhonov et al. 2017b).

A tribute to Slava would be incomplete without presenting the current understanding of the interaction of bicarbonate with PSII. Today, we have clear evidence for both acceptor and donor side effects of bicarbonate on PSII. The bicarbonate bound to the non-heme iron, between quinones Q_A and Q_B, plays an important role in electron and proton transfer reactions (Wydrzynski and Govindjee 1975; Shevela et al. 2012; Brinkert et al. 2016). In addition, bicarbonate ions also have clear effects on the water-splitting (oxygen-evolving) side of PSII, as suggested in numerous studies by Alan Stemler and Slava Klimov (see Klimov et al. 1995a, b, 1997a, b; Wincencjusz et al. 1996; Allakhverdiev et al.

Fig. 11 Left to right: Slava Klimov, Johannes Messinger, Dima Shevela, and Katrin Beckmann at the 2008 Ph.D. defense of Dima Shevela and Katrin Beckmann at Technische Universität-Berlin (Germany). Photo provided by Dima Shevela

Fig. 12 A 2000 photograph of (left to right): Vladimir (Vlad) Shuvalov, Alexandr Maljan, Alex Borisov and Slava Klimov at a conference. Photo provided by Klimov laboratory

1997a; Hulsebosch et al. 1998; Yruela et al. 1998; Klimov and Baranov 2001; Stemler 2002; Van Rensen and Klimov 2005). Bicarbonate ions are not tightly bound on this side (Tikhonov et al. 2017b), but act instead as mobile proton acceptors (Shutova et al. 2008; Koroidov et al. 2014). Additionally, they may stabilize the OEC against photoinhibition

Fig. 13 A 2001 photograph of the members of the "Laboratory of Photosynthetic Water Oxidation" (Pushchino, Russia). From left to right: Tatyana Smolova, Olga Zastrizhnaya, Alla Kazakova, Andrew Khorobrykh, Olga Pobeguts, Slava Klimov, Galina Abramova, Yurii Kozlov, Zoya Maevskaya, and Tatyana Antropova. Photo provided by Andrew Khorobrykh and Larisa Klimova

Fig. 14 A 2005 photograph of members of the Klimov laboratory. Left to right: Vasily Terentyev, Tatyana Smolova, Tatyana Antropova, Sergey Zharmukhamedov, Dmitrii Shevela, Galina Abramova, Slava Klimov, Yurii Kozlov, Vladimir Boichenko, Alla Kazakova, Olga Pobeguts, Zoya Maevskaya. Missing: Suleyman Allakhverdiev, Mikhail Khristin, Olga Zastrizhnaya, and Andrew Khorobrykh. Photo provided by Larisa Klimova

or thermoinactivation (Klimov et al. 1997, 2003). Bicarbonate is also known to facilitate the photoassembly process (Allakhverdiev et al. 1997a, b; Baranov et al. 2004; Ananyev et al. 2005; Dasgupta et al. 2008). *We miss Slava and would have liked to do more experiments together with him*. We end our reminiscence by showing a photograph of Slava Kimov after the doctoral defense exam of one of us (Dima Shevela) and Karin Beckmann in 2008 (see Fig. 11).

Fig. 15 Slava Klimov during a stay in the Institute of Botany (Beijing, China) April 2000. From left to right: Andrey Khorobrykh, Chong-qin Tang, Larisa Klimova, Slava Klimov. Photo provided by Andrey Khorobrykh

Fig. 16 **a** A 2005 photograph of Slava Klimov playing harmonica. **b** Another picture of Slava playing Bayan (a type of button accordion), in 2010, with his granddaughter Dasha dancing to his music. Photos provided by Larisa Klimova

Concluding Remarks

Slava Klimov was a brilliant scientist. We are particularly impressed with his discovery of "pheophytin" and the role of bicarbonate on the electron donor side of PSII, especially on the tantalizing evolutionary aspects of it (see reminiscence of Chuck Dismukes). Slava Klimov was a top scientist, a great mentor, team member, musician, gourmet, dancer, and above all a great human being. The *reminiscences* by Slava's wife Larisa, his first Ph.D. student Suleyman Allakhverdiev, Tatyana Savchenko, Jim Barber, Chuck Dismukes, Slim Samuelsson, Jian-Ren Shen, and

Dima Shevela (together with Johannes Messinger) tell the story of the man he was—a wonderful human being. Slava's life was in SCIENCE. Thus, we show a photograph with Vlad Shuvalov (author), Alex Borisov (a friend of ours), and Alexandr Maljan (Fig. 12); and two photographs of Slava with part of his research team in 2001 and in 2005 (Figs. 13 and 14). Figure 15 shows a photograph of his travel to China in 2000, whereas Fig. 16 is one of the most befitting photo(s) to end this Tribute to Slava, where he is playing his favorite instrument Bayan (a), and most importantly—to his grand-daughter (b). On behalf of the entire international photosynthesis community, we bid Slava our final "Good Bye" (Adieu), or better "Прощай" (Proshay).

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