PROTECTIVE ROLE OF SILICON IN LIVING SYSTEMS

[1,2,3]Biel K.Y., [1]Matichenkov V.V., and [1,2]Fomina I.R.

[1]Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia , [2]Biosphere Systems International, Tucson, Arizona 85755, USA , [3]Research Center for Food and Development, Hermosillo, Sonora 83000, Mexico

Corresponding author: Biel K.Y, E-mail: karlbiel@hotmail.com

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ABSTRACT

A brief review about the role of silicon in the soil-plant-animal system is presented, and the participation of silicon in stress tolerance promotion of organisms is discussed. It is hypothesized that the human body, as well as animals, plants and microorganisms, have a unique protective mechanism, which partially involves the mobile silicon compounds. According to our hypothesis, the function of silicon constituent can provide the additional synthesis of stress-protective molecules under genetical control but without "physical" participation of the genetic apparatus. This assumption is based on indirect experiments, and on a bases of subordination of two constituencies: a) response of genetic apparatus on stress, insuring synthesis of stress-protective compounds, such as antioxidant enzymes, stress-proteins, glutathione, phenols, and others antioxidants, etc., and b) on additional non-enzymatic formation of the same protective compounds on the matrixes of polysilicic acids. The active forms of silicon are considered as a matrix-depot for formation of compounds, which give assistance in any organism to maintain positive homeostasis under stress conditions.

INTRODUCTION

Medicine. In the early 20th century, amorphous silicic dioxide, silica, was the most commonly used pharmaceutical remedy in the world. It is well known that a silicon imbalance in the human body is accompanied by general metabolic disease and induces anemia, osteomalacia, shedding of hair, joint illness, and other diseases (Carlisle *et al.*, 1997; Voronkov *et al*., 1978). Silicon compounds can prevent atherosclerosis development; and problems such as headaches, cardiovascular and skin diseases, sicknesses of joints and osseous tissues have been treated successfully by silicon medications (Voronkov *et al.*, 1978; Birchall and Chapell, 1988; Kaufmann, 1995*a*; 1995*b*; Jugdaohsingh *et al.*, 2002; Perez-Grandos and Vaquero, 2002; Sripanyakorn *et al.*, 2004; McNaughton *et al.*, 2005).

It was shown that the concentration of silicon in blood increased several times around the wound (Voronkov *et al.*, 1978; Mayras *et al.*, 1980), and the bandage sodden by silicic acids hastened wound repair (Kuzin *et al*., 2000; Brown, 2002). It is also known that silicon concentration in the blood of pregnant women and in infants is increased (Voronkov *et al*., 1978; Kaufmann 1995*a*; 1995*b*; Van Dyck *et al.*, 2000).

As early as 1878, great Louie Pasteur proposed that "*therapeutic action of silica has a great future*" (see Voronkov *et al*., 1978). And Pasteur was right: the traditional medicineis again

returned to the application of silicon preparations, which comes in handy, and is not only absolutely safe for people, but also are very effective for treatment of a wide range of diseases.

Agriculture. Protection of agricultural plants against diseases and insect attacks by silicon compounds has been used for many centuries, or possibly, several thousands of years ago because even agriculturists of the Roman Empire and Ancient China were familiar with unique capacities of silicon remedies and successfully applied them. Today, the list of scientific publications related to the application of active forms of silicon for protection of plants against various stressors (nematodes, funguses, negative climatic conditions, etc.) amounts to over 4000 references (see ref. in Voronkov *et al*., 1978; Savant *et al*., 1997; Matichenkov *et al*., 2001*a*; 2001*b*; Ma and Takahashi, 2002; Matichenkov and Bocharnikova, 2004*a*; 2004*b*; and others).

Under stress conditions, the active forms of silicon have positive influences on the health of animals, fishes and birds (Carlisle, 1997). For example, small dietary supplement by Diatomaceous Earth, zeolite, silicon water, or other forms of active silicon harshly provides disease tolerance of the domestic animals, and decreases their death-rate (Carlisle, 1972; 1984; D'yakov *et al.*, 1990; Carlisle *et al.*, 1997). At the same time, the presence of active silicon supplements in food does not increase the level of silicon concentration in the blood of robust animals (Iler, 1979; Mayras *et al.*, 1980).

Previously, it was observed that wild animals aspire not only to take, as food diet, various clays, Diatomaceous Earth, and zeolite, but also to take up their residences close to wedging out high-silica soft minerals. The animals thus used these minerals as nutrition.

In the 1970's, the scientists of the Soviet Union and America proved the importance of silicon for improving the natural developing of the domestic and agricultural animals and birds; at least 6% of their fodder should be amorphous silicon dioxide (Carlisle, 1972; Voronkov *et al.*, 1978; D'yakov *et al.*, 1990; Carlisle *et al.*, 1997). It was also demonstrated that silicon promotes disease- and stress-tolerances of the domestic animals (Carlisle, 1984; Bgatov *et al.*, 1987; Anokhin *et al.*, 1997; Vladimirov *et al.*, 1998), disease-tolerance of fishes (Exley *et al.*, 1997; Camilleri *et al.*, 2003), and increases the rate of cancroids growth (Pellenard, 1969).

Microorganisms and plants. Silicon-rich compounds have a positive effect on growth and development of microorganisms (Al Wajeeh, 1999; Wainwright, 2005). In particular, silicon is one of the basic nutrient elements for phytoplankton, diatoms and cyanobacteria (Siegel and Siegel, 1973; Cha *et al.*, 1999; Brummer, 2003; Martin-Jezequel and Lopez, 2003; Velikova *et al.*, 2005; Tuner *et al.*, 2006). At the same time, silicon is a very important nutrient for organisms, which do not have as much silicon as diatoms and cyanobacters do. For example, the cultures of microorganisms are developing in the glass Petri dishes better than in plastic ones (pers. obs. and cons. with microbiologists).

The literature data testifies that silicon has a positive effect on the growth of a number of microorganism species (Mohanty *et al.*, 1990; Yoshon, 1990; Wainwright *et al.*, 1997; Soomro, 2000). We also observed increasing populations of various soil microorganisms when active silicon was applied to the grounds or to the soils, contaminated by oil or oil derivatives (Bocharnikova *et al.*, 1999).

The positive influence of silicon on plant growth and development has been known since Justius von Leibigh published his work (Leibigh, 1840) about mineral nutrition of plants. Today, the positive effects of silicon nutrition are estimated on various soils for the following cultivated plants: rice (*Oriza sativa* L.), sugar-cane (*Saccharum officinarum* L.), barley (*Hordeum vulgare* L.), wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.), rye (*Secale cereale* L.), sorghum

(*Sorghum vulgare* L.), corn (*Zea mays* L.), sunflower (*Helianthus annuus* L.), beans (*Vicia faba* L.), soy (*Glycine max* L.), trefoil (*Trifolium pretense* L.), lucerne (*Medicago sativa* L.), millet (*Panicum miliaceum* L.), tomato (*Lycopersicum esculentum* L.), cucumber (*Cucumis sativus* L.), marrow (*Cucurbito pero* L.), lettuce (*Lactuca sativa* L.), tobacco-plant (*Nicotiana tabacum* L.), sugar-beet (*Beta vulgaris* L.), lemon tree (*Citrus x limon* L., Burm. f.), tangerine-tree (*Citrus reticulate* L.), vine (*Vitis vinifera* L.), apple-tree (*Malus silvestris* L.), melon (*Cucumis melo* L.), and others (D'yakov *et al*., 1990; Savant *et al*., 1997; Epstein, 1999; Matichenkov *et al*., 2001; Ma and Takahashi, 2002; Matichenkov and Bocharnikova 2004*b*).

Summarizing the data about the influences of silicon fertilizers on plant productivity and soil fertility allows us to conclude:

1. Silicon enrichments provide the protective functions of plants on mechanical, physiological, and biochemical levels (Aleshin *et al*., 1987; Savant *et al.*, 1997; Ma and Takahashi, 2002; Belanger, 2005).
2. Agricultural activity results in deficiency of active silicon forms in plants and drives to the degradation soil processes (Matichenkov and Bocharnikova, 1994; Bocharnikova *et al.*, 1995; Matichenkov *et al*., 1999*a*).
3. Silicon fertilizers and silicon-rich soil amendments increase and retain phosphorus in accessible forms and results in facilitatation absorption of phosphorus by plants (Matichenkov, 1990; Matichenkov and Ammosova, 1994; Matichenkov, Bocharnikova, 2001).
4. Silicon nutrition could be applied as a lime material in acid soils (D'yakov *et al*., 1990; Savant *et al.,* 1997; Ma and Takahashi, 2002).
5. Silicon-rich soil amendments are able to optimize the physical properties of soils (Emadian and Newton, 1989; Matichenkov and Ammosova, 1994; Matichenkov and Bocharnikova, 2001).

Thus, the known facts show the positive influence of silicon on organisms throughout a certain general mechanism, which mostl likely connects with the self-protective function of living systems. Furthermore, it is logical to presume that the biochemical basis of this mechanism is uniform for all organisms.

FORMS OF SILICON

Silicon is the second most abundant element in the earth's crust, after oxygen, and its concentration is increased by a decrease of the lithosphere layer depth, and achieves the maximal value in the surface of soil (Reimers, 1990; Bashkin, 2005). In soil, the main part of silicon is presented as a silicon dioxide and various forms of aluminosilicates (Sokolova, 1985). Quartz, crystalline variety of silica, is characterized by stability to eolation (Orlov, 1985; Olier, 1990) and together with other macrocrystalline silicates [feldspar, plagioclase, pyroxenes] and secondary or clay silicon-containing minerals [kaolinite, vermiculite, smectite, and others] forms the skeleton of soil (Orlov, 1985).

Stability of silicon minerals to eolation is reflected in the classification of soil elements on the basis of their mobility, where the silicon is considered as an inert element (Polynov, 1952). However, in the same classification, silicon is also attributed to the group of mobile elements. In soil, solutions are permanently present in the mono- and polysilicic acids and organo-silicon compounds, which have high chemical and biological activity (Matichenkov, 1990; Matichenkov,

Calvert *et al.*, 2001; Matichenkov and Bocharnikova, 2004*a*; 2004*b*). Thus, the soil silicon consists of two main groups – inert elements and biogeochemically active compounds.

Figure 1 presents the classification of silicon compounds, in which special attention has been focused on biogeochemically active forms of silicon from the solid and liquid soil's phases (Matichenkov *et al.*, 1999*a*; 1999*b*). Traditionally (Sokolova, 1985), the silicon compounds in the solid phases of soil are classified on the bases of mineralogical structure, and are a priori considered as inert. But silicon compounds of the liquid phases are considered as active because they have numerous physico-chemical and biological properties. Undoubtedly, these active silicon forms are presented in the tissues of living organisms.

Monosilicic acid is a weak inorganic acid with a slight buffering capacity at pH ≈ 7.0. This acid can react with ions of aluminum, iron, calcium, manganese, magnesium and heavy metals (Bocharnikova *et al.*, 1995; 1999; Matichenkov and Bocharnikova, 2001). Monosilicic acid is also able to replace phosphate anions from the calcium, iron, and aluminum phosphates (Matichenkov, 1990; Matichenkov and Ammosova, 1994); this process results in facilitating phosphate uptake by plants and soil microorganisms (Yoshida, 1975; Trevors, 1997).
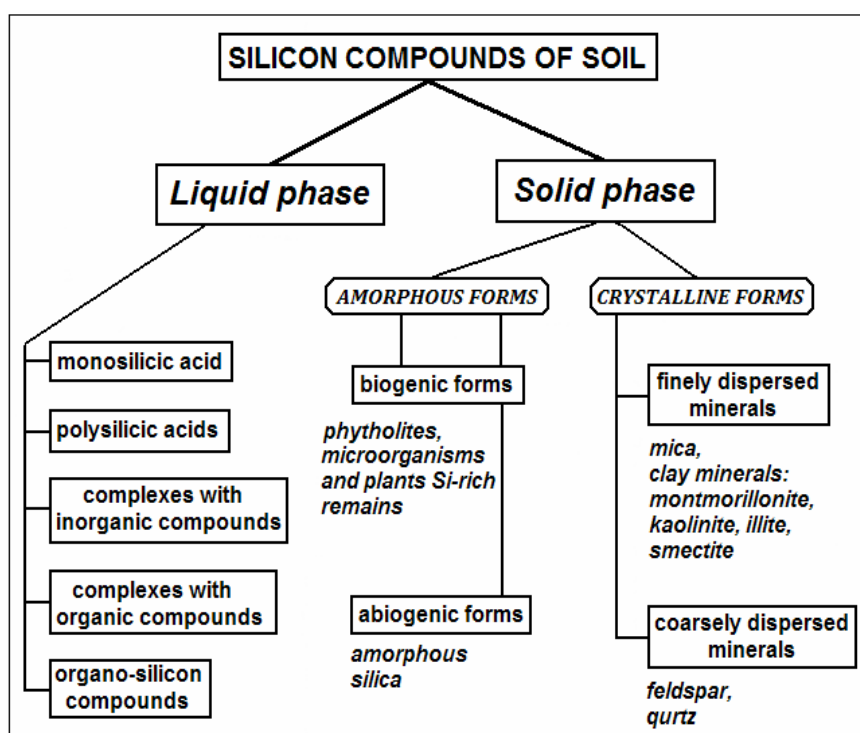

Figure 1: Forms of silicon compounds in soil (Matichenkov *et al.*, 1999*a*).

Polysilicic acids are compounds which consist of two or more silicon atoms linked by siloxane bonds in a line [-Si-O-Si-], with hydroxyl groups bonded with silicon atoms (Iler, 1979).

There are two groups of polysilicic acids in nature: 1) oligomers of silicic acid are contained from two till several hundred of silicon atoms per one molecule. They also were named as low-molecular weight polysilicic acids. It was believed that in diluted solutions (in most of natural waters, soil waters, lakes, rivers, and ocean waters), these compounds are unstable, and are found as intermediates between monosilicic acid and high-molecular weight polysilicic acids (Iler, 1979; Dietzel, 2000; 2002); 2) high-molecular weight polysilicic acids are containing till several thousands of silicon atoms per one molecule (Davies, 1964; Varshal *et al.*, 1980; Stumm and Morgan, 1996). These acids are chemically inert, but

nonetheless can influence the physical properties of soils (Yatsynin, 1989; Matichenkov *et al.*, 1994).

Chemical inertness of polysilicic acids is specified by the ability of their molecules "to twist" and by this way to compensate the negative charges, which are formed during dissociation of hydroxyl groups (Iler, 1979). Polysilicic acids are also able to form silicon bridges between soil particles (Yatsynin, 1994). These bridges, due to permanent changing of soil humidity, undergo-dehydration with formation of silicon dioxide.

The processes of periodical drying-wetting of soils are formatting the siliceous films on a surface of practically all soil minerals. And exactly this film is the main source of monosilicic acid, when moisture comes upon the soil.

Formation of polysilicic acids occurs as the monosilicic acid's molecules condensation (Iler, 1979). Though this process is poorly investigated, however, it is known, that in open water-bases the process can go, if the concentration of monosilicic acid is above 100 mg Si/liter (Iler, 1979). But usually, in the soil solutions the concentration of monosilicic acid is not higher than 1–50 mg Si/liter (Matichenkov, 1990). Theoretically, in such diluted solutions polysilicic acids should be depolymerized. Nevertheless, that does not happen (Varshal *et al.*, 1980; Alvarez and Sparks, 1985; Matichenkov, 1990; Matichenkov and Shnaider, 1996; Matichenkov *et al.*, 1997).

We suppose that the formation of polysilicic acids and their stable existence are due to the location of anti-ions in the diffusion layer surrounding the mineral's surface. And only in this layer is it possible to permanently keep the high concentration of monosilicic acid, which is formed during the dissolvment of siliceous films following condensation to polysilicic acids (Frolov, 2004).

High molecular-weight polysilicic acids are also able to form the gels with stable structure, and the colloids containing nucleus with silica microcrystals inside it (Iler, 1979).

The ratio between mono- and polysilicic acids is usually stable in various soils or water-mineral systems (Matichenkov and Shnaider, 1996; Matichenkov *et al.*, 1997; Matichenkov and Bocharnikova, 2001). However, this ratio could be varied by coming in or out of soluble silicon compounds, as well as by changing the mineralogical composition or the conditions for-secondary minerals formation. Similar processes take place on the surface of soil microorganisms (Matichenkov, Calvert *et al.*, 2001).

The discussion about presence of organo-silicon compounds and soluble complexes with non-organic and organic ligands in soil solutions has been expounded in some publications as well (Fotiev, 1971; Matichenkov and Snyder, 1996).

SILICON CYCLE IN SOIL–PLANT SYSTEM

Biological cycle of silicon on our planet is the most intensive in terrestrial ecosystems where plants uptake silicon in the range from 20 to 7000 kg Si/he/year (Matichenkov and Bocharnikova, 1994). Silicon is the 4th most abundant element in plant biomass, after oxygen, carbon, and hydrogen (Kovda, 1956; Perelman, 1975; Bazilevich, 1993).

As noted above, the plants and soil microorganisms are able to uptake only monomers of silicic acid and its anions (Yoshida, 1975; Ma, 2003). In larger plants, this process takes place through the roots and leaves. However, the silicon is distributed within the plant irregularly, according to the needs of the organism (see below).

Absorbed molecules of monosilicic acid may be polymerized and by this way participate in the formation of organo-silicon compounds (Figure 2). In their turn, polysilicic acids in plants

are able to be dehydrated with the formation of *phytholites* – amorphous silicon dioxide with complicate configuration. These phytholites are located within plant cells and in the intercellular space (Dobrovolsky *et al.*, 1988; Gol'eva, 2004).

It was demonstrated that the size, structure, and quantity of phytholites depend not only on the presence of silicon-forms available in soil, but also on the soil humidity, temperature, and the availability of other nutritional elements (Gol'eva, 2001; Hodson *et al.*, 2005). It should be noted that the formation and rate of growth of phytholites in plants are controlled by specific proteins (Harrison, 1996; Perry and Keeling-Tucker, 2000).
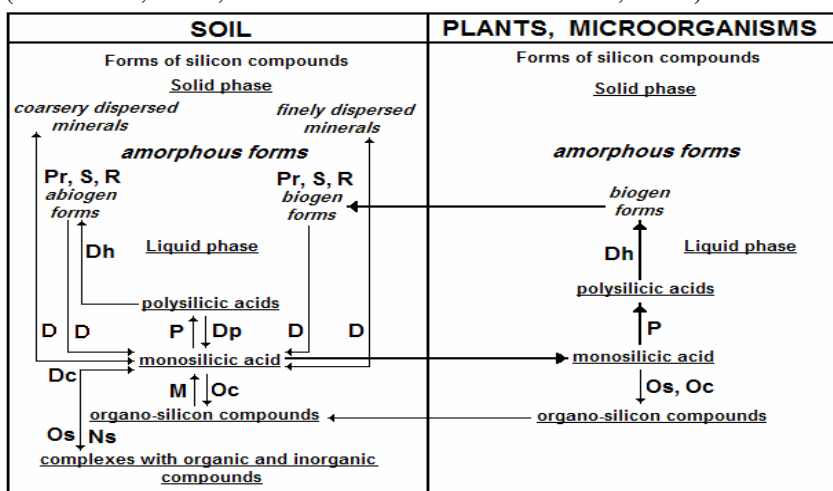
After the plants decay or their pulling-down, the biogenic silicon-forms (polysilicic acids, phytholites, organo-silicon compounds, etc.) are transported into the soil, where it is subjected to processes of dilution and/or decomposition. The final product of the silicon cycle process is the monosilicic acid, which once again involves the biological cycle and the influences of a number of physical-chemical and biological soil properties (Matichenkov and Bocharnikova, 1994; Bashkin, 2005).

It was distinguished that *eluvial* and *accumulative* types of silicon cycles, in which biologically active silicon forms are either accumulated in soil or are permanently moving out of the soil (Matichenkov and Bocharnikova, 1994). Both of these processes are initiated by the anthropogenic and natural factors (Matichenkov and Ammosova, 1994, Matichenkov *et al*., 1994, Matichenkov and Bocharnikova, 1994).

The phenomenon of *silicatization* in nature should also be noted. Under this process, the replacement of carbon atoms takes place in the soil or ground (from the remains of plants and animals) by silicon atoms (Milnes and Twidale, 1983; Cid *et al.*, 1988). The opportunity of such replacement is conditioned by the high concentration of monosilicic acid in the soil solution.

Silicon and Flora

The intensity and type of silicon cycles in native *soil-plant* systems are connected not only with the presence of active silicon forms in the parent material (Olier, 1990; Bashkin, 2005), landscapes, and secondary minerals (Kovda, 1956), but also with the type of plant association (Bazilevich, 1993; Matichenkov and Bocharnikova, 1994). For example, the plant associations with the predomination of scanty silicon species such as pine forest and meadow non-crop grasses are formed on the active-silicon depleted soils (Lanning and Eleuterius, 1981; Bocharnikova and Matichenkov, 2006). On the other hand, the intensive silicon cycle embraces a lot of active silicon forms in

Figure 2. Silicon cycle in system soil–plant–microorganisms.

Note: D – dissolving, Pr – precipitation, P –polymerization, Dp – depolymerization, Dh – dehydratation, S – salt formation, R – replacement of inorganic anions, Oc – formation of organo-silicon compounds, Ns – formation complexes with inorganic compounds, Os – formation complexes with organic compounds, Dc – decomposition of complexes, M – mineralization of organo-silicon compounds.

formation of the crop associations or mixed wood (Bazilevich, 1993; Matichenkov and Bocharnikova, 1994). The accumulation and moving out of the soil silicon compounds determine the succession of plant communities (Bocharnikova and Matichenkov, 2006).

This determination causes increasing stress sensitivity of silicon-accumulative plants at silicon-deficient conditions. On the other hand, a sufficient amount of active silicon forms grants for *silicophilic* plants more chances in competitive activity with silicon-non-accumulative species.

The majority of agricultural lands of the world have a deficiency in active silicon forms (Matichenkov and Bocharnikova 1994; Matichenkov *et al*., 1999*a*; 1999*b*; 2001; Matichenkov and Bocharnikova, 2004*a*; 2004*b*; Snyder *et al.*, 2006) due to the principle of agricultural activity – removing nutrient compounds from the soil. Usually, deficiency of macroelements such as P, N, K, and Ca is partially restored by mineral and organic fertilizers, but the lack of silicon is not compensated. It's estimated that the movement of silicon from the ground is ranged between 30– 7000 kg Si/ha/year. As a result, the upper soil horizon has a deficiency of active silicon; and, consequently, the trophic chain: *agricultural plants–farm animals–people* feels a serious deficiency of silicon.

Localization of Silicon in Plants

Distribution of silicon between plant organs is not equal and may vary from 0.001% in the pulp of fruit to 10–15% in the epidermal tissues (Voronkov *et al*., 1978). According to the total silicon content, the plants are subdivided into two big groups: *silicophiles* [silicon-accumulative plants] and *non-silicophiles* [silicon-non-accumulative plants]. *Silicophiles* are the species which has 1% or more of silicon per total dry mass, while *non-silicophiles* has less then 1% of silicon per dry mass (Epstein, 1999; Ma and Takahashi, 2002). Usually, the main amount of silicon is located in needles, husks, bark, and some others organs (Ma and Takahashi, 2002; Snyder *et al.*, 2006). The high content of silicon was also shown in root caps (Hodson, 1986; Ma *et al.*, 2001), where monosilicic acid is polymerized into polysilicic acids, which further are crystallized into microcrystals of amorphous silica.
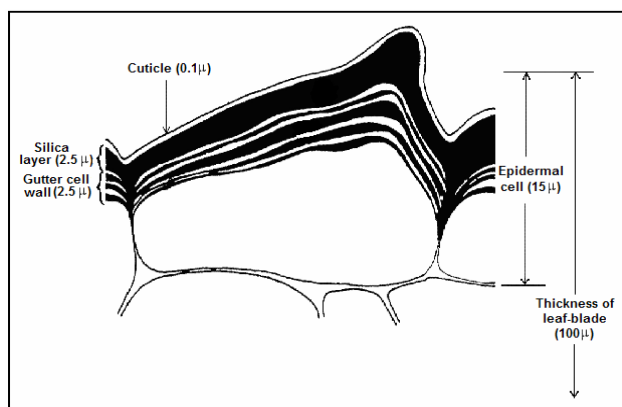
It is possible that microcrystals of silica play a role of "mechanical drill" in the root system. Indirectly, it was confirmed by the fact that under the deficiency of silicon nutrition, the formation of the secondary and tertiary plant's roots is sharply decreased (Matichenkov *et al.*, 1999*b*; Matichenkov *et al.*, 2001*b*; Matichenkov andBocharnikova, 2004*b*).

Figure 3. Scheme of epidermal cell of the leaf of *Oriza sativa* (Yoshida, 1975).

Absorbed molecules of monosilicic acid are accumulated in the epidermal tissues (Yoshida, 1975; Hodson and Sangster, 1989) and form the silicon-cellulose envelope where silicon is bonded with pectin and calcium (Waterkeyn *et al.*, 1982). As a result, the double cuticular layer (Figure 3) protecting and mechanically strengthening the plants is formed (Yoshida, 1975; Ma, 2003). This layer also prevents dehydration of the leaves (Emadian and Newton, 1989).

We speculated that the higher plants have a special mechanism for selective uptake of monosilicic acid from the soil solution. Indirectly, this idea was confirmed in various experiments. For example, Ma and Takahashi (2002) showed that *Oriza sativa* L. and *Lycopersicum esculentum* Mill. [grown hydroponically with presence of silicon compounds] may decrease concentration of monosilicic acid in nutrient solution from 50 to 5 mg Si/liter. In our experiment, *Hordeum vulgare* L. absorbed monosilicic acid from soil solution (2-20 mg Si/liter) and collected this compound in roots up to 500-520 mg Si/liter plant sap (Matichenkov *et al.*, 2005). Therefore, plants are really able to absorb monosilicic acid from the diluted solutions.

Because roots are containing not only monosilicic acids, but also polysilicic acids (Table 1), and, at the same time, it is known that plants are not able to absorb polysilicic acids from solutions (Epstein, 1999; Ma and Takahashi, 2002). Thus, it may be logically assumed that polymerization of the monosilicic acid molecules occurs inside of the root cells; and this process is started immediately after the uptake of monosilicic acid by the roots (Figure 4).

Forms of Silicon in Plants

Until recently, it was considered that about 90% of total silicon is present in plants as amorphous silicon dioxide – phytholites and epidermal films (Savant *et al.*, 1997; Epstein, 1999; Ma and Takahashi, 2002). This point of view was a subject of much controversy and was based on the "chemical rules" and chemical properties of silica (Iler, 1979). According to silicon chemistry, the occurrence of monosilicic and polysilicic acids of high concentrations is impossible in water or other solutions. In particular, it was known that at pH < 8 the amount of monosilicic acid in natural solutions is usually ranged between 0.1–100 mg Si/liter. Further increase of the monosilicic acid concentration initiates its polymerization or its precipitation in a form of amorphous silica (Iler, 1979).
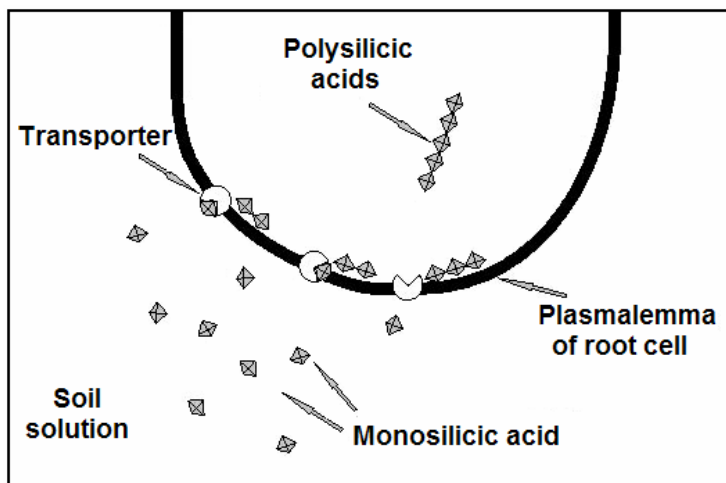

Figure 4. Hypothetical scheme of silicon uptake by plants: molecules of monosilicic acid penetrate into the cells of root filaments and are immediately polymerized into polysilicic acids.

However, it was supposed that such conditions are not characteristics for the intracellular and intercellular spaces of terrestrial plants (Medvedev, 2004), and therefore practically all polysilicic acids in

plants should coagulate with the formation of microcrystalline lattice of silicon dioxide (Iler, 1979; Yatsinin, 1994). As a result, despite the absence of actual data about the real concentration of soluble silicon in plants, physiology has "created" the point of view that plants tissues have a very low concentration of mono- and polysilicic acids.

And relatively recently, Japanese scientists demonstrated in the sap of *Oriza sativa* the existents of mono- and polysilicic acids at concentrations of 100–600 and 2000–3000 mg Si/liter, respectively (Ma, 1990; Ma and Takahashi, 2002). Our measurements (Table 1) are in agreement with these data. Table 1 shows that 30-70% of the total silicon compounds from different parts of *H. vulgare* are presented as polysilicic acids; content of monosilicic acid also is high and can be around 1-5% of the total plant's silicon.

Table 1. Content of monosilicic and polysilicic acids in different parts of *Hordeum vulgare* L.

Part of the plant	Monosilicic acid		Polysilicic acids		Total silicon content, mg Si/kg dry mass
	mg Si/liter plant sap	% from total silicon content	mg Si/liter plant sap	% from total silicon content	
Leaf	100-400	1.0-5.0	2700-5000	30-55	9000-12000
Node of stem	130-200	1.6-2.5	3800-5000	40-62	8000-9000
Interstitial space	350-400	4.3-5.0	3500-5700	40-70	8000-9500
Root	500-520	3.0-4.0	5000-8000	30-53	15000-19000

Note: Plant material [fresh mass of 0.1-0.2 g] was ground with a mortar and pestle in distilled water at room temperature and centrifuged for 15 min at 6000 g [Centrifuge T-30, Janetzky, Germany] to precipitate colloids and solid particles. Concentration of monosilicic acid was immediately determined in the supernatant samples by the method developed by Mallen and Raily (see, Iler, 1979). This method allows eliminating the affect of phosphate anions on the monosilicic acid measuring. Our modification allows to measure monosilicic and polysilicic acids separately. For this remained supernatant was treated as described earlier (Matichenkov *et al.*, 1997) to depolymerize polysilicic acids, and concentration of monosilicic acid was determined again as noted above. The difference between the second and the first measurements shows amount of polysilicic acids in tested solution. Concentrations of silicon compounds are expressed per liter plant sap; sap volume per kg fresh mass of the leaves was measured especially. Total silicon content was analyzed in the dried plant material according to Elliot and Snyder (1991). Each measurement was made in 8-12 independent replications.

Thus, we can establish a fact that up to 75% of silicon in plant occurs in the form of water-soluble mono- and polysilicic acids. Undoubtedly, the high concentration of these compounds is stipulated for the important role of silicon in vital plant functions.

Silicon and Water Storage in Plants

An important property of silicon is the ability to accumulate and store the water within the organism throughout, forming polysilicic acids and their gels. The model experiment showed that one atom of silicon is able to hold up to 146 molecules of water (Table 2). We estimated that about 20–30% of the total silicon in organism may be involved in the process of maintaining internal water reserve. For example, under optimal silicon nutrition, the medium-latitude culture *H. vulgare*, usually containing around 1.2–1.4% of silicon per dry mass, is able to store only with silicon assistance from 6-37 g water per 100 g fresh mass of the individual plant.

The capability of silicon to hold water is very important for tropical and arid plants, which are usually *silicophiles* (Ahmad *et al.*, 1992; pers. obs., 1986-2007). From this stand point, it makes sense to assume, that *silicophiles* have a high tolerance to drought, in part because during the drought season, they can use "extra" water, which was collected in plants with silicon "assistance" during humid season. At least, some of our data is in agreement with this.

Table 2. Content of water molecules and silicon atoms in different gels, formed from silicic acid.

Gel number	Silicon, % from total gel mass	H_2O, % from total gel mass	H_2O/Silicon, molecules/atom
1	1.28	97.9	146
2	1.60	97.7	119
3	2.40	97.1	82
4	3.20	96.6	63
5	4.80	95.3	40

Note: Standard silicic acid [16% silicon, product of TerraTech LLC] at 24 ^oC and atmospheric pressure of 765 mm mercury was mixed with water and mineral acids [HCl, H_2SO_4, and others] in different proportions until steady-state gels were formed. Final amounts of water molecules and silicon atoms in gels were calculated on the basis of initial amounts of the compounds, which participated in the gel(s) formation, *n*=10.

In particular, the special experiment with woody tropical species *Hura crepitans*, *Hibiscus elatus*, *Ceiba pentandra*, and *Clitoria racemosa*, preserved during the long-term drought and maintained in the tropical mesocosms of Biosphere 2 Center [Columbia University, Arizona, USA], has argued for such believing. The analyses showed that water potential (Rascher *et al.*, 2004) and total water content in leaves of these trees, even in the middle of the day(s) (Figure 5) were not decreased of the essence, even when the rainy season was changed by the long-term season of the air and soil drought.

SILICON AND PLANTS RESISTANCE TO EXTREME ENVIRONMENTS

The number of publications, related to how active silicon compounds influence on plant growth and development, suggest the existence of the total mechanism, by which silicon improves plant stress-tolerance (Cherif *et al.*, 1994; Savant, *et al.*, 1997; Ma and Takahashi, 2002; Belanger, 2005). This mechanism seems to be universal, that even, for example, optimization of silicon nutrition, it will induce plant resistance against biogenic [infections, mycosis, insect injurious, etc.] and abiogenous [low or high temperature, salt stress, heavy metals, drought, etc.] factors (Bocharnikova *et al.*, 1999; Savant *et al.*, 1997; Matichenkov and Bocharnikova, 2004*a*; 2004*b*; Belanger, 2005; Snyder *et al.*, 2006).

There are several suppositions about the protective role of silicon in plants. In particular, the thickening of the epidermis, increasing chemical stability of DNA, RNA, and molecules of chlorophyll(s), functional activation of organelles, optimization of transport and redistribution of compounds within the plant, and others (Voronkov *et al.*, 1978; Aleshin, 1982; Aleshin *et al.*,

1987; Matichenkov, 1990; Savant *et al.*, 1997; Ma and Takahashi, 2002; Matichenkov and Kosobryukhov, 2004) can support the involvement of silicon in numerous adaptive responses of the plants.
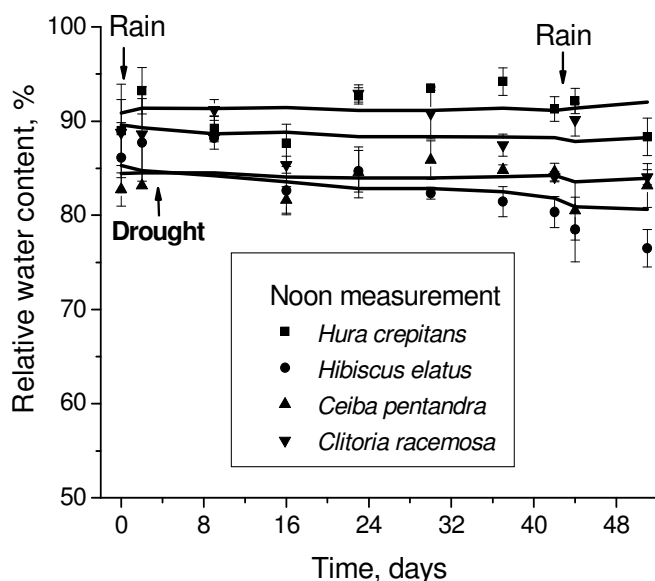

Figure 5. Relative water content in the middle of the days in the leaves of tropical woody cultures *Hura crepitans*, *Hibiscus elatus*, *Ceiba pentandra*, and *Clitoria racemosa* during the long-term drought, maintained in tropical mesocosms of Biosphere 2 Center [Columbia University, Arizona, USA]. Data points represent the mean ± SE, *n*=3-4.

But we speculate that all of these "adaptations" are the consequence of functioning of uniform protective mechanism, part of which is connected with the active silicon forms. Our opinion is indirectly supported by the fact that stress-tolerance of plants is increasing with rising silicon content within the tissues (Matichenkov *et al.*, 1999*b*; 2000). Moreover, as we found in the experiment with *Distichlis spicata* growing under high salinity, the highest amount of silicon was collected in the organs, which were more "suffering" over salty stress (Matichenkov, Bocharnikova *et al.*, 2007). We also hypothesize that living organisms have a special ability to coordinate absorption and rapid redistribution of silicon into the parts of the body, exposed to stress.

Silicon as Matrix for Organic Compounds Synthesis

In the mid 20th century, Russian scientists (Strelko *et al.*, 1963; Vysotsky *et al.*, 1967) had discovered and determined the possibility of catalytic synthesis of the organic compounds on silicon gel matrix. According to authors' data, the challenge of synthesized molecules from silicon gel matrix and conservation of matrix allowed to realize non-limiting low-temperature synthesis of initial molecules from more primitive organic "row material". On the basis of that V.V. Strelko and co-workers (1963) even advanced an idea that "…*the reactions of amino acids polycondensation, concentrated by adsorption on the silica surface, could lead to formation of pre-proteins and might play an important role in origin of life on the Earth*".

In modern organic chemistry, the polycondensation technology is developed in greater detail. According to general opinion, if during formation of silicic-gel certain organic molecule are present in the solution, the the silicic-gel surface has a possibility to hold the "print" matrix from this initial "molecule-former". Afterwards, if the "molecule-former" would be removed, such "print" on the silicic-gel surface becomes to be a "matrix or the center of replication" for synthesis of initial molecules. It is important to note that the "silicic acid-gel-matrixes" are playing the role of catalyzer in a number of reactions which are necessary for organic synthesis.

Some of them are: cycle formation, cyclization, rearrangements, reduction and/or oxidation, condensation, hydratation and/or dehydratation, formylation, protection of functional groups, and others (Banerjee *et al.*, 2001). At present time, many chemical and pharmaceutical companies are using this approach for synthesis of complex molecules.

HYPOTHESIS ON SILICON PARTICIPATION IN PROTECTION OF LIVING ORGANISMS UNDER STRESS CONDITIONS

Premises of Hypothesis

The possibility of biochemical compounds synthesis on the gels of polysilicic acids within living cell was not considered until now. The general reason for that, as we mentioned above, was conception, that in living organisms the polysilicic acids are existing in very low concentrations, or even do not exist totally.

However, the new data allow being in doubt about such conclusion. In particularly , the results, presented in Table 3, showed the high concentration of mono- and polysilicic acids in the leaves and stems of *D. spicata*, even when the plants were grown in a sand which had a very low concentration of water-soluble forms of silicon; it was ranged around 1.0 – 2.5 mg Si/kg sand.

In this experiment, the content of silicic acids [sum of mono- and polysilicic acids] of leaves and stems was 514 mg Si/kg fresh mass and 893 mg Si/kg fresh mass, respectively; inside the cells [in symplast] the content of silicic acids was higher than outside the cells [in apoplast] (Table 3).

During next experiment we examined the same parameters, but after 12 days of silicon fertilization throughout *D. spicata'* root system. In this case, the content of silicic acids of leaves and stems increased more than 40-67% (Table 3).

The Figures 6 and 7 illustrate the dynamics of mono- and polysilicic acids release from apoplast and symplast of *D. spicata* leaves and stems. It is clear that silicon fertilization induces accumulation of silicic acids in stem apoplast, and in symplast of the leaves and stems. Peculiarities of silicon accumulation and redistribution between plant organs we will describe in detail in a special publication (Matichenkov *et al.*, 2007). But here it is important to note, that shoots of plants are able to accumulate the water-soluble silicon forms in amount, sufficiently enough for silicon creative job in organism.

The additional pre-suppositions for organic compounds synthesis on gels of polysilicic acids in living cell are following:

• Active silicon forms moving into the living systems increase their stress-tolerance (Cherif *et al.*, 1994; Savant, 1997; Epstein, 1999; Ma and Takahashi, 2002; Matichenkov and Bocharnikova, 2004*a*; 2004*b*; Belanger, 2005);

• It has been found a specific protein (transporter), which regulates absorption of silicon from environment, and its redistribution within the plants (Ma *et al.*, 2006);

• Plants absorb silicon from the environment only in the form of monosilicic acid (Yoshida, 1975; Ma and Takahashi, 2002);

• Depending on plant species and type of tissue, the total silicon content in plants varies, on average, from 0.2 to 1.5% of dry mass (Epstein, 1999; Ma, Takahashi, 2002);

• In plants the silicon exists in the forms of mono- and polysilicic acids, amorphous silica [phytholites], and organo-silicon compounds. Percentage of mono- and polysilicic acids may rich 1-2% and 10-70% from the total silicon content, respectively (see Table 1);

• Water-soluble silicon compounds in plants purposefully redistributed directly into the parts and/or organs, which are exposed to stress (Matichenkov *et al.*, 2000; Matichenkov and Bocharnikova 2004*a*; 2004*b*; Matichenkov, Bocharnikova *et al.*, 2007);

• Polysilicic acids gels are able to form matrixes from organic "molecule-formers". These "matrixes" could carry out low-temperature synthesis of new molecules which are equal to "molecule-formers". The precursors for this synthesis may be chemically more simple organic components (Strelko *et al.*, 1963; Vysotsky *et al.*, 1967; Banerjee *et al.*, 2001).

Table 3. Content of mono- and polysilicic acids in leaves and stems of *Distichlis spicata.*

Part of the plant	Monosilicic acid		Polysilicic acids	
	Apoplast	Symplast	Apoplast	Symplast
	Silicon, mg Si /kg fresh mass			
	No silicon fertilization			
Leaf	34	165	326	368
Stem	19	117	58	320
	After silicon fertilizers			
Leaf	42	223	227	487
Stem	20	197	104	395
*LSD$_{05}$	5	15	15	20

Note: *Distichlis spicata* plants were grown in plastic pots (20×50×20 cm) with sand at temperatures of 22-24 $^{\circ}$C /17-19 $^{\circ}$C [day/night], and natural illumination. Soil salinity was simulated by irrigation of water with 10 g/liter of Na^+ as NaCI. Plants were watered by regular water containing no more than 0.10-0.15 mg Si/liter. Fertilizers (MiracleGro: www.miracle-gro.com) were added into ground 1-2 times per month. For the experiments, leaves and stems were cut into 2.0-2.5 cm length segments and placed to the flasks with distilled water; the plant material/water ratio was ranged from 1/100 to 1/200 (w/w). The flasks were shaken up by mixer for 25 h at room temperature. Content of mono- and polysilicic acids in apoplasts of leaves an stems was determined after sequestrating sampling of water aliquots (1-5 ml) during 0, 1, 5, 15, 30, 60, 180, 360, and 1440 (min) shaking. Then, plant material was grinded with mortar and pestle till homogenous substances and mixed with initial solutions; the flasks were shaken additionally for 60 min [total time for extraction of water-soluble fractions of silicon was 1500 min]. Content of mono- and polysilicic acids was measured again. The difference of the values between after grinding of solid material and before grinding of solid material was considered as the concentration of these compounds in the symplast. * LSD$_{05}$, the least standard deviation, *n*=4.

Hypothesis

During endeavor (ontogenesis) of total realization of genetic information, the organisms (Biel *et al*., 1990; Biel and Fomina, 2005) usually feel deficiency of nutrient elements or energetic resources, or are affected by negative climatic factors, diseases, and other stressful pressures. At such conditions the living systems are spending substantial part of energy for maintenance, adaptation and defense against internal and external problems. As a result of that, the plants [and others organisms as well] are usually slowed in development, and do not realize interior potential. In principle, the situation may be improved by supplying organism with

essential nutrition and by creating optimal environment and internal conditions. However, in real life this way is not practicable, especially in a large-scale agriculture.

Improvement could be achieved, if the responsibility for the part of repairing, metabolic and protective functions would be shifted from genetic apparatus to the other system(s).
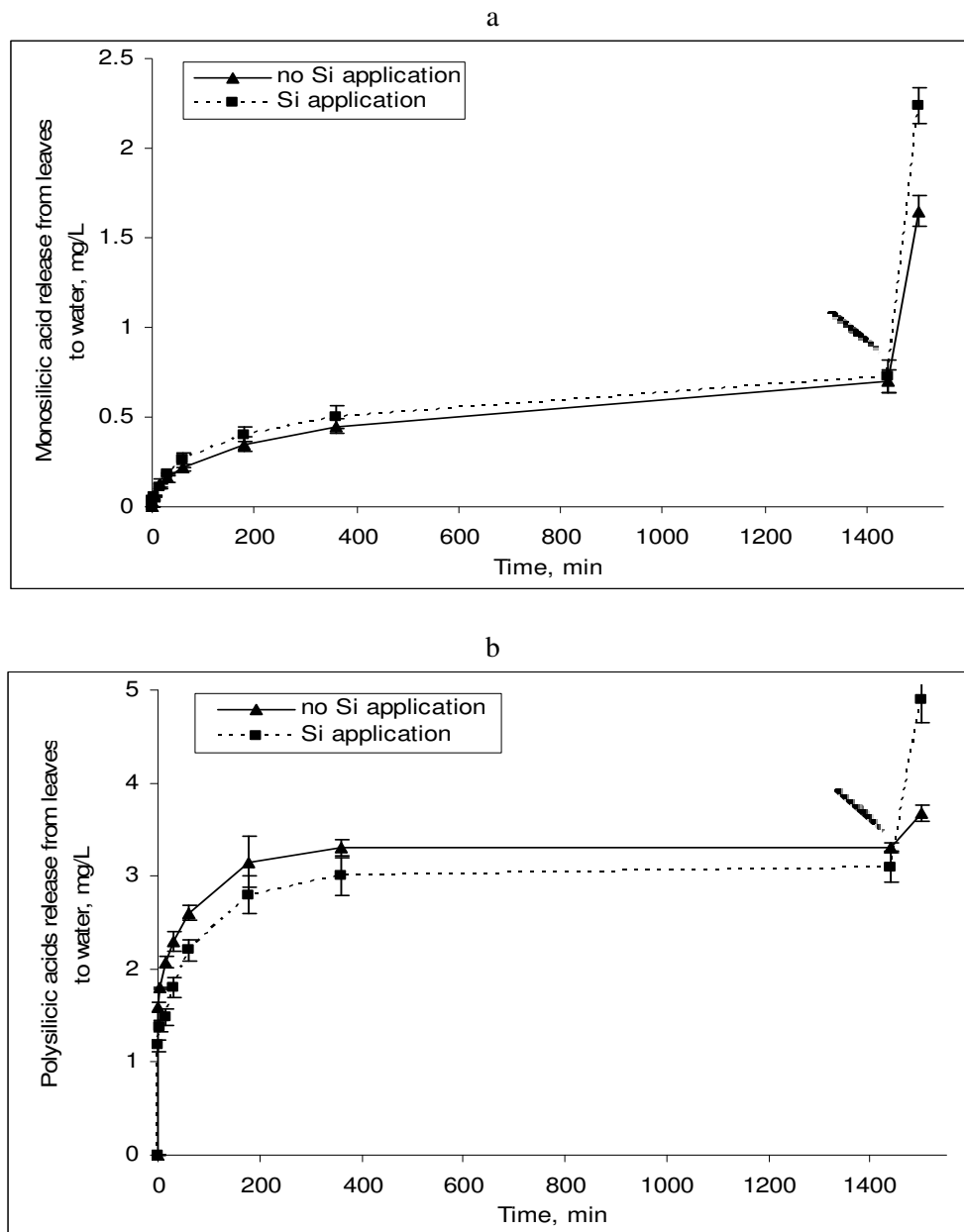

Figure 6. Dynamics of washing out of mono- (a) and polysilicic (b) acids from the leaves of *Distichlis spicata* grown without silicon fertilizers (▲) and with silicon fertilization (■), added to substrate 12 d before measurements.

Note: Arrow shows the moment of grinding of the leaves and further returning leaf homogenate to initial water-soluble fraction. The total silicon content has been measured after 1 h in the same volume. Description of details is presented in the note of Table 3. Data points represent the mean ± SE, *n*=4.

Figure 7. Dynamics of washing out of mono- (a) and polysilicic (b) acids from the stems of *Distichlis spicata* grown without silicon fertilizers (▲) and with silicon fertilization (■), added to substrate 12 d before measurements.
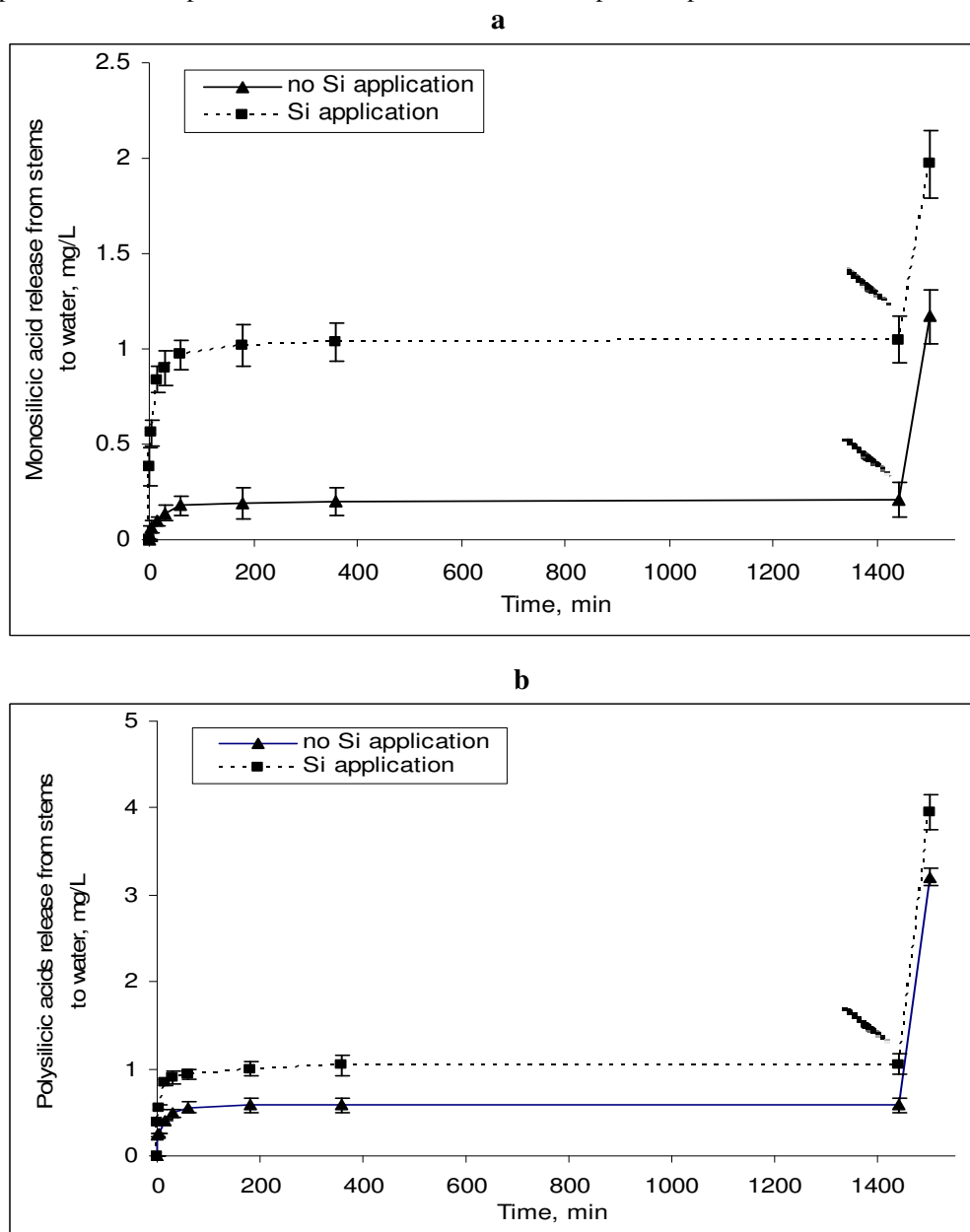
Note: Arrow shows the moment of grinding of the stems and further returning stem homogenate to initial water-soluble fraction. The total silicon content has been measured after 1 h in the same volume. Description of details is presented in the note of Table 3. Data points represent the mean ± SE, *n*=4.

Using the plants like example, we'll consider one of such system, although it is most likely that this mechanism is universal and functioning in all organisms, which are living now on our Planet.

Silicon uptake – Molecules of monosilicic acid, located in soil, penetrate across the root's plasmalemma [cell "sluice"] inside of the cells and are immediately condensed into active chains of polysilicic acids (Figure 4). Then the silicon compounds are distributed within all plant.

Silicon distribution – Some part of silicon compounds goes to epidermal layer, root caps, cell walls, and other tissues and organs for synthesis of phytholites and other silicon-containing structures. The second part of silicon is used to form polysilicic acids gels – the basis of further low-temperature synthesis of organic compounds. The third part of absorbed silicon is preserved and stored at the normal conditions as polysilicic acids or their gels with non-active surface within the cells and in the intercellular space.

Synthesis of organic compounds on the polysilicon matrixes at optimal conditions – Silicon compounds, located inside of the cells, are shaped into polysilicic acid gels. At certain moment, into activated polysilicon-gel is delivered the appropriate molecule-former [protein, simple or complicated protective compounds, and so on], which creates in polysilicic-gel the replica-matrix of itself (Figure 8). After printing and moving out replicating substance, modified polysilicic acid as a "gel-plate" becomes to be able to do catalytic synthesis of molecule-formers' copies from simpler structural blokes and components, located in cytoplasm.

Silicon-dependent synthesis of protective compounds during stress – After external irritation, the signal system is switching on the mechanism of stress identification. Simultaneously, organism additionally uptakes the silicon from the environment and transports it to stressed area. After receiving the information about type of stress, the nuclear founds adequate response for providing synthesis of correct protective compounds; it could be stress-proteins, antioxidant enzymes, antioxidants and others products (Figure 8). Then, the synthesized stress protective molecules are transported to the stressed aria(s) where they play protective roles, and are also used as molecule-formers for additional synthesis of their copies on the polysilicon matrixes.

However if an organism has a strong stress or many different stresses simultaneously, the rate and quantity of synthesizing stress-response-material(s) may not be sufficient enough to solve the problem because some other vitally-important functions should be done in organism at the same time. As a result of escalating energy deficiency and informational resources, the synthesis of "routine" compound, essential for cells is slowed down or even ceased.

We suppose that in living cell some of the protective compounds can move to the activated polysilicic acids gels, and are printed to form "matrixes" as molecule-former(s). Then, these "former(s)", after creation of itself replica in polysilicic acid gel, are transported to stressed-zones. At the end, the silicon-gel-matrixes begin to clone the same molecules from the "at hand material" of cytoplasm. At such cooperation the silicon-gel-matrixes give to organism the possibility [on a background of the stress] to release informational-commanding resources and part of energy for cell functioning in former "before-stress" regime. Thus, additional synthesis of protective compounds can carry out on polysilicic acids-gel-matrixes without direct participation of the genetic apparatus.

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New Technologies

High pollution level of the environment and other negative consequences of human civilization bring up a question about the manner and conditions of humanity's survival. The application of synthetic drugs and pesticides initiates a number of negative consequences, which are now sensed by everybody. For example, antibiotics are not only killing pathogenic microorganisms, but also destroying the patients's immune system. Fungicides kill in soil and on the plants surface, together with pathogenic fungus, the useful organisms. Absolutely unwarrantable to apply in agriculture insecticides: while trying to protect the plants against insects, people provide penetration of the toxins inside of animals and, as a consequence – to human body. And, it is absolutely unallowable [in modern stage of genetic engineering development] to introduce genetically modified organisms into agriculture, food industry, pharmacology, and other fields because such organisms are the harbor for a number of unstudied consequences and frequently negative for humanity.
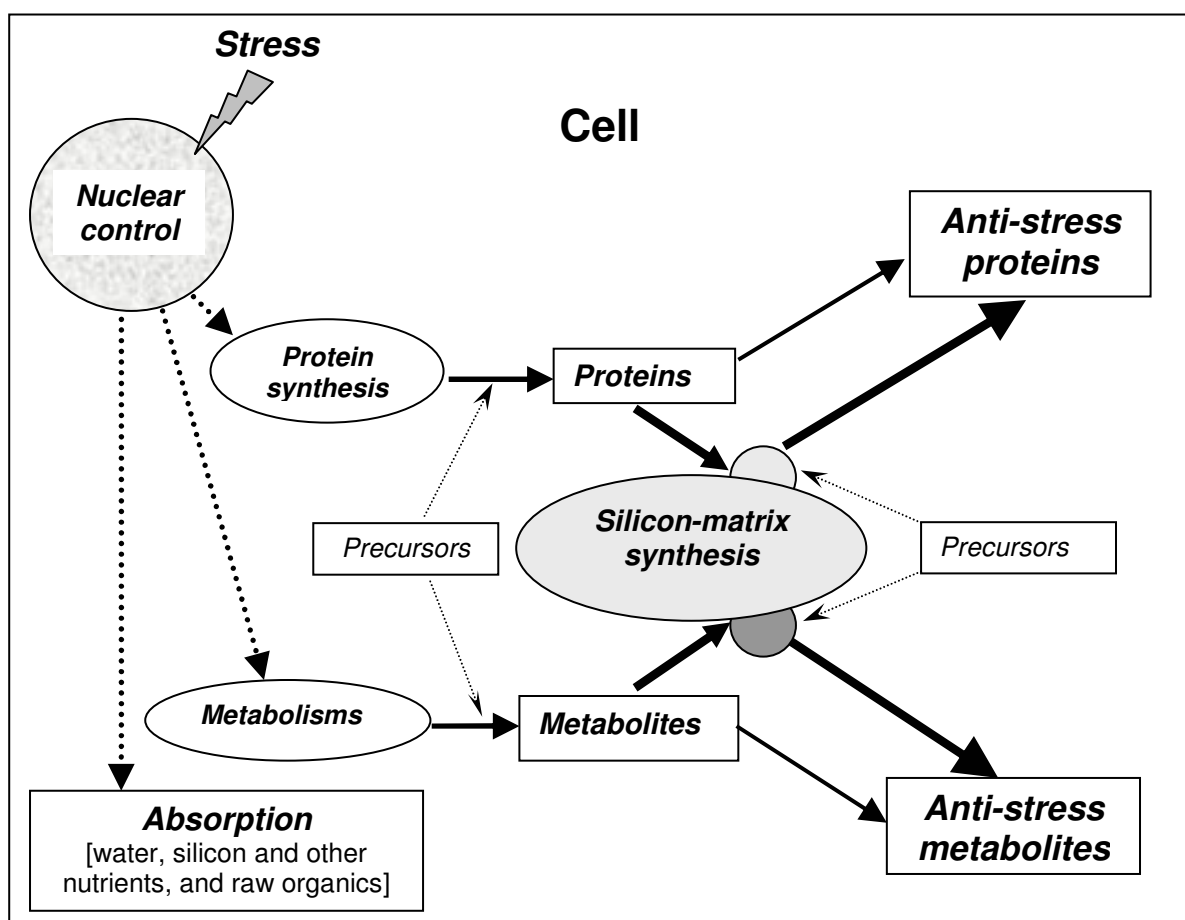

Figure 8. Hypothetical scheme of the universal auxiliary stress-protective mechanism of living systems with participation of the movable silicon compounds.

The way out from this situation, in some cases, could be using of silicon compounds, although we are far a way from conclusion that silicon is "panacea from all troubles". We are sure that competent application of silicon compounds may help to solve some large-scale problems, and to modify whole series of economically-important technologies. Below we have presented some of really solvable actual problems:

• Planetary problem of fresh water deficiency [the most of which is used for irrigation] can, in part, be solved by corrective application of silicon fertilizers, because the "activated" silicon facilitates a decrease of irrigation water amount on 30–50% without diminution of quantitative and qualitative crops characteristics (Matichenkov and Kosobryukhov, 2004; Snyder *et al.*, 2006)

• The application of silicon compounds, which facilitates plants tolerance to infection and are often more affective than fungicides and insecticides, will allow a decrease in the use the pesticides in agriculture (Datnoff *et al.,* 1991; Savant *et al.,* 1997);

• The application of silicon fertilizers promotes plant tolerance to high/low temperatures, saline intoxication, and etc., and as a result, permits guaranteed yields enriched with silicon compounds under extreme environment (Matichenkov and Kosobryukhov, 2004; Snyder *et al.*, 2006);

• Consumption of the foodstuffs with high level of silicon compounds makes people and animals stronger against diseases and unfavorable environment. Furthermore, an overdose of silicon compounds is not possible in principle, because the extra dose is transforming into an inert form – silica, which quickly moves out from the organism (Voronkov *et al.*, 1978; Iler, 1979; D'yakov *et al.*, 1990).

CONCLUSION

Silicon increases the level of resistance of living systems to stress(es), and does not toxically influence the organism. Active silicon forms are possible purposefully with low cost and without interference of the structure of genetic apparatus, to create conditions which are necessary for optimal use of the Program of Realization of Genetic Information (Biel et al., 1990; Biel and Fomina, 2005). Our proposition can be one of the directing criteria for detection of the way(s) "to switch on" the silicon-protective function in cell with using natural materials and internal reserves of organism.

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