



How does the ocean acquire its chemical composition?

Over the geological era, the chemical state of the ocean determines its ability to absorb atmospheric carbon dioxide gas, and therefore to contribute to the Earth climate regulation. Its state depends on the balance between sources and departures of any element delivered to the ocean, both terms extremely difficult and complex to quantify. This article reviews the state of knowledge on dissolved and particulate contributions to the ocean issued from the land-ocean interface (continental flux) on one hand and from the oceanic crust – ocean interface (hydrothermal flux) on the other hand.

GET IN TOUCH WITH THE OCEAN

Over the last 150 years, the concentration of carbon dioxide gas has increased exponentially due to human activities, leading to global warming. At present, the ocean is able to sequester 25% of the annual anthropogenic carbon dioxide flux. Its potential as a sink depends on its chemical state on a global scale. However, the ocean exchanges continuously heat and matter with its surrounding superficial terrestrial envelopes, which are the atmosphere, the polar ice sheets and the continental and oceanic crusts. These exchanges highlight the crucial role played by the ocean in our environment. The characterization and the quantification of these exchanges remain, nevertheless, a major challenge for oceanographers.

Geochemistry may provide important answers on the nature of these exchanges. The chemical composition of the ocean reflects the balance of element budget between 1) inputs – “sources” from continental weathering, atmosphere-ocean interaction, hydrothermal reactions at the ocea-

nic crust – ocean interface and anthropogenic sources, and 2) outputs – “sinks” from secondary mineral precipitation, sediment burial, evaporation and biological and physico-chemical processes acting within the water column (Figure 1). The first global marine geochemical budget proposed in the late 1970’s suggested that hydrothermal fluxes were of the same order of magnitude as those issued from the continental sources (Edmonds *et al.*, 1979). Nowadays, the element budget of the ocean is continuously questioned and debated because major progresses have been achieved to observe the natural environment. One of the fundamental missions of oceanographers is to better constrain element fluxes delivered to the ocean and to define their behavior within the marine realm. In other words, it is necessary to fully comprehend global biogeochemical cycles by means of quantifying element fluxes of continental and hydrothermal origin - a step that cannot be ignored to assess response of these cycles to global climate change.



OCEAN MUCH MORE THAN SALTED WATER

Geochemists aim at tracing the transport, dispersal and behavior of each chemical element within the oceanic domain. The ocean is composed of water and salt, which has a relatively homogeneous chemical composition. The salinity of seawater is at about 35 grams per liter of water but may vary from place to place around the globe (10 g/l measured for the Baltic Sea compared to 275 g/l for the Dead Sea). The chemical composition of seawater is dependent upon the mean residence time of each element within the ocean. The oceanic residence time represents the total oceanic inventory of any element divided by its annual flux - whether as sources or sinks - into the ocean. All major elements, which are chemically inert also known as conservative elements, have residence time in the order of millions years - much longer than the 1000 years necessary to mix the entire ocean. In contrast, minor elements whose distribution may be modified by chemical reactions (oxydo-reduction, adsorption, ...) and the biological activity, both acting within the oceanic domain, have residence times spanning from several decades up to several thousand years. These trace element species of seawater become important indicators in our understanding of the chemical composition of the ocean,

simply because their contrasted and distinctive distributions and behaviors witness the processes acting on their distribution. Therefore, by analyzing modern seawater masses as well as geological materials, which faithfully record the isotopic composition of ocean water, it is possible to assess the variation/evolution of element inputs to the ocean both in time and space. Unfortunately, such approach has strong limitation as it is impossible neither to determine the origin of these fluxes, nor to identify potentials mixing and exchanging processes. This hindrance is overcome by combining chemical element abundances with their respective isotopic systems whether derived from natural radioactive decay (Sr, Nd, Hf, Pb) or stable (O, C, N, Li, Cr, Fe, Mo,...).

To summarize, our understanding of global biogeochemical cycles have made significant steps forward over the last few years by corroborating elemental and isotopic approaches to a number of chemical elements displaying distinctive responses to the natural environmental conditions. Among the most recent discoveries, the continental contribution and hydrothermal fluxes are about to be completely re-assessed (Jeandel and Oelkers, 2015; Resing *et al.*, 2015; Chavagnac, 2015).

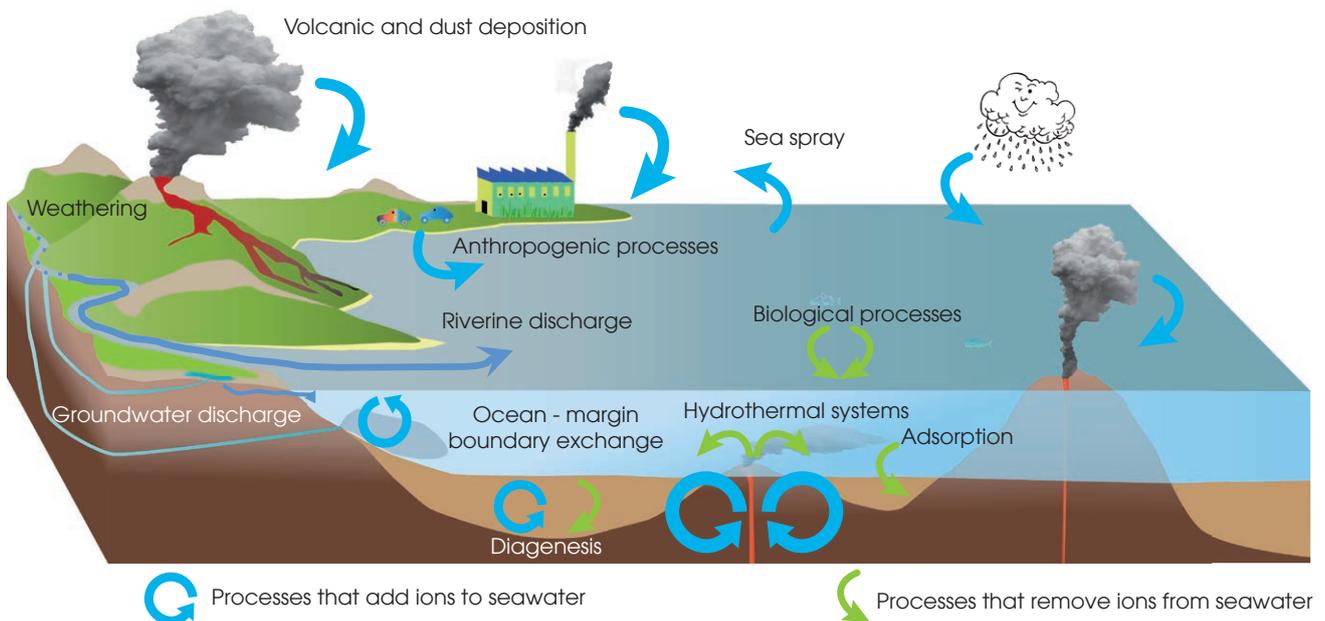


Fig. 1 — Major sources and sinks of chemical elements controlling the chemical composition of the ocean.



FLUXES BETWEEN THE CONTINENTS AND THE OCEANS

Young to old emerged continental surfaces are undergoing modern mechanical and chemical alteration processes. The continental-derived erosion products enter the marine realm either as dissolved phase or particulate matter (organic or mineral) and are transported by winds or rivers. Although the preferential sites of continent-ocean interactions take place along coastal areas, winds and oceanic currents enable the oligotrophic ocean to be widely affected. Until recently, the oceanic elemental budget was based solely on two main types of contributions: dissolved phases of rivers and rainwaters together with a fraction of a few percent (according to the element) due to dust dissolution. This fraction may induce an important but local disruption: for example, export of particulate organic carbon in the Equatorial Atlantic Ocean may be increased by 4 folds during dust storm originating from the Sahara, because surface seawaters are suddenly fertilized by iron – a nutrient element provided by this matter (Chavagnac *et al.*, 2007). However, this type of contribution is sporadic both in time and space, compared to continental shelves and oceanic margins, which are major outlets of eroded matter coming from the continent. Indeed, the fluvial flux of suspended particulate matters is 50 times more important than the atmospheric one (Milliman and Farnsworth, 2011). However, once deposited these sediments undergo chemical reactions, which release chemical elements to seawater whereas others are scavenged or trapped. As a result, sediments act both as a sink and a source of elements or chemical compounds for the open ocean. Determining the net fluxes of element contribution to the ocean is a major challenge, even more difficult to assess as the continent – ocean interface is also the one, which conveys the anthropogenic contributions. The most recent studies suggest that the sediments are an important source of chemical elements such as iron - a source, which is overlooked thus far (Jeandel and Oelkers, 2015; Tagliabue *et al.*, 2014). The recent improvements in our understanding of element fluxes between the continent

and the ocean will have an immediate effect on biogeochemical models, in particular those describing the global carbon cycle. This illustrates how oceanographic research is still alive and still likely to debate.

HYDROTHERMAL FLUXES

Hydrothermal circulation is due to the penetration and percolation into the oceanic crust and deep-sea sediments of seawater. Along its pathway, numerous chemical reactions take place and alter the surrounding rocks leading to the complete conversion of initial seawater into an acid, reduced and hot hydrothermal fluid (up to 410°C). Thus, some of the seawater major elements such as magnesium are stored in the substratum for secondary mineral formation – it is a Mg sink, whereas metallic trace metals (Fe, Mn, Cu, Zn,...) and alkali metals are enriched by several order of magnitude (up to 10⁶) – this is a source. At the seafloor, high temperature hydrothermal fluid mixes with the surrounding deep seawater being neutral, oxygenated and cold, producing the formation of a hydrothermal plume – process giving the nickname of “black smokers” to these systems. A high proportion of hydrothermal dissolved metals fluxes (>90%) precipitate as sulfur, sulfate, poly-metallic and oxy-hydroxide particles, dragging along their way other seawater dissolved trace elements which are absorbed on surface particles (REE, V, P, ...). Besides, the hydrothermal iron source can be detected and traced in the seawater column from its emission site at ridge axis over a distance of more than 4300 km (Resing *et al.*, 2015). Consequently, element balance of the ocean is not as simple as that in terms of sinks and sources. All remain to be determined which key factors – organic or mineral – control the behavior of any elements in the marine domain. Hydrothermal systems of high temperature are located at ridge axis and volcanic arcs. The latter are associated with large underwater volcanoes whose summits may be located a few hundred meters below ocean surface, thereby modifying the chemical composition of the upper most portion of seawater.



Alongside these hot fluid circulations, there is the occurrence of cold fluid circulation (<100°C) within ridge flanks and subducting oceanic plates. Cold hydrothermal fluids exhibit chemical compositions that are drastically different from those of black smokers, as they are basic, enriched in alkali metals but extremely depleted in metallic trace metals. These low-temperature hydrothermal systems are still unknown (geographical extension, temporal variability of chemical fluxes,...) because they do not generate physical and chemical anomalies in the seawater column as do “black smokers”, detectable and traceable by modern oceanographic instruments available to us at present. To detect the occurrence of low-temperature hydrothermal system at the deep-sea is an extremely difficult task to fulfill. Still, these systems may be of fundamental importance to oceanic element budget and global biogeochemical cycles.

In less than 5 decades of research, there has been the discovery of the first manifestations of hydrothermal activity at the deep sea, to that of a wide inventory of phenomena, both at high and low temperature. It is evident that fluid flow in the oceanic crust and marine sediments is a phenomenon of great diversity and acting on a global scale. However, its implications on the chemical composition of the oceanic crust and the ocean remain poorly understood as evidenced by few constraints of heat and mass transfer. For example, it is estimated that the amount of water flowing off ridge axis is 10 to 100 times greater than that associated with hydrothermal systems at ridge axis (Bickle and Elderfield, 2004; Elderfield and Schultz, 1996). A better quantification of hydrothermal fluxes can only be achieved if the characterization of the geometry and motor (tectonic? thermal? other...) of hydrothermal circulation together with the mechanisms of seawater-rock interactions are fully understood.

REFERENCES

- BICKLE M. and ELDERFIELD H. – *Hydrothermal Fluxes in a Global Context*. In *Hydrogeology of the Oceanic Lithosphere*. Eds DAVIS E. and ELDERFIELD H., Cambridge University Press, 677-690, 2004.
- CHAVAGNAC V. – *When the Crusts Meet the Ocean...* Habilitation à Diriger des Recherches, Université de Toulouse, 201pp, 2015.
- CHAVAGNAC V., WANIEK J.J., ATKIN D., MILTON J.A., LEIPE T., GREEN D.R.H., BAHLO R., HAYES T.E.F. and SCHÜLTZ-BULL D.E. – *Source of Lithogenic Derived Element Fluxes to the Deep Subtropical North East Atlantic Ocean*. *Geophysical Research Letters*, 34, L21604, doi:10.1029/2007GL030985, 2007.
- EDMOND J.M., MEASURES C., MAGNUM B., GRANT B., SCLATER F.R., COLLIER R., HUDSON A., GORDON L.I. and CORLISS J.B. – *On the Formation of Metal-Rich Deposits at Ridge Crests*. *Earth Planetary Science Letter*, 46: 19-30, 1979.
- ELDERFIELD H. and SCHULTZ A. – *Mid-Ocean Ridge Hydrothermal Fluxes and the Chemical Composition of the Ocean*. *Annual Review of Earth and Planetary Sciences*, 24: 191-224, 1996.
- JEANDEL C. and OELKERS E.H. – *The Influence of Terrigenous Particulate Material Dissolution on Ocean Chemistry and Global Element Cycles*. *Chemical Geology*, 404 : 41-51, 2015.
- MILLIMAN J.D. and FARNSWORTH K.L. – *River Discharge to the Coastal Ocean. A Global Synthesis*. Cambridge University press. 382 pp, 2011.
- RESING J.A., SEDWICK P.N., GERMAN C.R., JENKINS W.J., MOFFETT J.W., SOHST B.M. and TAGLIABUE A. – *Basin-Scale Transport of Hydrothermal Dissolved Metals across the South Pacific Ocean*. *Nature*, 523(9), doi : 10.1038/nature14577, 2015.
- TAGLIABUE A., WILLIAMS R.G., ROGAN N., ACHTERBERG E.P. and BOYD P.W. – *A Ventilation-Based Framework to Explain the Regeneration-Scavenging Balance of Iron in the Ocean*. *Geophysical Research Letters*, 41, 7227-7236, 2014.