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The Biogeochemical Cycle of Silicon in the Ocean

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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).

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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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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