

Chemistry of Biogenic Carbonates and application of LA-ICP-MS

In isotope measurements

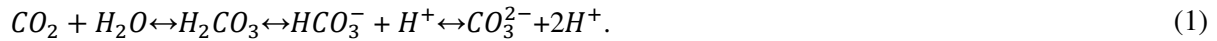
By:

Amin Alibakhshi

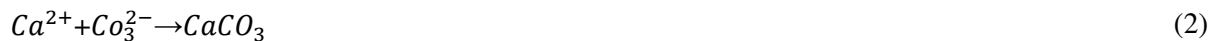
GEOMAR Helmholtz Center of Ocean Research Kiel

aalibakhshi@geomar.de

Calcium carbonate ($CaCO_3$) is used by many marine organisms to construct exo- and endoskeletons and include the main source of marine biogenic carbonates. Biogenic carbonates can record and provide many useful information about the environment in which they are formed. Formation of calcium carbonate which is known as calcification is achieved through transportation of calcium ions and dissolved inorganic carbons by a series of active or passive mechanisms to the calcification sites which are typically located in specialized cellular compartments, tissues, or tissue interfaces. Common dissolved inorganic carbons can be found in the seawater in the form of carbon dioxide (CO_2), bicarbonate ion (HCO_3^-), or carbonate ion (CO_3^{2-}) which their incorporation in calcium carbonate formation can be shown as follows:



Meanwhile, the transport mechanisms for moving the calcium and dissolved inorganic carbons as well as the preferred form of dissolved inorganic carbon is highly diverse among various calcifying organisms which makes it impossible to achieve a general calcification model. The general chemistry of biogenic calcium carbonate formation can be written in the form of:



which as clearly inferred from thermodynamics, influenced by temperature, salinity and pressure, in addition to the concentration of ions. However, Bach [1] showed that calcification can be inhibited by high concentration of proton ions and the calcification rate and the success of calcifying in ocean organisms often is affected by the concentration of carbonate ions (CO_3^{2-}) and carbonate ion dependent $CaCO_3$ saturation state (Ω_{CaCO_3}) which is defined as follows:

$$\Omega_{CaCO_3} = \frac{[Ca^{2+}]_{seawater} [CO_3^{2-}]_{seawater}}{K_{sp}^*}, \quad (3)$$

$$K_{sp}^* = [Ca^{2+}]_{saturated} [CO_3^{2-}]_{saturated}. \quad (4)$$

Bach also showed that HCO_3^- is the main form of dissolved inorganic carbon used in biogenic calcium carbonate formation and is preferred against carbonate ions by marine calcifying organisms.

Solubility of biogenic carbonates is one of the important aspects in studying and reconstruction of past ocean history. Clearly, less soluble carbonates are more preferred due to lower possibility of occurrence of diagenesis. Two main forms of calcium carbonate are calcite and aragonite which have different crystallography and solubility. The presence of magnesium in the crystallographic structure of carbonates seems to play an important role in their solubility. While Bach [1] claimed that aragonite is more soluble than calcite, Bischoff et. al., showed that calcites with inclusions of higher than 8-12 mol % magnesium are more soluble than aragonites and their low Mg counterparts [2]. The kinetic and solubility of biogenic carbonates were elaborately studied by Gehlen et. al. [3] [4]. They studied the [63-150 micron] size fraction of sediments. They reported an average reaction rate of $n=2.3 \pm 0.4$. According to their work, as a result of pressure increase concurrent with temperature decrease, the solubility of calcium carbonates increases with depth. Therefore, aragonite as the more soluble structure, disappears from the sedimentary record at shallower depths compared with calcite.

According to the above considerations, brachiopods due to their low magnesium calcite structure, are one of the most informative and useful ocean organisms in reconstruction of ocean history. Therefore, they are less prone to diagenesis compared with bivalves which are composed of aragonite and/or high magnesium calcite. Parkinson et. al., studied different species of brachiopods [4]. They showed that fibrous secondary or prismatic tertiary shell layers of the articulated Terebratulida and Rhynchonellida species were in oxygen isotopic equilibrium with ambient seawater and therefore can provide records of ocean temperature. However, the primary layer supposed to be affected by the vital effects i.e. all fractionation and changes in isotope ratio of the environment due to biological aspects of the organism. Furthermore, they showed that carbon isotopes composition in all layers is highly affected by vital effects and cannot be a good proxy for the past reconstruction.

As discussed before, biogenic carbonates can provide many useful information about the history of ocean as well as earth. This can be achieved via studying the isotopic concentrations and their ratio in the biogenic carbonate which are briefly introduced in this report.

Temperature reconstruction

Magnesium to calcium ratio is shown to be a good proxy for sea-surface temperature [5]. This elemental ratio increases with temperature increase. As magnesium and calcium both possess long oceanic residence times, their ratio may be considered to be constant over glacial/interglacial timescales. Furthermore, since the concentration of foraminiferal oxygen isotopes which can also provide some information about ambient temperature is highly influenced by the isotopic composition of seawater which is a function of ice volume and local salinity differences, the combination of these two isotopes can provide information about the variations in isotopic composition of seawater over time.

Studying the Mg/Ca ratio in benthic foraminifera from 31 high quality multicore tops by Bryan et. al., revealed a reduction in this proxy with increase in temperature [6]. They attributed this sensitivity reduction to Mg/Ca suppression at high carbonate ion concentration and suggested a modification on this effect by Li/Ca ratio. Temperature reconstruction in biogenic carbonates using lithium and calcium isotopes and their ratio were also studied by Marriot et. al [7]. According to their work, Li fractionation is almost temperature independent and as Li doesn't involve in vital processes, the concentration of this isotope can be a good proxy of the Li concentration in the ambient. Furthermore, they showed that Li/Ca ratio increases as temperature decreases with a sensitivity of 4% per degree centigrade.

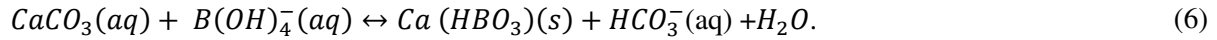
In other works, it has been shown that strontium to calcium ratio in coral, coccolithophores and foraminifera can be a good proxy for sea surface temperature [8]. Marshall et. al. however showed that this proxy doesn't always provide accurate information about the sea surface temperature as can be highly affected by vital effects specially at stress conditions either from a temperature or nutrient viewpoint [9].

pH reconstruction:

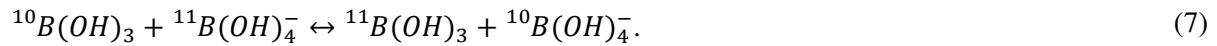
Boron isotopes are the most reliable proxies for the reconstruction of pH [10, 11]. Boron has two dominant aqueous species $B(OH)_3$ and $B(OH)_4^-$ which their relative proportions are controlled by pH as implied from the following relationship:



Borate is supposed to be the primary specie to incorporate into biogenic carbonates as follows:



Furthermore, the distribution of isotopes between the two aqueous species defined via:



has a rate constant of a little greater than unity which means that ^{11}B tends to be enriched in $B(OH)_3$ compared with ^{10}B . Therefore, studying the fractionation of boron isotopes which is pH dependent can provide information about the history of pH.

Brief introduction to LA-ICP-MS [12]

LA-ICP-MS is one of the robust techniques in direct measurement of isotopes ratios and their variation in solid samples. Briefly stated, in LA-ICP-MS a high power laser shut ablates the sample and vaporize and pulverize the atoms at the surface. Then, the generated aerosols are carried using a carrier gas to the inductively coupled plasma (ICP). The ICP converts the sample aerosols to a gas flow of charged ions. It consists of a three layer coaxial tube known as plasma torch and an external radio frequency generator. The gas flowing through the outset layer is called cooling gas which is applied to enhance the cooling of torch wall and avoid its melting. The gas which passes through the second layer is called auxiliary gas which is applied to avoid the contact of plasma with the torch and also to fix the sample gas in the center. The central tube contains sample gas which is the sample aerosols which is carried to the plasma torch.

The last step is measuring isotopes ratios of the generated plasma flow of sample via mass spectrometry and according to their charge to mass ratio.

One of the greatest challenges in the method of LA-ICP-MS is elemental fractionation and matrix effect. Elemental fractionation includes all processes which result in different isotope ratios in the sample compared with the real one in the solid surface. Many aspects can affect the elemental fractionation such as laser power, wavelength and pulse width, type of carrier and washing gas, their ratio and flow rate, power exerted on ICP and so on which should be optimized considering the sample and type of isotopes which are measured. Matrix effect is also measuring different isotope ratios for the sample with the same ratio of those isotopes but different matrices.

Isotope measurement using LA-ICP-MS

Measurement of Sr isotopes variations has been one of the earliest and most widely studied applications of LA-ICP-MS. The methodology of LA-ICP-MS for Sr isotopes measurement is driven by three main factors: (1) attaining high Sr signals, (2) accounting for interfering elements and molecules and (3) minimizing elemental and potential isotopic fractionations generated from the laser ablation process including fractionation effects generated from the laser pit. Ramos et al. demonstrated that relatively accurate $^{87}Sr/^{86}Sr$ ratio can be obtained via LA-ICP-MS, while precision depends on the analyte matrix [13]. They studied the possible isobaric interferences in Sr measurement and methods to modify them.

They showed that the interference of Ca dimmers (e.g. $^{44}\text{Ca } ^{33}\text{Ca}^+$) and Ca argides (e.g. $^{44}\text{Ca } ^{40}\text{Ar}^+$) in Sr isotopes is negligible. They also obtained the same results for Fe oxides (e.g. $^{54}\text{Fe } ^{16}\text{O}_2^+$), Ga and Zn oxides.

For Erbium which is one of the rare earth elements, they showed that the interference can be considerable and must be corrected. Erbium has two isotopes which interferes with Sr measurement: $^{168}\text{Er}^{2+}$ which interferes with ^{84}Sr and $^{170}\text{Er}^{2+}$ which interferes with ^{85}Rb and the later applies to correct interferences of ^{87}Rb contribution to signal of ^{87}Sr . To modify the interference of these isotopes, the intensity of $^{167}\text{Er}^{2+}$ measured at mass 83.5 as well as $^{167}\text{Er}^{2+} / ^{168}\text{Er}^{2+}$ and $^{170}\text{Er}^{2+} / ^{168}\text{Er}^{2+}$ ratios determined on analyzing 1ppm Er solution is applied.

Ytterbium is one of the other interfering doubly charged ions which is modified in the same approach as in Er modification monitoring the isotopes of $^{171}\text{Yb}^{2+}$ and $^{173}\text{Yb}^{2+}$.

Krypton is another element present in Ar pass through the plasma torch and He carrier gas. The interference of Kr can be modified by subtracting the signals observed before firing the laser in the baseline than the observed signal after firing the laser.

Rubidium is of other major source of isobaric interference. To take into account this interference, the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio and the natural $^{85}\text{Rb}/^{87}\text{Rb}$ ratio are measured to calculate a mass bias uncorrected $^{85}\text{Rb}/^{87}\text{Rb}$ ratio. This unbiased ratio is then used in addition to the ^{85}Rb intensity to calculate the ^{87}Rb contribution to mass 87.

Fietzke and Eizenhauer presented bracketing standard method to measure the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio with ppm precision for the first time [14]. They proved the accuracy of the method for the inorganically precipitated aragonite samples prepared under temperature control between 10 and 25 C and also the natural coral samples from a proxy calibration study.

Through a modified measurement and new data reduction strategy using the dynamic responses of the simultaneously collected isotope signals, Fietzke et al. could achieve a reproducibility of 19 ppm for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in carbonates [15]. They observed no interference of doubly charged ions and calcium dimmers as well as for Y and hydrates. They reported 5 times improve in precision in measurement of Sr isotopes ratios through LA-ICP-MS.

In addition to Sr isotopes, Fietzke et al. have reported accurate measurement of Boron isotopes via LA-ICP-MS [16]. Boron has two stable isotopes, ^{10}Br (19.9%) and ^{11}Br (80.1%) and due to its volatility and the high relative mass difference between isotopes (ca. 10%), it can be considerably fractionated in different environments []. The analytical challenges of boron isotope ratio measurement are inability to use double or triple spike methods because it has only two stable isotopes. Furthermore, contamination and lack of an appropriate solid-state matrix standard are other challenges. The novelty of the method they applied was using a 193nm excimer, new data reduction strategy and data collection using Faraday cups instead of multi-ion counting. They showed that on contrary to SIMS method, there is no matrix related offset between soda-lime glass and carbonates through the new method they used. Therefore, soda-lime glass standards were introduced as a new and adequate reference material for boron isotope ratio measurements.

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