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The Biogeochemical Cycle of Silicon in the Ocean

Bernard Quéguiner

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Preface

Biology, chemistry, physics, mathematics, geosciences, and social sciences provide us with the tools necessary to understand the past, present, and future of the world. These tools allow us to build concepts that are not necessarily accurate but seem sufficiently developed for us to consider them as paradigms. The ancient cosmology of our Western society has long been satisfied with seeing planet Earth as a flat object, a paradigm sufficient for understanding the environment perceived by humanity at that time. We must always keep in mind the approach of Descartes, and progress in our analysis and knowledge of objects in the environment, whilst maintaining the humility essential for knowing that we can sometimes be wrong and that there are limits to our understanding.

Geochemistry is the science or study of the elemental chemical composition of Earth, the chemical speciation of the elements in the dynamic aspect of their transfers (= fluxes) between different compartments (= stocks). Whether or not life has little influence on the deep geochemistry of our planet[1], it is a feature of its external envelope, and may be unique on the Universe scale. Biological mechanisms have emerged progressively, acting as drivers of the basic dynamics of matter regarding the chemical composition of fluid envelopes and the upper mantle rocks as well as element fluxes between these compartments under a variety of chemical species. How do we explain the elemental

1 Although the discovery of "active" microorganisms within the deep sedimentary layers is likely to change this concept in the near future.

composition of our atmosphere and its evolution on a geological time scale without referring to the emergence and development of life on Earth? This question also applies to the hydrosphere and, particularly, the oceans, whose chemical composition changes on that same scale, which are closely associated with the chemical structure of the primordial Earth and the evolution of living organisms. How do we explain the formation and composition of not only sedimentary rocks, but also of metamorphic rocks and even some crystalline rocks of variable nature over geological eras, evading the role of life on land and in the oceans? This short list of questions is not exhaustive and is provided here as an example; it reflects the direction of thinking from the first naturalists to modern scientists involved in studies of the Earth's environment that ultimately led to the definition of a new, eminently multidisciplinary science: biogeochemistry. This can therefore be defined as the science whose objects are the elemental chemical composition of the Earth, the chemical speciation of its components, stock dynamics of the main reservoirs and fluxes between them, under the simultaneous control of physical, chemical and biological reactions. Such a wide program underlines the inclusiveness of biogeochemical studies, whether it be through the establishment of working concepts on the global scale or through the definition of experimental sampling schemes and processing of supporting data of such concepts! Therefore, biogeochemistry occupies a special place among other more mono-disciplinary sciences.

The global carbon cycle is at the center of current concerns of biogeochemists because biogeochemistry is inseparable from climate science. The concept of the biological pump perfectly illustrates this case. Autotrophic organisms living on the surface of our planet are indeed responsible for the annual fixing of around 120 Gt[2] of carbon in almost equal proportions between the continents and oceans. In the oceanic compartment, diatoms, microalgae with siliceous cell walls, are responsible for nearly half of the primary production. This is one of the reasons why, albeit belatedly, marine biogeochemists became interested in the silicon cycle. Furthermore, despite the importance of primary marine production, only a small proportion of organic carbon formed is finally deposited and buried in deep sediments. Indeed, through

2 Gt: unit, a gigatonne (109 t), equal to a petagram (Pg, 1015 g).

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heterotrophic respiration, but also through that of autotrophs, the bulk of primary marine production is returned to the atmosphere as CO_2 on short time scales ranging from minutes to years. This is one reason why the biological pump plays a smaller role than the physical pump in the annual cycle of carbon, the latter being responsible for more than 90% of the carbon annually swept along in the oceans by CO_2 dissolution in surface water and subduction during the formation of intermediate and deep water. However, the carbon carried away by the physical pump will not be permanently sequestered, as the return of the deep water to the surface by the global thermohaline circulation will release it again to the atmosphere as CO_2, on time scales less than 1,200 years. Ultimately, the biological pump will play the key role because, although less than 0.5% of the carbon fixed in surface waters accumulates in deep sediments, it is the only way to isolate carbon over geological time scales.

The biological pump is a set of processes responsible not only for the processing and vertical advection of dissolved organic material, but also for the passive sedimentation flux of particulate organic material and associated biominerals as well as the active transport by the nycthemeral migration of zooplankton. This definition taken from Robinson *et al.* [ROB 10] underlines the unique role played by organisms in the pelagic realm, from bacteria to mesozooplankton. In this book, we will focus on a group of particularly important organisms for the functioning of the biological pump. These organisms represent a functional group of "biomineralizers" using silicon and are therefore dependent on the availability of this element to be able to develop. Several groups of organisms are represented here, but the diatom group is undoubtedly the one that plays the major role. Understanding the mechanisms that will govern the ability of diatoms to use the silicon cycle is therefore essential to understand their role in the biological carbon pump.

Bernard QUÉGUINER
April 2016

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1

The Chemical Forms of Silicon in the Marine Domain

1.1. The element "silicon"

Silicon (symbol Si, atomic number 14) is not found in its native state[1], but in the form of silicates it is the most abundant element in the Earth's surface (about 28%), after oxygen. Its name comes from the Latin word *silex*, meaning stone. Lavoisier had suspected its existence in 1787, but it was not until 1811 that it was discovered by Gay-Lussac and Thénard. In 1823, Berzelius isolated silicon in a sufficient state of purity to be able to approach its study. Natural silicon is a metalloid that actually corresponds to a mixture of three stable isotopes.

Isotope	Atomic mass	Abundance (% atoms)
^{28}Si	279,769,265,325	92,223
^{29}Si	28,976,494,700	4,685
^{30}Si	2,997,377,017	3,092

Table 1.1. *Natural atomic masses and abundances of three stable isotopes of silicon [HAY 16]. The weighted average atomic mass of natural silicon is equal to 28.08549871*

1 Several chemical methods, however, are used to prepare elemental silicon, particularly from the reduction of SiO_2 at very high temperatures (~2000°C).

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The silicon element also presents 20 radioactive isotopes [AUD 03]; the most frequently reported (and used) in biogeochemistry are ^{31}Si, with a period of 2.62 h (transmitter β^-, maximum energy of 1.49 Mev), and ^{32}Si, known as a cosmogenic isotope, with a period of 132 years (transmitter β^-, maximum energy of 0.22 Mev).

1.2. Orthosilicic acid

Dissolved silicon in seawater is present in various chemical forms, eventually available to living organisms. The most abundant form is orthosilicic acid, which has the molecular formula H_4SiO_4 and is a tetraprotonated acid. The four protons in aqueous solution may be successively released during the formation of a series of monosilicate anions: $H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSiO_4^{3-}$ and SiO_4^{4-}.

In an aqueous saline solution at room temperature, the major forms of orthosilicic acid are H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, and other anions can be overlooked [ING 78]. At a pH value close to that of seawater, only the undissociated form and the first deprotonated form may co-exist, the second being largely in the minority.

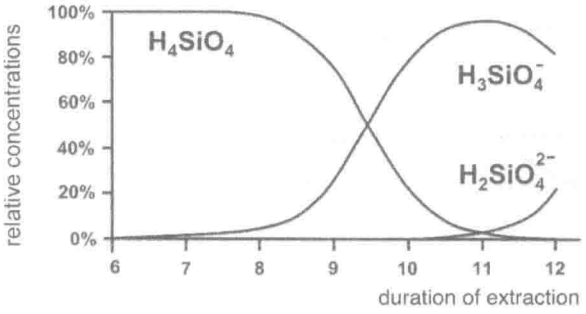

Figure 1.1. *Relative distribution of the majority of the chemically dissolved species of silicon under thermodynamic conditions comparable to seawater (0.6 M NaCl, 25°C) as a function of the pH of the solution*

Thermodynamic constants for acid–base reactions of orthosilicic acid in saline solution (25°C, 0.6 M NaCl salinity, i.e. ≈34.5) were

determined by Sjöberg *et al.* [SJÖ 81]. They allow us to calculate relative concentrations of the different species of orthosilicic acid with the formulation by Riedel and Nelson [RIE 85]:

$$\frac{\left[H_3SiO_4^-\right]\cdot a_{H^+}}{\left[H_4SiO_4\right]} = 10^{-9,47} \qquad [1.1]$$

$$\frac{\left[H_2SiO_4^{2-}\right]\cdot a_{H^+}}{\left[H_3SiO_4^-\right]} = 10^{-12,6} \qquad [1.2]$$

where a_{H^+} is the activity of protons.

The dissolved silicon is equally likely to react with metal cations such as Ca^{2+} and Mg^{2+}. The values of the equilibrium constants determined by Santschi and Schindler [SAN 74] show that for the pH values of seawater and the usual concentrations ($[H_4SiO_4]_{total} \leq 10^{-4}$M; $[Ca^{2+}] \leq 10^{-2}$M; $[Mg^{2+}] \leq 5\ 10^{-2}$M), the complexes formed are quite negligible. However, the possible formation of such complexes under acidic pH must be considered when preparing the stock solutions used in the different incubation experiments (and acidification solutions during purification for the removal of metals may result in the formation of such complexes).

Another aspect of silicon chemistry, which is often overlooked, is the possible formation of complexes with $Fe_{(III)}$. As noted by Ingri [ING 78], these complexes can be present in significant quantities in natural freshwaters and must be taken into account in limnological biogeochemical cycles. In the marine environment, given the low concentrations of mineral iron, the formation of these complexes can be ignored.

1.3. Particulate silicas

The global silicon cycle is governed by the fluxes between dissolved and particulate stocks. The latter is represented by a geological component (the lithogenic silica) and a biogeochemical

component (biogenic silica or opal). As part of this work, we will focus mainly on biogenic silica and biogeochemical exchanges controlled by the biological production processes and the physicochemical process of dissolution from tests of organisms with siliceous walls.

1.3.1. *Lithogenic silica*

The silica contained in rocks and the different forms of silicates that make them up are collectively referred to as lithogenic silica. Given the existence of different crystalline forms, lithogenic silica thus defined has variable physicochemical properties, particularly with respect to the dissolution by basic solvents (including seawater). The geochemical role of silicates is essential because they represent more than 90% by weight of the Earth's crust. These silicates are quasi-regular tetrahedrons of the general formula $(Si, Al)O_4$, the centers of which are occupied by atoms of Si or Al and the tips by O. There are different types of three-dimensional structures, the details of which can be found in books on crystallography. In summary, in tectosilicates, tetrahedra form a three-dimensional framework, $(Si, Al)_xO_{2x}$, wherein each of the oxygen atoms is shared by two tetrahedrons. When the centers of the tetrahedra are all Si atoms, the network, which is electrically neutral, has the formula SiO_2 and corresponds to different forms of lithogenic silica such as quartz, tridymite and cristobalite. If some of the Si atoms are replaced by Al atoms, the structure is a macroanion whose negative charge is compensated by cations, such as in feldspars, feldspathoids or zeolites. Phyllosilicates (micas, chlorites, clay minerals, etc.), which are easily cleavable, are characterized by plane sheets of tetrahedrons associated with three of their tips, wherein the degrees of substitution of silicon by aluminum may vary. Quartz, and its many varieties, is by far the most important species; it is also one of the major minerals of many rocks – especially igneous rocks – which are found in excess (saturation) or deficit in silica. The process of alteration of igneous rocks, however, results in the formation of clay minerals, collectively referred to as aluminosilicates, mainly as phyllosilicates. The

mineralogical composition of these different forms of lithogenic silica will control their susceptibility with respect to the dissolution in the marine environment. The dissolution of lithogenic silica thus has a high variability at the regional level.

1.3.2. *Biogenic silica*

Biogenic silica is the fraction of particulate silica produced by living organisms. It has an amorphous, that is to say non-crystalline, structure in which aluminum atoms can sometimes be substituted for silicon atoms. In biogenic silica, disordered tetrahedra are coordinated with water molecules (Figure 1.2).

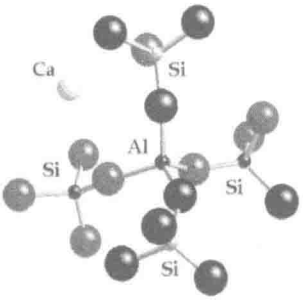

Figure 1.2. *Structural model of biogenic silica. Al enters the network structure while preserving the three-dimensional environment resulting from sharing tetrahedra SiO_4. The substitution of Si^{4+} by Al^{3+} generates a negative charge. Chemical analysis of the diatom frustule suggests charge compensation by Ca^{2+} cations [GEH 02]*

Biogenic silica is a hydrated polymer having a degree of hydration that varies depending on the nature of the material. Hecky *et al.* [HEC 73] indicated that diatoms can produce a range of amorphous silica structures of the general formula (SiO_2, nH_2O). In oceanic sediments, the average formula of biogenic silica is (SiO_2, 0.4 H_2O) according to Mortlock and Froelich [MOR 89]. The degree of hydration of biogenic silica also seems to play an important role in the dissolution processes. Biogenic silica also contains a number of

organic molecules originating from the process of polymerization and mainly composed of proteins and polysaccharides. This organic matter can be preserved in sedimentary opal and represents a material of choice for paleoceanography, especially allowing us to trace the evolution of the isotopic ratios of carbon and nitrogen (e.g. [CRO 02]).

2

Techniques for Studying Stocks and Fluxes

2.1. Techniques for the chemical analysis of silicon

The determination of orthosilicic acid is generally carried out by spectrophotometry according to the colorimetric method of Mullin and Riley [MUL 55], adapted by Strickland and Parsons [STR 72].

Leblanc [LEB 02] conducted a review of the main methods for the determination of particulate silica. The dosage of biogenic silica in the marine environment is relatively recent in oceanography, as it was introduced in the late 1950s by Goldberg [GOL 58]. Early techniques that have been implemented (X-ray diffraction, infrared spectroscopy, digestion with hydrofluoric acid (HF) and colorimetric analysis of orthosilicic acid) were not selective and did not allow us to discriminate between biogenic silica and lithogenic silica.

Several techniques are available today, according to the type of material being looked at: filtered samples on 0.6 micron porosity polycarbonate membrane (for samples of the water column and some sediment traps, including drifting traps) or concentrated samples after lyophilization (for sediment samples or some benthic sediment traps, including fixed traps deployed for long periods).

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