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HISTORY AND BIOGRAPHY

In memory of Vladimir Anatolievich Shuvalov (1943–2022): an outstanding biophysicist

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Abstract
We present here a tribute to one of the foremost biophysicists of our time, Vladimir Anatolievich Shuvalov, who made important contributions in bioenergetics, especially on the primary steps of conversion of light energy into charge-separated states in both anoxygenic and oxygenic photosynthesis. For this, he and his research team exploited pico- and femtosecond transient absorption spectroscopy, photodichroism & circular dichroism spectroscopy, light-induced FTIR (Fourier-transform infrared) spectroscopy, and hole-burning spectroscopy. We remember him for his outstanding leadership and for being a wonderful mentor to many scientists in this area. Reminiscences by many [Suleyman Allakhverdiev (Russia); Robert Blankenship (USA); Richard Cogdell (UK); Arvi Freiberg (Estonia); Govindjee Govindjee (USA); Alexander Krasnovsky, jr, (Russia); William Parson (USA); Andrei Razjivin (Russia); Jian- Ren Shen (Japan); Sergei Shuvalov (Russia); Lyudmilla Vasilieva (Russia); and Andrei Yakovlev (Russia)] have included not only his wonderful personal character, but his outstanding scientific research.

Keywords Primary photochemistry · Reaction centers · Charge separation · Photosystem I · Photosystem II · Cytochromes · Femtosecond spectroscopy · Delayed light emission

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Personal life, education, and early research

Vladimir Anatolievich Shuvalov was born on October 13, 1943, in Omsk, Siberia. He passed away in Moscow on January 8, 2022. Figure 1 shows his 2005 portrait. He is survived by his wife Tatyana and two sons, Andrei, and Sergei. Vladimir's parents were engineers at an aircraft manufacturing plant in Omsk during World War II (Shuvalov 2015). After the war, the family moved to Moscow, where he graduated from high school in 1960 and entered the Department of Biophysics at the Biology and Soil Faculty of the M.V. Lomonosov Moscow State University. The Biophysics Department had a special educational program that combined substantial education in biology with serious courses in mathematics, chemistry, and physics as well. Shuvalov's experimental work began in 1963 in collaboration with Alexander Krasnovsky Jr. (his groupmate), under the supervision of Professor Felix F. Litvin, who provided a unique chemiluminometer with a cooled photomultiplier and photon-counting electronics for their research (see Litvin 1960). This device was very useful for training and understanding how photomultipliers and photon-counting systems work. However, it was extremely inconvenient to use. By mid 1964, Vladimir had designed another photochemiluminometer that was much easier to operate and speeded up his research. At this initial stage of the research, Vladimir and Alexander worked in close cooperation, which helped both to learn faster. Both investigated delayed light emission (DLE) of leaves (for the discovery of DLE, see Strehler and Arnold 1951). Part of their joint work was published in two papers in 1966 (Litvin et al. 1966; Litvin & Shuvalov 1966); these were Vladimir's first publications. He received his higher education diploma, which is comparable to the MS degree in the USA, in Biophysics in 1965. Soon thereafter, he joined the *aspirantura* (approximately equivalent to a post-graduate program in the USA) of the A.N. Bach Institute of Biochemistry at the Russian Academy of Sciences (RAS), under the joint guidance of Professors A.A. Krasnovsky, Sr, and F.F. Litvin. However, Vladimir's main research was done at Moscow University, where he received his *Candidate-of-Science* degree (approximately equivalent to a Ph.D) in Biophysics in 1969. His thesis dealt with the '*afterglow*' (delayed light emission) from chlorophyll during photosynthetic electron transfer (Shuvalov and Litvin 1969).

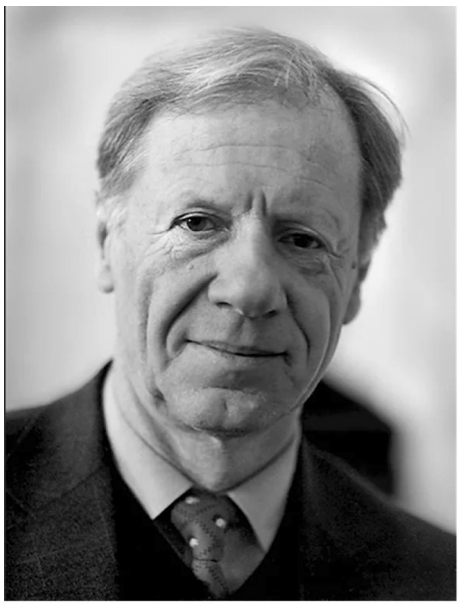

Fig. 1 A portrait of Vladimir A. Shuvalov, ~2005; source: Photosynthesis laboratory, Pushchino

Scientific career, positions held, and recognition

From 1965 to 1972, Shuvalov worked as a junior researcher at the A.N. Bach Institute of Biochemistry, Moscow. In 1973, he moved to Pushchino (Moscow region) where he first had the position of a *Senior Researcher* in the group of Professor Krasnovsky at the Institute of Photosynthesis and soon thereafter, he was appointed as *Vice Chair* of this group. In 1979, this group was transformed into the laboratory of primary processes in photosynthesis at the Biological Research Center. Shuvalov became the head of this laboratory (see Fig. 2). Just before this, he was invited by Bacon Ke, in USA, to work as a postdoc at the Charles F. Kettering Research Institute (Yellow Springs, Ohio), For his research at that time, see Shuvalov et al. (1979a,b), and for the life and work of Ke, see Govindjee et al. (2021). In 1980, William Parson invited him to do nanosecond–picosecond measurements on bacterial reaction centers at the University of Washington, Seattle (see the *Reminiscence* of William Parson).

Shuvalov received his Doctor of Science degree in Biophysics in 1982 for the study of primary processes of light energy conversion in photosynthesis. He guided and mentored many scientists in Pushchino during the 1980s, and in 1986, he was invited by Louis N.M. Duysens, in the Netherlands, to do picosecond measurements on photosynthetic reaction centers (RCs) in Leiden (for results, see Shuvalov and Duysens 1986, and Shuvalov et al. 1986; for the life of Duysens, see Govindjee and Pulles 2016).

In 1987, Shuvalov became the Head of the Department of Photobiophysics at the A.N. Belozersky Institute of Physical–Chemical Biology, Moscow State University. For his research in the overall area of '*Biophysics of Photosynthesis*', he received two major recognitions in 1991: (1) the *State Prize of the USSR* for the discovery of the

Fig. 2 Members of the laboratory of the primary processes in photosynthesis, Pushchino, late 1970s. Standing (left to right): Vyacheslav (Slava) Klimov, Vladimir Shuvalov, and Alexander Klevanik. Sitting (left to right): Tatyana Volshukova, Lyudmila Erokhina, and Irina Ganago. *Source* Photosynthesis laboratory, Pushchino

molecular mechanisms of photochemical transformations of chlorophylls in the reaction centers of photosynthesis; and (2) corresponding membership of the Russian Academy of Sciences in the section of chemical and biological sciences. From 1996 through 2017, he served as the Head of the Institute of Basic Problems in Biology of the RAS (formerly the Institute of Photosynthesis of the USSR Academy of Sciences); during part of this period (1997–2013), he also served as the Director of the Pushchino branch of the Moscow State University. He became a full member of the Russian Academy of Sciences in 1997, a Foreign Honorary Member of the American Academy of Arts and Sciences, and a member of the American Chemical Society and the Society of Plant Physiologists (USA) in 1998, an Honored Professor of Moscow State University and a member of the Order of Friendship in 1999, a member of the German Academy of Naturalists Leopoldina in 2002, and received the Order of Honor, the state award of the Russian Federation. In addition to all the above, Shuvalov served as a frequent reviewer for several journals including *Photosynthesis Research*, *Comparative Biochemistry and Physiology*, *Biochemistry* (Russian), *Biophysics* (Russian) and *Biological Membranes* (Russian).

Vladimir Shuvalov participated actively in many photosynthesis conferences in Russia as well as abroad. Figure 3 shows an informal photograph with a few other participants on a sight-seeing trip during a break at the 1991 Gordon Conference on "Biophysical Aspects of Photosynthesis" (Chair: Robert Blankenship), which was held at the Proctor Academy, Andover, NH, USA.

Research

Vladimir Shuvalov pursued research with great energy and personal dedication. His work led to important contributions to our understanding of the energetics, dynamics, and mechanism of the conversion of light energy into charge-separated states in both photosystems I and II of oxygenic organisms as well as in the reaction centers (RCs) of photosynthetic bacteria. It also provided new information on the cytochromes of photosynthetic systems. Shuvalov authored or co-authored well over 200 papers (see below for selected papers) and two books (i) on the *primary conversion of light energy during photosynthesis*, 1990, and (ii) on the *conversion of solar energy in the primary act of charge separation in the reaction centers of photosynthesis*, 2000.

As head of two research groups, one at the Institute of Basic Biological Problems of RAS in Pushchino (see Fig. 4 for a group photograph of the Pushchino group in 2008), and the other at the Department of Photobiophysics of the A.N. Belozersky Institute of Physical–Chemical Biology of Lomonosov Moscow State University (see Fig. 5 for his photograph with Victor Nadtochenko

Fig. 3 Gordon Research Conference on Photosynthesis, 1991. From left to right: Andrew Shreve, Andres (Andy) Karplus, Vladimir Shuvalov, Giuliana Zannetti, Slava Klimov, Thomas (Tom) G. Owens, and Alexander Ganago. *Source* Photosynthesis laboratory, Pushchino

Fig. 4 Members of the Laboratory of Primary Processes in Photosynthesis, Pushchino 2008. **Standing**, from left to right: Ravil Khatypov, Anatoliy Shkuropatov, Ilgiz Galiulin, Lyudmila Vasilieva, Vladimir Shuvalov, Anton Khmelnitsky, and Tatyana Khmelnitskaya. **Sitting**, from left to right: Olga Kaminskaya, Valentina Shkuropatova, Lyudmila Erokhina, and Tatyana Volshukova. *Source* Photosynthesis laboratory, Pushchino

Fig. 5 A 2011 photograph at Moscow State University. Left to right: Victor Nadtochenko, Alexey Semenov and Vladimir Shuvalov. *Source* Alexey Semenov

and Alexey Semenov), Shuvalov was a powerful driving force for introducing diverse experimental techniques, including pico- and femtosecond transient absorption spectroscopy (Shuvalov and Klevanik 1983; Streltsov et al. 1995; Khatypov et al. 2012), photodichroism and circular dichroism spectroscopy (Shuvalov and Asadov 1979), light-induced FTIR spectroscopy (Zabelin et al. 2011), and hole-burning spectroscopy at liquid helium temperatures (Shuvalov et al. 1988). His group also used site-directed mutagenesis and membrane protein crystallization (Fufina et al. 2007; Vasilieva et al., 2012), as well as selective chemical modification of RC chromophores (Shkuropatov and Shuvalov 1993; Shkuropatov et al. 1999). Further, affinity immobilization of bacterial RCs on a metal surface was used to investigate photoinduced charge transfer of electrons from immobilized RCs to metallic electrodes (Katz et al. 1989).

Shuvalov's many scientific accomplishments include, chronologically, the following discoveries: (i) 1976: in bacterial reaction centers (bRC), bacteriopheophytin (BPh) is an electron acceptor that precedes the ubiquinone electron acceptor Q_A; (ii) 1977–2008: in the Photosystem II (PSII) RC, pheophytin (PheoD1) and chlorophyll (ChlD1) are electron acceptors before Q_A; (iii) 1978: in bRC, bacteriochlorophyll B_A is the electron acceptor before BPh; (iv) 1986–2010: in Photosystem I (PSI), a Chl *a* is a primary electron acceptor reduced within 100 femtoseconds; and (v) 2012: in bRC, primary charge separation may occur in femtoseconds (120–180 fs) within the excited P870, P* (see Carpentier and Allakhverdiev 2015). Selected results of these studies are discussed below. (For a background on the molecular mechanism of photosynthesis, see Blankenship (2021), and for an overview on photosynthesis, see Shevela et al. (2019).)

Studies of bacterial reaction centers

(by Lyudmila Vasilieva and Anatoly Shkuropatov)

Prior to X-ray diffraction analysis of RC crystals, Shuvalov and Asadov (1979) described the pigment organization in the RCs of the purple bacterial species *Blastochloris* (formerly *Rhodopseudomonas*) *viridis*. Their analysis was based on the optical properties of RCs, using expressions for dipole and rotational strengths in molecular aggregates. Measurements of absorption spectra, photodichroism and circular dichroism spectra of isolated RCs under various redox states at 100 K provided values for intermolecular distances and interaction energies of the pigments. A model was obtained of the arrangement of two bacteriochlorophyll (BChl) molecules constituting the primary electron donor, two monomeric BChl molecules, and a photochemically active bacteriopheophytin (BPh) (Shuvalov and Asadov 1979). This model was later supported by the X-ray crystallographic data (Deisenhofer et al. 1984).

Using transient absorption spectroscopy to study native bacterial RCs (Shuvalov et al. 1978; Shuvalov and Klevanik 1983) as well as RCs modified to contain plant pheophytin instead of bacteriopheophytin (Shkuropatov and Shuvalov 1993; Kennis et al. 1997), Shuvalov and his coworkers had a major share in the description of the currently widely accepted two-step model of primary charge separation, $P^* \rightarrow P^+B_A^- \rightarrow P^+H_A^-$, where P^* is the excited primary electron donor, B_A is a monomeric BChl, H_A is the active BPh, and superscripts + and − denote oxidized and reduced radicals.

Yakovlev et al. (2002a,b) showed that femtosecond excitation of the primary electron donor (the BChl dimer P) induces low-frequency vibrations leading to the rotation of small groups (presumably, H_2O) that modulate the energy of electron transfer from P* to B_A (see Andrei Yakovlev's reminiscences below). Yakovlev et al. (2005) later established that a water molecule (HOH55) located near the 9-keto group of the BChl B_A in the crystal structure plays a particularly important role in the primary photochemistry, and that its removal in the (M203) GL mutant RC slows electron transfer from P* to B_A. Yakovlev et al. (2003) had suggested previously that one of the main factors determining the high efficiency and the direction of primary charge separation in purple bacterial RCs is a combination of coherent electron transfer from an excited primary electron donor P* to B_A and an incoherent change in nuclear coordinates due to reorientation of the hydroxyl group of tyrosine M210.

Khatypov et al. (2010, 2012) suggested that relaxation of the excited P* on a femtosecond time scale leads to the formation of a short-lived internal charge transfer state of the bacteriochlorophyll dimer ($P_A^+P_B^-$). Then, Khmelnitsky et al. (2013) found evidence for a long-lived mixed P*($P_A^+P_B^-$) state when electron transfer to the primary acceptor B_A was largely prevented by increasing the midpoint redox potential of P by ~ 260 mV. Based on the results of femtosecond studies of electron transfer from P* to B_A in a series of *Rhodobacter sphaeroides* mutant RCs with increased redox potentials of the primary electron donor, Khmelnitsky et al. (2013) estimated the free energy change between P* and $P^+B_A^-$ to be 60 ± 10 mV at physiological temperatures.

Over the last 20 years, Shuvalov and his coworkers in Pushchino focused on structure–function relationships in photosynthetic RCs of *R. sphaeroides* using site-directed mutagenesis (Fufina et al. 2007, 2013; Leonova et al. 2011). Data obtained by combining this method with biochemical and biophysical approaches led to new information on the role of axial ligation in the spectral and redox properties of the BChls. Following this, Fufina et al. (2019) and Khristin et al. (2020) discussed the correlation between the structures of the chromophores and the nature of their ligands. In addition, the crystal structures of several mutant RCs were resolved with high resolution (Vasilieva et al. 2012; Fufina et al. 2015; Selikhanov et al. 2022).

Primary events in photosystems I and II

(by *Alexey Semenov and Victor Nadtochenko)*

Beginning in 2006, Vladimir Shuvalov intensively collaborated with the research laboratories headed by Oleg Sarkisov and later Victor Nadtochenko at the N.N. Semenov Institute of Chemical Physics (Russian Academy of Sciences) and by Alexey Semenov at A.N. Belozersky Institute of Physical–Chemical Biology (Moscow State University). A unique pump-probe setup with 10 fs resolution over a broad UV-VIS-NIR spectral range was developed at the Institute of Chemical Physics and used to study the primary events in photosystems (PS) I and II. Shuvalov's experience and knowledge greatly contributed to the planning of experiments and interpretation of the results obtained in this period, which resulted in publication of more than a dozen papers (cited below).

Studies of PS I pigment-protein complexes from the cyanobacteria *Synechocystis* sp. PCC 6803 led to a new understanding of the primary events of charge separation in this reaction center. It was shown that conversion of a delocalized exciton into a charge-separated state between the primary (electron) donor in PS I (P_{700}) and the primary (electron) acceptor Chl (A_0) proceeds within ~ 100 fs. These results were obtained by the pump–probe technique with 20-fs low-energy pump pulses tunable in the spectral region of the red shoulder of the Chls' Q_y absorption bands (Shelaev et al. 2010; Cherepanov et al. 2017). This approach allowed direct excitation of reaction center Chl molecules with minimal involvement of light-harvesting antenna pigments. The data obtained were rationalized with an adiabatic three-state model that included the Chl dimer P_{700} and two symmetrically arranged chlorophyll molecules nearest to A_0. The main events under the experimental conditions used included very fast (< 100 fs) charge separation with the formation of the $P_{700}^+A_0^-$ primary ion-radical pair in about half of the RCs, a ~5-ps energy transfer from excited antenna Chl* in the remaining part of RCs, and electron transfer to the phylloquinone acceptor A_1 within ~ 25 ps with the formation of the secondary radical pair $P_{700}^+A_1^-$.

A similar approach was used to study the primary events in spinach photosystem II (PS II) core complexes excited at 710 nm at room temperature. The initial step of charge separation, with a time constant of ~ 1 ps, was ascribed to electron transfer from the Chl dimer P_{680} to the monomeric Chl_{D1} in the D1 protein subunit, with the formation of the ion-radical pair $P_{680}^+Chl_{D1}^-$. The subsequent electron transfer from Chl_{D1}^- to pheophytin ($Pheo_{D1}$) occurred in 13 – 14 ps and resulted in the formation of the secondary ion-radical pair $P_{680}^+Pheo_{D1}^-$. (An alternative mechanism of charge separation with Chl_{D1} as the primary electron donor and $Pheo_{D1}$ as the primary acceptor cannot be ruled out at cryogenic temperatures and in the presence of external acceptors.) The next electron transfer from $Pheo_{D1}^-$ to the primary plastoquinone electron acceptor (Q_A) occurred in ~ 250 ps in good agreement with previous measurements (Shelaev et al. 2011; Nadtochenko et al. 2014).

Studies on cytochrome (Cyt) *b559*

(by *Olga Kaminskaya*)

Vladimir Shuvalov was also interested in the function of the non-covalently bound cytochrome component of the PSII reaction center, Cytb-559, whose reduced alpha band peak is midway between 559 and 560 nm and whose properties and related studies have been recently reviewed (Cramer and Zakharov 2022). Shuvalov's research began in collaboration with the research groups of Gernot Renger and Athina Zouni. (For the life and work of Renger, see Siggel et al. 2016.) Investigation of the redox properties of Cyt *b559* began with redox titrations of the heme protein in PS II preparations of higher plants with different degrees of structural complexity—PS II membrane fragments, oxygen-evolving PS II core complexes, and D1-D2-Cyt *b559* complexes (Kaminskaya et al. 1999, 2005; 2007b; Kaminskaya and Shuvalov 1994). It was shown that the frequently observed three-component redox pattern of Cyt *b559* in PS II membrane fragments, represented by high-, intermediate- and low-potential (HP, IP, LP) forms, transforms irreversibly to a homogenous LP state upon solubilization of PS II. A single redox form of Cyt *b559* with an intermediate E_m value was found in a preparation of PS II complexes from *Thermosynechococcus elongatus* (Kaminskaya et al. 2005). In the latter preparation, a refined value of the Cyt *b559* α-band extinction coefficient was determined; this work established the Cyt *b559*/PSII stoichiometry to be 1:1 in higher plants, where the crystal structure of PS II had not yet been determined.

Photoinduced redox transitions of Cyt *b559* were observed in dehydrated films of PS II membrane fragments by Kaminskaya et al. (2003) and Kühn et al. (2005). These studies revealed that a decrease in relative humidity leads to reversible replacement of water oxidation by photooxidation of Cyt *b559*. In dehydrated films, oxidized Cyt *b559* was shown to undergo photoreduction in a DCMU-insensitive manner, with endogenous components (Chl and carotenoid) acting as electron donors (Kaminskaya et al. 2003). These data suggested the existence of an intrinsic electron-transfer pathway from Q_A^-/$Pheo_A^-$ to oxidized Cyt *b559*, bypassing Q_B. Photoreduction of Cyt *b559* in dehydrated PS II membrane films closely corresponded to the formation of a trapped state with an oxidized Chl molecule in samples of D1-D2-Cyt *b559* complexes frozen under illumination (Kaminskaya and Shuvalov 1994).

Further work on Cyt *b559* by Shuvalov and coworkers addressed possible functional interactions between the heme protein and plastoquinone (PQ) molecules in the thylakoid membrane. Kaminskaya et al. (2007a) showed that several chemical compounds cause concentration-dependent negative shifts in the E_m of the high-potential (HP) form of Cyt *b559* without affecting the forms of the cytochrome with a low or intermediate E_m. These findings indicated that a binding site distinct from the Q_B site exists for externally added DCMU, dinoseb, CCCP and TPB (and, presumably, also for the internal PQ) in the vicinity of the heme group of Cyt *b559*. The specific accommodation of lipophilic anions suggested that this site has a polar nature and is probably different from a buried plastoquinone site (Q_C) that was found in PS II from the cyanobacterium *T. elongatus* (Guskov et al. 2009). The proposed quinone site near HP Cyt *b559* that specifically binds lipophilic anions was later named Q_D (Kaminskaya and Shuvalov 2013). (The presence of two quinone sites in PS II in addition to Q_A and Q_B had been suggested earlier (see Kruk and Strzalka 2001) based on studies of photoreduction and dark oxidation of Cyt b559 in Triton X-100-solubilized PS II membrane fragments.)

Kaminskaya and Shuvalov (2013) found that oxidized Cyt *b559* of PSII membrane fragments is reduced by either endogenous or added plastoquinol in a biphasic manner. These results indicated the existence of two kinds of redox equilibria between Cyt *b559* and plastoquinol in different time domains. The first sub-second phase of Cyt *b559* reduction was attributed to one-electron redox equilibrium between the oxidized Cyt *b559* and the PSII-bound plastoquinol. The proposed Q_D quinone site near the heme group of the oxidized Cyt *b559* was suggested to be the site of deprotonation and one-electron oxidation of plastoquinol; further, the slow phase of Cyt *b559* reduction by quinols probably reflects redox equilibration of Cyt *b559* with the quinone pool.

A key step in understanding the so-called '*Cyt b559 enigma'* is the interpretation of the characteristic three-component redox titration pattern (HP, IP, LP) observed in chloroplasts and PS II membrane fragments (Horton and Croze 1977; Thompson et al. 1989; Kaminskaya et al. 1999). This property had been attributed to the presence of three conformational forms of Cyt *b559* heme, depending on the microenvironment. Kaminskaya and Shuvalov (2016, 2018) offered an alternative interpretation of the redox heterogeneity of Cyt *b559*: electrostatic interactions of Cyt *b559* with a singly protonated plastoquinone bound in the buried Q_C site causing three redox components to appear in the redox titration curve of structurally homogenous Cyt *b559*. In this model, the singly protonated plastoquinone species at the Q_C site is suggested to allow fast entrance and output of electrons at the level of the Q_C in equilibrium with Cyt *b559*, ensuring conditions of the Cyt *b559*-mediated cyclic electron flow around PS II (Kaminskaya and Shuvalov 2016).

Reminiscences

We provide here reminiscences from Sergei Shuvalov (Vladimir's younger son), followed by some of his coworkers, and other scientists in the order in which they were received. These reminiscences mention many of Shuvalov's research contributions (some not mentioned above) as well as his outstanding personal qualities.

Sergei Shuvalov (131043@gmail.com)

My father was a very progressive person in all areas of activity that he undertook, and there were many such in his life in addition to science. He played the piano beautifully and was fond of tennis and skiing (see Supplementary Material). When I was a child, he helped me design a model aircraft with great interest. He was a very well-read and educated person with a broad outlook. I am infinitely grateful to him for instilling in me this ability to be interested in everything not superficially, but to dive deep into the problem, explore it, achieve certain results, and go forward, no matter what. Everyone who was close to him was infected by his incredible interest in life, which was always creative.

Suleyman Allakhverdiev (suleyman.allakhverdiev@gmail.com)

We have lost a unique man of science. I do not have sufficient words to describe the superb qualities of Vladimir Shuvalov. His unassuming nature, simple life, honest, straightforward, ego-less personality, respect for the intellectuals and finally his commitment to quality research in science made him a scientist beyond compare.

On October 2, 1977, I came from Baku (Azerbaijan) to Pushchino (Moscow Region, USSR) for my Ph.D. thesis, and I joined the group led by Academician A.A. Krasnovsky and Vladimir A. Shuvalov. I worked on an investigation of pheophytin (Phe) in photosynthetic reaction centers (RCs) of photosystem II (PSII) with Slava Klimov, Vladimir Shuvalov and A.A. Krasnovsky as my supervisors. At that time only two papers on pheophytin had been published (Klevanik et al. 1977; Klimov et al. 1977). These were very exciting times!

In 1978, Vladimir Shuvalov and then Slava Klimov went first to the Charles F. Kettering Lab in Yellow Springs, Ohio, USA, to work with Bacon Ke (1978–1979), and then with William (Bill) Parson (1980–1981), at the University of Washington, where they performed additional experiments on the role of pheophytin (Phe) in PS II. Before their visit to USA, Shuvalov, Klimov and I submitted and published several papers in Russian (Klimov et al., 1978, 1979a,b, 1980a, b, 1986). The experimental evidence for the participation of Phe, and the energetics and kinetics of electron transport in PSII were summarized in my Ph.D. thesis (Allakhverdiev 1984; also see Allakhverdiev et al. 2018). 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 (Allakhverdiev et al. 2018).

During 1977–1986, together with Alexander A. Krasnovsky, Vladimir Shuvalov, Slava Klimov, Sasha Klevanik and Professor Gertz 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 atoms acting in the electron-transfer reactions of PS II. We concluded that the water-oxidizing complex on the (electron) donor side of PS II contains four atoms of Mn. Reconstitution of the Mn-cluster after a complete removal of Mn from PS II preparations had been achieved using Mn(II) as well as various artificial Mn-organic complexes. We studied the magnetic interaction of Mn with Phe^{-} and $P680^{+}$ and evaluated the distance between the main components of PS II. The immersion depths of the main components of PS II RC in thylakoid membranes were also analyzed and published in several papers (Klimov et al. 1982, 1985, 1990; Allakhverdiev et al. 1983, 1986, 1989a, b, 1994; Kulikov et al. 1983).

I worked in Professor Norio Murata`s lab in Japan from 1995 to 2007. Shuvalov visited us there in 2001, and we investigated the role of a cytochrome, cyt cM. We showed that this cytochrome is synthesized under low-temperature stress and that it might carry electrons directly to $P700^{+}$ in photosystem I (PS I). The expression of the cyt cM gene in *Synechocystis* sp. PCC 6803 is known to be induced under low temperature. Our spectrophotometric studies revealed that light absorbed by PS I oxidized cyt cM in cells that had acclimatized to a low temperature, and that the absorbance changes associated with this process were absent in mutants lacking cyt cM. The kinetics of the oxidation and reduction of P700 before and after acclimation of *Synechocystis* cells to low temperature suggested that cyt cM might, indeed, donate electrons to photooxidized P700 (Shuvalov et al. 2001).

In 2014, we organized a conference ''Photosynthesis Research for Sustainability-2014 in honor of Vladimir Shuvalov'' in the city of Pushchino, Moscow Region; it was dedicated to him on his 70th birthday (see Allakhverdiev

et al. 2014; also see https://icprs.ru/ and, Carpentier and Allakhverdiev 2015).

The contributions of the group and laboratory headed by Vladimir Shuvalov had a great impact on our understanding of the primary processes of photosynthesis of both plants and bacteria. Shuvalov made unique contributions to the basic principles and details of charge transfer processes, beginning in the femtosecond time scale. His collaborative spirit can be easily judged by his research with many scientists in Russia as well as in other countries: Germany (Ulrich Heber, Gernot Renger); UK (Richard Cogdell); Japan (Norio Murata); The Netherlands (Jan Amesz, Louis N.M. Duysens, Peter Gast, Arnold J. Hoff, Hans van Gorkom, and Rienk van Grondelle), and in the USA (Bacon Ke and William Parson).

Richard Cogdell *(Institute of Molecular Cell and Systems Biology, Glasgow*; Richard.Cogdell@glasgow.ac.uk)

I first met Vladimir (whom we called Vlad) in the mid-1970s in Moscow at a small meeting. We were both rather young then and had been working independently on the primary reactions in purple bacterial reaction centers. He had been working in Russia and I had been working with William (Bill) Parson and Roderick (Rod) Clayton in the US. (For life and work of Clayton, see Wraight 2014.) We had very similar results and had come to the same conclusions! Luckily, we were proved to be correct when much later the structure of the reaction center was determined by Hartmut Michel, Johann Deisenhofer, and Robert Huber. We became good friends but due to the political situation then we were not able to meet up so frequently. But I always admired his work. His data were always excellent, and his interpretations were always well founded on that data. I will miss his warm smile and his thoughtful, incisive questions.

William Parson *(University of Washington; parsonb@u.washington.edu)*

It was my good fortune to have Vlad Shuvalov spend nine months in Seattle in 1980 and 1981. We immediately became good friends. He was an exceptionally well-rounded person who enjoyed classical music and hiking in the mountains in addition to science. He was both a skilled pianist with a taste for Chopin's romantic compositions and a daring skier, and I understand that he also distinguished himself on the tennis court. During the winter, he took the bus to the ski runs at Snoqualmie pass almost every weekend. He particularly liked the expert slope at Alpental, partly because of its technical challenge. I remember the smile and deep voice with which he described the steep drop at Alpental as "*very nice*!".

It was an exciting time for studies of photosynthetic reaction centers. We knew that bacterial reaction centers contained four molecules of bacteriochlorophyll (BChl), of which two (P870) acted as the photochemical electron donor. We knew they also contained two molecules of bacteriopheophytin (BPh), two quinones and a non-heme iron atom. We had studied the $P870^{+}BPh^{-}$ radical pair that formed within a few picoseconds when reaction centers were excited with a short flash of light, and in collaboration with Dewey Holten, Craig Schenck and Maurice Windsor we had explored the kinetics and temperature dependence of electron transfer from the BPh to a quinone. But Deisenhofer, Michel and Huber's elucidation of the crystal structure was four years in the future, and we still had no idea how the electron carriers were arranged. The role of the other two BChls was a complete mystery, and it was this that most piqued Vlad's curiosity. By measuring the spectrum and temperature dependence of $P870^{+}BPh^{-}$ when further electron transfer to the quinone was blocked, Vlad obtained evidence that a $BChl^{-}$ radical was in thermal equilibrium with BPh^{-}, suggesting that $P870^{+}BChl^{-}$ could be an intermediate in the formation of $P870^{+}BPh^{-}$ (Shuvalov and Parson 1981a). The energetics of the excited state (P*), $P870^{+}BChl^{-}$ and $P870^{+}BPh^{-}$ appeared to be consistent with this view.

Vlad also studied the triplet radical-pair and the more localized triplet state that formed by spin rephasing and back-reactions from the singlet $P870^{+}BPh^{-}$ (Shuvalov and Parson 1981b), and for comparison, he examined triplet excited states of BChl in vitro and in photosynthetic

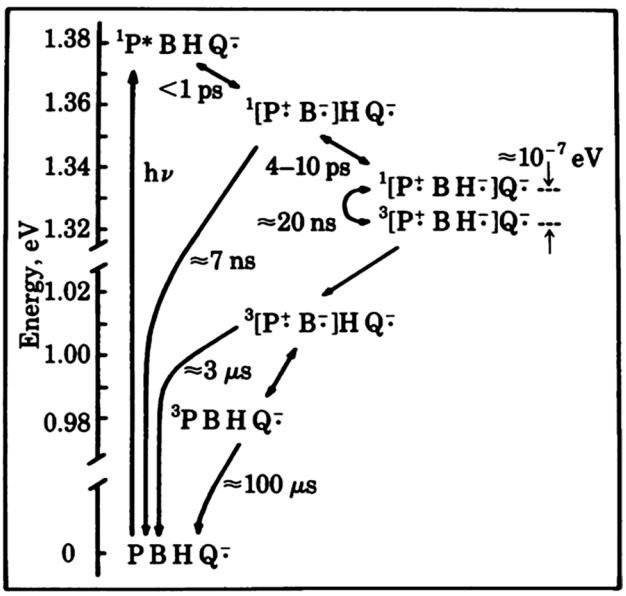

Fig. 6 A scheme of the light-driven electron-transfer reactions in purple bacterial reaction centers. P = P870 (BChl dimer); B = monomeric BChl; H = BPh; Q = quinone. *Reproduced from* Shuvalov and Parson (1981a)

bacterial antenna complexes (Shuvalov and Parson 1981b). Measurements of thermal excitation back to fluorescent excited singlet states allowed him to determine the energies of the triplet states. Figure 6 describes the energetics and kinetics of the initial charge-transfer reactions and triplet states as we understood them then (Shuvalov and Parson (1981a).

Klimov joined us for a week during Vlad's time in my lab, bringing a preparation of photosystem II from Bacon Ke's lab. This led to what I think was the first evidence for the formation of a $P680^{+}Phe^{-}$ radical pair in photosystem II similar to the $P870^{+}BPh^{-}$ of bacterial reaction centers (Shuvalov et al. 1980). During a hectic week of experiments, Vlad and Slava somehow also found time to take up sailing and join the University's sailing club.

Two things particularly impressed me about Vlad's skills as a scientist. First, he had essentially no energy barrier for starting new experiments. On several occasions after we had discussed some potentially interesting experiments that would require building new apparatus, I left the lab in the evening thinking that the experiments would take some time to get started. When I returned in the morning, I found a note on my desk with experimental results and Vlad's characteristic exclamation, "*Very interestingly*!" He had not only built the equipment but made the measurements and even had an interpretation of the results.

Vlad's second remarkable quality was his sharp eye for small details that other investigators might easily have overlooked as noise in the experimental results but that he realized could be a key to something important. His observations on thermal equilibration of $P870^{+}BChl^{-}$ and $P870^{+}BPh^{-}$ were typical in this regard, as were his later pioneering observations on vibrational motions and relaxations in reaction centers.

Vlad's identification of $P870^{+}BChl^{-}$ as an intermediate in photosynthetic charge separation was not without controversy. Jacques Breton, Jean-Louis Martin and their coworkers could not reproduce his absorbance measurements showing clear formation of $BChl^{-}$ on subpicosecond time scales. Both groups defended their observations tenaciously, and as far as I know the discrepancy was never resolved. However, subsequent experimental and computational work by many investigators provided increasingly convincing evidence that $P870^{+}BChl^{-}$ was a real intermediate in the sequence, and Jacques Breton agreed with that. When Jacques and I visited Pushchino (Russia) for a symposium on the occasion of Vlad's 65th birthday, he entertained us very kindly, treating us to an excellent performance of Verdi's *Requiem* in Moscow.

Sadly, my own last emails to Vlad were to explain my objections to his proposal that the initial excited state (P870*) in reaction centers relaxes to an internal charge-transfer state ($P_B^{+}P_A^{-}$) before it transfers an electron to the neighboring BChl (see Parson 2020). I learned only later that he was by then too ill to reply. However, Vlad's coworker Andrei Yakovlev did respond to my messages, and we enjoyed a fruitful exchange of ideas.

Vlad was an extraordinary person. It was both a pleasure and a continuing education to work with him.

Andrei Yakovlev (Moscow State University; yakov@genebee.msu.su)

I met Vladimir Shuvalov in 1990, when he invited me as a young postdoc to investigate the primary processes of photosynthesis in a new laboratory that he had 'created' and headed at the Belozersky Institute of Physico-Chemical Biology, Lomonosov Moscow State University. Our small team was engaged first in the construction of a femtosecond spectrometer, and then in measurements of the dynamics of ultrafast charge separation processes in the reaction centers of bacterial photosynthesis. Looking back, I understand that working with Shuvalov had a strong influence on me and ultimately shaped me as a researcher. He was a man infinitely devoted to science and infinitely fascinated by it. His mighty enthusiasm charged me with positive energy for many years and allowed me to overcome many difficulties in my life. Shuvalov combined the features of a great scientist, a real intellectual, and a very bright, extraordinary person. I remember our conversations with him; they would begin with a discussion of current affairs, especially the newly obtained scientific results. Then the range of issues discussed would expand; Shuvalov willingly shared with me his inexhaustible knowledge of biology and biophysics. His invariable thesis was the importance of studying photosynthesis as the basis of life on Earth, as well as the unique opportunity to engage in the true creativity that science provides. Using the advantage of his erudition and life experience, Shuvalov showed the talent of a real mentor. He corrected my mistakes very patiently and tactfully and at the same time persistently pushed me to do independent work and instilled confidence in my abilities. All this happened easily and democratically, accompanied by jokes. Only now, having lived for many years, do I realize how lucky I was to have such a person as Shuvalov in my life. I will miss him very much, and the memory of this amazing person will remain with me forever.

Studies of the primary processes of photosynthesis in bacterial reaction centers (RCs) were in the sphere of interest of V.A. Shuvalov for many years. He led this research in the Department of Photobiophysics of the Belozersky Institute of Physicochemical Biology (Lomonosov Moscow State

University). Below, I briefly summarize the main results of these studies, most of them obtained using the femtosecond high-sensitive differential spectrometer constructed in his laboratory. As a result of studying the femtosecond dynamics of the IR (Infrared) absorption band of the monomeric bacteriochlorophyll anion B_A^-, direct evidence was obtained for the involvement of B_A in the primary charge separation in native RCs from *Rhodobacter sphaeroides* and *Chloroflexus aurantiacus* (Yakovlev et al. 2000, 2002a, 2002b, 2003). A similar conclusion was obtained for several mutant RCs from *R. sphaeroides* (Yakovlev et al. 2009, 2010a, 2010b, 2011). Thus, Shuvalov's assumption was confirmed that BChl B_A is the primary electron acceptor, and the $P^+B_A^-$ state is the primary state with separated charges in these RCs. Based on the results on the temperature dependence of the delayed fluorescence of pheophytin-modified RCs from *R. sphaeroides R-26*, Shuvalov and Yakovlev (1998) found that the free energy level of the primary state with separated charges $P^+B_A^-$ is lower than the free energy level of the excited state of the P* dimer by ~ 550 cm^{-1}. The position of the free energy level of $P^+B_A^-$ below the analogous level of P* creates conditions for the participation of B_A in electron transfer from P*.

Direct experimental evidence that collective motions of nuclei (in the form of a wave packet) in the excited state of the P* dimer influenced the primary charge separation in native and mutant RCs from *R. sphaeroides* and in native RCs from *C. aurantiacus* was obtained by Shuvalov and Yakovlev (2003) and by Novoderezhkin et al. (2004). It was shown that oscillations in the populations of primary states with separated charges reflect reversible transitions of the nuclear wave packet from the potential energy surface of P* to similar surfaces of photoproducts. Characteristic low-frequency modes of nuclear motions associated with electron transfer were revealed through our experiments (Yakovlev et al. 2002a, 2002b, 2003). It was shown that the crystallographically determined water molecule HOH55, located near BChl B_A in the RCs from *R. sphaeroides*, has a strong effect on electron transfer from P to B_A (Yakovlev et al. 2005). The presence of water HOH55 accelerates the primary charge separation by ~ 4 times, and its rotation, initiated by femtosecond excitation of P, modulates the population of the $P^+B_A^-$ state with a frequency of 32 cm^{-1} and multiple other frequencies. An analysis of the effect of water HOH55 on the electron transfer with the help of M203-site mutants revealed an effective path of electron transfer from P* to B_A along the chain of polar groups of atoms N–Mg(P_B)–N–C–N(HisM202)–HOH55–O=(B_A). The key role of tyrosine M210 located near P and B_A in *R. sphaeroides* RCs in the process of primary charge separation and stabilization of separated charges was demonstrated by Shuvalov and Yakovlev (2003) and Yakovlev et al. (2003). It was shown that the dramatic slowdown of the primary electron transfer reaction in mutant RCs that do not contain tyrosine M210 is accompanied by a lack of stabilization of the separated charges in the $P^+B_A^-$ state. It was shown that introduction of tyrosine in the M197 position of mutant RCs that lack tyrosine M210 does not compensate for the absence of tyrosine M210 and does not significantly change the difference

Fig. 7 Vladimir A. Shuvalov and Andrei G. Yakovlev, 2011, Faculty of Biology, Lomonosov Moscow State University. *Source* A. Yakovlev

between the free energies of P* and $P^+B_A^-$. In RCs from a mutant of *R. sphaeroides* and in those from *C. aurantiacus*, a reversible electron transfer to the inactive B-branch of cofactors, caused by the coherent motion of the nuclear wave packet, was discovered (Yakovlev et al. 2006). This transfer precedes the similar coherent electron transfer in the photoactive A-branch by 60–80 fs. The occurrence of coherent electron transfer in the B-branch does not depend on the presence or the absence of conditions for the usual, incoherent transfer, but is determined mainly by the dynamics of the wave packet.

In memory of Vladimir Shuvalov, we show, in Fig. 7, a 2011 photograph of two of us together in Moscow.

Lyudmila Vasilieva (Institute of Basic Biological Problems RAS, Pushchino; lyu_v@yahoo.com; vsyulya@mail.ru)

In 1998, after several years of work in Tsukuba, Japan, I planned to return to Pushchino, and I informed Prof. Vladimir Shuvalov about my experience in applying genetic methods to work with purple bacteria. He responded warmly to my proposal, although at that time there was no experimental facility for such work in his laboratory and even in the entire Institute. With the active support of Shuvalov, we organized a group that began to work first on site-directed mutagenesis of *R. sphaeroides* RCs, and later crystallization of the mutant complexes. Use of femtosecond spectroscopy in combination with genetic approaches made it possible to obtain new results regarding the mechanisms of primary electron transfer in the RCs of purple bacteria (Yakovlev et al. 2003, 2006; Shuvalov et al. 2006; Khatypov et al. 2008, 2012). There is no need to say that the main ideas for these studies were proposed and promoted by V.A. Shuvalov himself. After 2015, a serious illness did not allow him to actively participate in scientific work, but he led his laboratory in Pushchino, until 2019. All members of the laboratory who have worked with him for many years acutely felt the loss of Academician Shuvalov, and will honor his memory for a long time.

Jian-Ren Shen (Okayama University, Japan; shen@cc.okayama-u.ac.jp)

It is really sad that Prof. Vladimir A. Shuvalov has passed away. He was a great scientist and warm-hearted, easy-to-go person. I knew his name from his famous work of pheophytin of photosystem II many years ago and was able to see him at the 2014 Conference of "Photosynthesis Research for Sustainability" when I visited Pushchino. He highly appreciated our work on the structural analysis of photosystem II. His contributions to the photosynthesis research expand to the electron donors and acceptors of bacterial reaction centers, photosystem I and photosystem II mostly through ultra-fast absorption and fluorescence spectroscopy, which is a highly sophisticated technique; it was highly expensive especially in early days. Shuvalov's passing away is definitely a great loss of the photosynthesis community, and I pray for the repose of his soul.

Arvi Freiberg (Institute of Physics, University of Tartu, Tartu, Estonia; arvi.freiberg@ut.ee)

In my memory, Vladimir (or Vlad as many friends used to call him) remains as an intelligent looking man with low, friendly voice talking to his colleagues at the conference coffee break time. When arguing, he used to look straight into your eyes characteristically inclining his head. His manner of wearing a (regularly grey-colored) suit was natural, not a necessity of his high scientific standing or administrative status. These qualities were rather rare among men of his generation. Despite his modesty, Vlad also had a great sense of humor. I once complained to him that our measurements on reaction centers using different methods quite disagreed with each other, while the data obtained with separate techniques complied very well with the published results. "Why did you do those other measurements, in the first place? " asked Vlad cunningly. Yet the problem remains to be solved. All of us miss Vladimir -as a person and as a researcher.

Govindjee Govindjee (gov@illinois.edu)

I met Vlad Shuvalov each time I visited Russia for various photosynthesis conferences. I have the highest regard for him both as a person and as a scientist. He was always very thorough, cordial, and extremely polite in his discussions –often, we talked about the primary photochemistry in oxygenic photosynthesis since in 1979 we had made our first measurement, on picosecond timescale, in Photosystem I (see e.g., Fenton et al. 1979), and in in 1989, in Photosystem II (see e.g., Wasielewski et al. 1989). Vlad always pointed out to me the pros and cons in judging the identity of the species involved in his as well as in our experiments. For a review that covers all aspects of the primary photochemistry in oxygenic photosynthesis, including the work of Shuvalov, see Mamedov et al. (2015). It has been a pleasure to have known Vlad as a wonderful person, a great friend, and a top scientist. I certainly miss him.

Alexander Krasnovsky (phoal@mail.ru)

Vladimir and I entered Moscow university at the same time and were students in the same research group. In a very short time, we became very close friends and maintained a wonderful relationship up until the end. During our student days, we spent much time together and did many things besides science. When the time came to start research work, my

father directed me to F.F. Litvin. After a while, Vladimir also joined this group. So, during many years we worked in one room and in one research group in close cooperation. In the beginning, we both studied Strehler-type delayed luminescence of plant leaves and jointly published two papers, in 1966, under Litvin's supervision. Later, I decided to shift to work on isolated chlorophylls in solution, and most of my studies were devoted to photochemiluminescence of chlorophyll molecules in vitro. Vladimir continued with real photosynthetic systems, and his doctoral thesis dealt with delayed luminescence of plant leaves. We all miss Vladimir Shuvalov.

Robert Blankenship (reblankenship@gmail.com)

I first met Vlad Shuvalov in 1980 at the Gordon Research Conference that Bill Parson had organized in California. After that first time, we would see each other at various conferences over the years and became friends, although we never worked together or published any papers together. Perhaps the most memorable interaction I had with Vlad was in 1990. The US National Academy of Sciences and Russian Academy of Sciences had organized a trip for a group of Russian scientists. One of their stops was to Arizona State University, Tempe, AZ, where I was a faculty member. I served as the local host. Over the course of several days, we took the delegation to the Grand Canyon and some other typical Arizona destinations. It was fun to get to know Vlad and the other members of the Russian delegation in a more relaxed setting. We all miss Vlad as a highly friendly person and as a top biophysicist of our time.

Andrei Razjivin (Belozersky Research Institute of Physico-Chemical Biology, Lomonosov Moscow State University, Moscow, Russian Federation; razjivin@belozersky.msu.ru)

With Vladimir Shuvalov, I had a chance to argue about important issues, to write articles together, and to visit with each other at conferences in the late 1970s and early 1980s. In 1975, my research supervisor Alexander Yurievich Borisov concluded that phase fluorometry had exhausted its possibilities for studying the primary processes of photosynthesis. He suggested that I, an engineer-physicist by education, construct a spectrometer with nano- or picosecond pulse excitation. Breton and Geacintov (1980) had already used ultrashort laser pulses in the visible region to excite photosynthetic samples, but we wanted to excite reaction centers (RCs) selectively in their longest-wavelength absorption bands to distinguish processes of charge separation from energy transfer. We managed to solve this problem in 1977 (Akhmanov et al. 1977). The following year, Shuvalov et al. (1978) also described selective excitation of RCs in the long-wavelength band, beginning a controversy between us concerning the interpretation of the data. Shuvalov believed that they had seen electron transfer through the monomeric BChl as he had predicted (cf. Shuvalov and Asadov 1979). I thought we had observed nonlinear processes associated with multi-photon excitation. To solve this dilemma, we carried out joint measurements and published results that took both possibilities into account (Akhmanov et al. 1980; Borisov et al. 1980). Our scientific interests diverged after that, as I began to study the transfer of excitation energy in light-harvesting antennas and Shuvalov continued research on charge-separation processes.

Working with Vladimir Shuvalov and meeting him at seminars and conferences, I was always amazed by his intuition and clarity of thought. In the mid 1980s he became head of the Department at our institute. He supported me on many occasions, especially in the early 1990s when Vladimir Novoderezhkin and I were working on a model of BChl ring aggregates in bacterial light-harvesting antennas. We all marvel Vladimir Shuvalov both as a person and a scientist.

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Supplementary Material
for

In memory of Vladimir Anatolievich Shuvalov (1943—2022): An outstanding biophysicist

by

Lyudmila G. Vasilieva , Olga P. Kaminskaya , Andrei G. Yakovlev, Anatoly Ya. Shkuropatov , Alexey Yu. Semenov , Viktor A. Nadtochenko , Alexsandr A. Krasnovsky, Jr., William W. Parson, Suleyman I. Allakhverdiev & Govindjee Govindjee

We present below three informal photographs of Vlad that gives us a glimpse of his personal fun side. Figure S1 shows him wearing Caucasian highlander clothes, Figure S2 shows him as a sports -and a family person, skiing together, and Figure S3 shows him, in a dancing mood, at a restaurant – with his wife Tatyana Dolgova, who, kindly provided us these wonderful photographs.

Fig. S1 . Vladimir Shuvalov, 1988, during a vacation in the Caucasus (Caucasia) , wearing the national clothes of a Caucasian highlander.

Fig. S2. Vladimir Shuvalov (on the left) with his family, ~2002, at a Skii resort in Russia. Next to Vlad is Artem Dolgov, then Tatyana Dolgova, and a family friend.

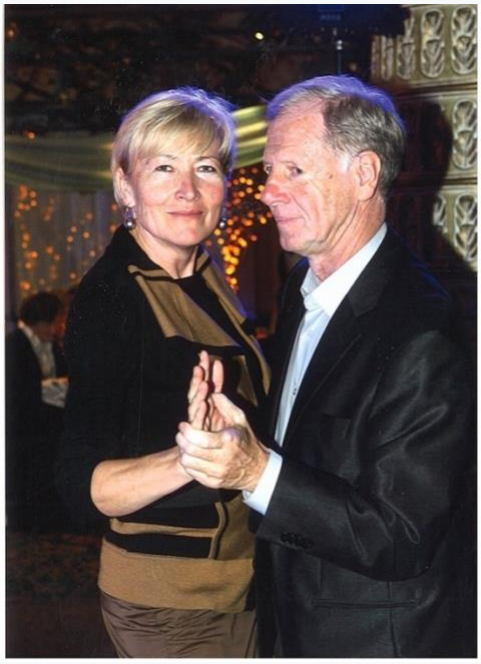

Fig. S3. Vladimir Shuvalov and Tatyana Dolgova, 2009, in a dance posture, in a restaurant in Russia