Invited paper

Silicon everywhere

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Abstract — The paper discusses the ubiquity of silicon and its compounds in the geo-chemical structure of the Earth. The dominant role of mineral oxidized compounds of silicon as the building material of the primordial magma, metamorphic and sedimentary rocks is also shown. The reader's attention is also attracted to the numerous varieties of silicon compounds valued for their intrinsic beauty. Finally, methods of silicon production for electronics purposes are briefly addressed.

Keywords — silicon, silica, quartz, geo-chemical structure.

The ubiquity of silicon is a characteristic feature of the geo-chemical structure of the Earth. The popular slogan: "Earth – silicon planet" is thus fully justified. Silicon is, beside oxygen, the most common element of the external, solid part of the Earth also known as the earth crust or lithosphere. Its average content is estimated to be in the range of 26–29 per cent by weight depending on the adopted calculation method. The mineral silicate fraction is also the dominant component of the chemical composition of meteorites. This indicates a privileged position of silicon in the primordial matter of the Solar System.

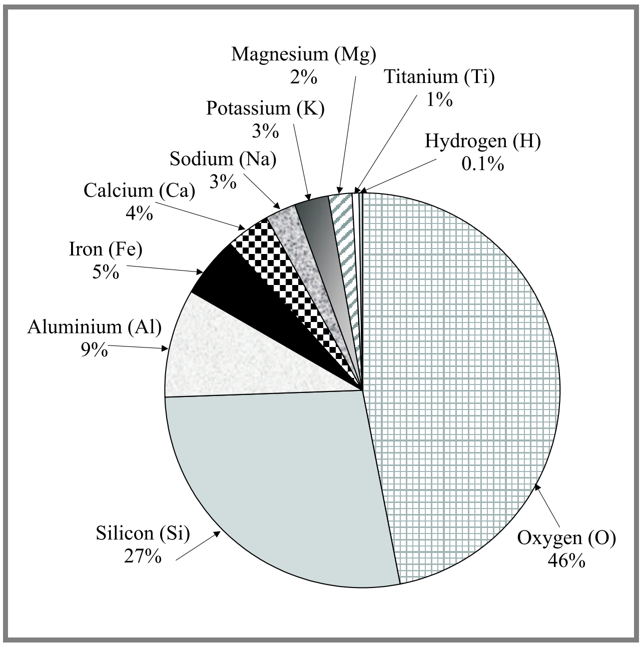


Fig. 1. Composition of the lithosphere.

It should be noted that few elements only contribute significantly to the lithosphere. Based on thousands of analyses it is estimated that the average content of those elements (expressed in per cent by weight – see Fig. 1) is following.

Oxygen and silicon have, therefore, an enormous advantage over the next 6 elements that constitute merely a few per cent of the lithosphere. It is, thus, no accident that these elements are considered to be the main rock-forming components.

Fig. 2. Natural quartz crystals.

Silicon does not exist naturally in its pure form. It is almost always oxidized, the most often as silicon dioxide SiO_2 also known as silica (Fig. 2). Silicon is extremely oxyphilic and its bonds to oxygen in silicate crystal lattices are very durable in all geo-chemical conditions. $[SiO_2]^4$-anions are the basic component of the silicate crystal structure (Fig. 3).

Together with aluminosilicates, silicates form the biggest family of minerals, constituting 87 per cent (!) of the components building the lithosphere. Rough estimates of the average content of the rock-forming minerals in the lithosphere are thus unambiguous, as indicated in Table 1.

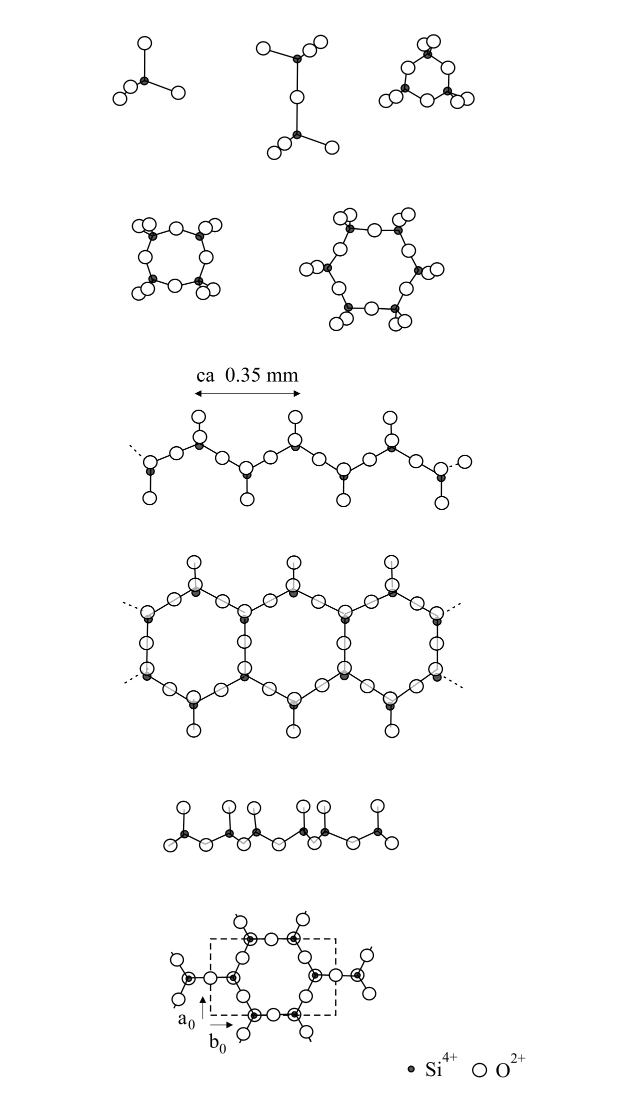


Fig. 3. Basic structures of the silicon-oxygen anions in silicate crystal lattices.

The real "power" of silicon may be fully appreciated only when the information presented in Table 1 is taken into account. It is thus clear that silicon is rightly considered as one of the most important lithophilic elements. In other words, mineral oxidized compounds of silicon are the dominant building material of the primordial magmatic rocks, such as the most widespread granite and basalt that form the core of the lithosphere. Silica is also abundant in metamorphic rocks and is easily found in sedimentary ones. In short, it is present in every geo-chemical environment. In oceanic and fluvial waters significant amounts of extremely diluted silica (fluvial waters – 25–30 g/t, oceanic waters – 6 g/t) are present, too. Silica may reach higher concentrations with the help of certain live organisms building silica skeletons. Such valuable minerals as diatomaceous earth or diatomites are created from clusters of the skeletons of certain single-cell algae known as diatoms (*diatomae*). The organogenic siliceous rocks include also radiolarites (formed of clusters of protozoa called radiolaria) and spongiolithes (consisting of *silicispongiae*). The presence of silicon in the tissues of live organisms is a separate issue. Silicon is especially abundant in certain plants where unusual combinations of silicon and organic compounds are observed.

Table 1
Average content of rock-forming minerals in the lithosphere

Mineral	Simplified chemical composition	Percentage by weight
Feldspars	$Ca[Al_2Si_2O_8]$; $Na[AlSi_3O_8]$; $K[AlSiO_3O_8]$	58
Quartz	SiO_2	12.5
Pyroxenes	Ca, $(Mg,Fe)_2[Si_2O_6]$	12.0
Mica	$K(Mg,Fe,Mn)_3$ $[(OH)_2AlSi_3O_{10}]$	3.5
Olivines (chrysolites)	$(Mg,Fe)_2[SiO_4]$	2.6
Amphiboles	$Ca_2(Mg,Fe)_5$ $[(OH)Si_4O_{11}]_2$	1.7
Silty minerals	$Al_4[OH_8/Si_4O_{10}]$ (example)	1.0

Compounds of oxidized silicon are the basis of extremely numerous mineral forms with very different structural, morphologic, physical and chemical properties. Minerals belonging to the group of silicates and aluminosilicates are the most common rock-forming minerals that are also valued in practical applications that include all areas of material culture and technology. The very beginnings of the use of silica go back to the Paleolithic Age, where the ability to fabricate flint tools was the measure of the technological progress. Nowadays synthetic single crystals of quartz and silicon wafers are simply indispensable for the sophisticated technology of the materials required by modern microelectronics and optoelectronics.

One of the most efficient ways to obtain pure silicon is to use minerals belonging to the class of spatial silicates, especially SiO_2, which forms in itself a separate group of minerals. Numerous polymorphic varieties include **tridymite**, **cristobalite** and the most common **quartz** taking a high-temperature form (hexagonal α-quartz stable in the range of 573–850°C) and a low-temperature one (trigonal β-quartz stable at temperatures below 573°C) (Fig. 4).

Let us also mention numerous varieties valued for their color, that is transparent and colorless *rock crystal*, dark-brown *smoky quartz*, black *morion*, violet *amethyst*, yellow *citrin* and *rose quartz*. Many colorful varieties of quartz take their colors from the inclusions of other minerals, e.g. asbestos (*cat's eye*), krokidolit (*tiger's eye*), actinolite (*prase*), green micas (*aventurine quartz*) or rutile spine (*rutilated quartz – hair of Venus*). Cryptocrystalline varieties of quartz belonging to the chalcedon group take many

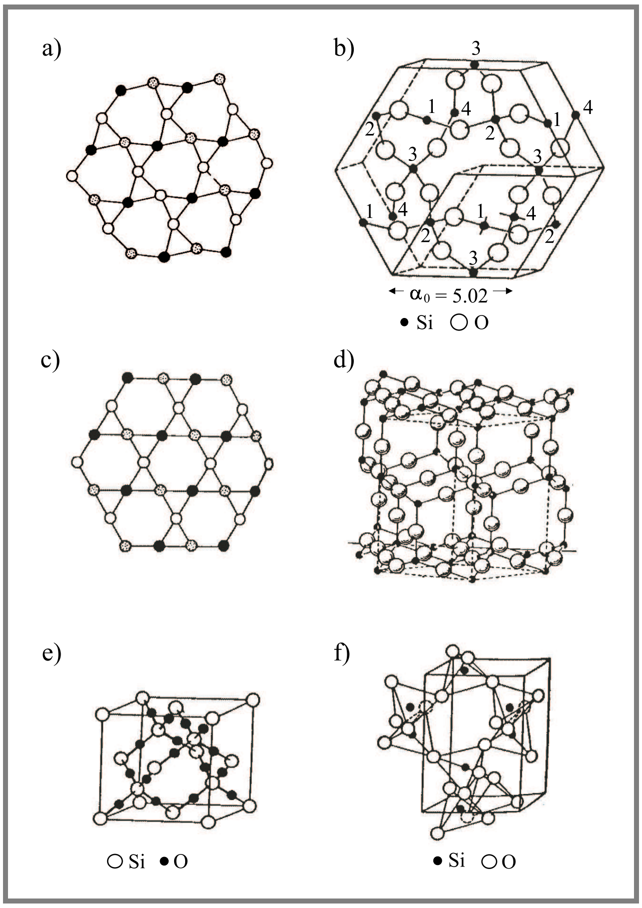


Fig. 4. Fundamental structures of polymorphic SiO_2 varieties: (a),(b) quartz β; (c) quartz α; (d) trydymite α; (e) cristobalite α; (f) cristobalite β.

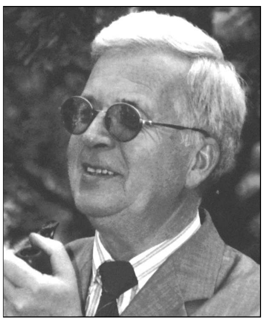
different forms, such as multicolored and layered agate (Fig. 5) and onyx, jasper with diversified colors, green *chryzopras*, red *carnelian* and *sardonyx*, and finally common *flint*. In the world of minerals amorphous varieties of pure silica are found, too, mostly in the form of opals, and significantly less often as a silica glass formed as a result of melting of quartz sand during atmospheric discharge (the so-called *fulgurite*). Finally, let us mention very specific mineral forms of silica clusters – *geyserites*, deposited around certain hot, volcanic sources and geysers.

Fabrication of high-purity silicon (above 99.997 per cent of Si) for electronics requires, of course, the use of complex and time-consuming technologies of extensive processing of raw materials, that is production of second generation minerals. Regardless of the intricacy of the processing or synthesis, natural minerals are always the basis. Vein deposits of quartz, quartzite or quartz sands are the fundamental and most often used source of metallic silicon. It should be noted that the content of silica in the sands and quartz sandstone may sometimes reach a peak value of 99 per cent due to the processes of erosion, water transport and sedimentation.

Technologically pure, metallic silicon is usually obtained by means of electro-thermal reduction of molten quartz or quartzite with carbon. It is used as a component of alloys and is also the basis for the production of silicon carbide (SiC), silicides and silicones. Silicon with semiconductor properties, as well as single crystals of silicon (doped or not), are obtained from polycrystalline silicon.

Fig. 5. Agate.

World resources of raw materials needed for the production of metallic silicon (quartz, quartzite, quartzite sands and sandstone) are enormous and practically unlimited. The only problem is high consumption of energy during the fabrication of pure silicon, which is important from the economic point of view.



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