# Vital effects in the context of biomineralization

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***Abstract***

Vital effects can be defined as biological processes overriding environmental signals, as recorded in geochemical signatures in biominerals. The nature and influence of these vital effects are poorly understood, particularly related to biogenic mineral formation. The aim of this review article is to highlight the complexity of the study of vital effects in the context of biomineralization. Improving our knowledge of vital effects will greatly contribute to a better interpretation of biogeochemical proxies for paleoenvironmental and paleoclimatic reconstructions, and the fundamental understanding of biomineralization itself.

***Key-words:*** Biogenic Carbonates, Trace Elements, Stable Isotopes, (Paleo-) Thermometry, Synchrotron

## *1. Introduction*

Biologically-controlled mineralization is the biomineralization process used by freshwater and marine invertebrates, including single-celled organisms such as foraminifera, to build up protective exoskeletons. Biogeochemical signals recorded in these biomineral structures, particularly in the case of carbonates, have been a main focus of study in Earth Sciences for more than half century. As biomineralization takes place, organisms record chemical changes in the surrounding environment. Subsequently, biogeochemical proxies can be 'extracted' to reconstruct past changes in environments in which organisms lived based on the fossil record. This idea portrays organisms as 'passive environmental recorders', but these biomineralization processes occur under a strict biological control *(Lowenstam & Weiner, 1989; Weiner & Dove, 2003)*. The influence of this biological control in the recording of environmental parameters, named as 'vital effect', was firstly described in the use of oxygen stable isotopes in biogenic calcium carbonates for (paleo-) thermometry *(Urey et al., 1951)*. Vital effects, therefore, can be defined as biological processes overriding environmental signals, as recorded in geochemical signatures in biominerals (Weiner & Dove, 2003). Almost since its first definition, vital effects has become a 'black box' term to explain any deviations from expected, theoretical / empirical equilibrium, geochemical values related to environmental factors *(e.g. ambient water temperature)*. Some of those deviations can be attributed to 'true' vital effects linked to biological processes, such as metabolism or physiology. However, in many instances, explanations can be directly related to the formation, including nucleation, growth and final emplacement, of biogenic minerals. Traditionally, the recording of environmental chemical signals in abiogenic mineralization has been assumed to be a valid model for biogenic biomineralization. Although biominerals 'meet the criteria for being true minerals' *(Weiner & Dove, 2003; p. 7)*, biomineralization is quite unique and different to inorganic mineralization. Therefore, the interpretation of biogeochemical signatures extracted from biogenic minerals could take in consideration data from inorganic mineralization, but also should be analyzed within the context of biomineralization.

The aim of this article is to analyze some biogeochemical information, frequently used in paleoenvironmental studies, from biogenic calcium carbonate minerals. The main focus of discussion is the biogenic mineral phase itself, including aspects such as crystal size and habit, which could provide a better understanding of vital effect mechanisms *(Weiner & Dove, 2003).*

Few selected examples are used to discuss trace element chemistry (Mg/Ca) and oxygen stable isotopes ($\delta^{18}O$) applied in (paleo-) thermometry, and trends in carbon isotope composition in mollusk shells as an example of the influence of 'true' vital effects. Finally, some outstanding biogeochemical questions in the context of biomineralization are provided to promote discussion and further future research venues.

## 2. Trace Elements

### 2.1. Mg/Ca thermometry: Where is the $Mg^{2+}$?

Organisms with skeletons of biogenic calcite can potentially record ambient seawater temperature via Mg/Ca ratios as in the case of foraminifera *(e.g., Lear et al., 2000; Elderfield & Ganssen, 2000; Lea et al., 2000)*. The use of Mg/Ca ratios represents an alternative to $\delta^{18}O$, and high resolution records can be obtained from different groups of marine invertebrates, such as bivalve molluscs and coralline algae, including ontogenetic series *(Fig. 1)*. Mg/Ca thermometry lies in the fact that the partition coefficient of $Mg^{2+}$ correlates with temperature based on laboratory experiments using inorganic calcite *(e.g., Katz, 1973; Burton & Walter, 1991)*. The principle is related to an increase in $Mg^{2+}$ substituting for $Ca^{2+}$ within the crystal lattice with an increase in temperature. This implies therefore, a thermodynamic process with no biological input. However, biomineralization processes involved in calcite formation occur under biological control, including the mineralogical incorporation of trace elements. In fact, physiological exclusion of magnesium has been reported in organisms that secrete calcium carbonate skeletons such as bivalves (*e.g., Lorens & Bender, 1977, 1980)* and foraminifera *(e.g., Nürnberg et al., 1996; Lea et al., 1999; Erez, 2003)*. Subsequently, this biological control has been related to the vital effects controlling the chemical composition of shells with respect to the use of Mg/Ca ratio as a seawater temperature proxy *(e.g., Klein et al., 1996; Vander Putten et al., 2000; Bentov & Erez, 2005)*.

Despite of numerous studies using Mg/Ca (paleo-) thermometry, the fundamental condition to have magnesium as a lattice component, substituting calcium, is not frequently tested for biogenic carbonates. It is usually assumed that magnesium can only be present in the crystallized mineral phase. Carbonate biomineral structures, however, are composed of strongly associated organic and mineral phases, even at nanoscale level. Thus, magnesium is often present bounded to organic components, such as

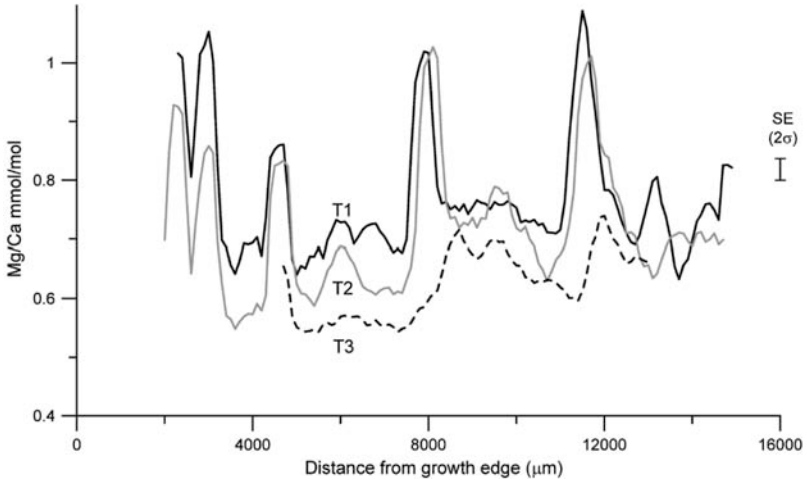


*fig. 1. Example of a high resolution Mg/Ca record, along parallel transects (T1, T2, and T3), throughout the ontogeny of one specimen of the bivalve mollusk Arctica islandica. Reprinted from Chemical Geology, Vol. 254, L.C. Foster, A.A. Finch, N. Allison, C. Andersson, L.J. Clarke, Mg in aragonitic bivalve shells: Seasonal variations and mode of incorporation in Arctica islandica, pp. 113-119, Copyright (2008), with permission from Elsevier.*

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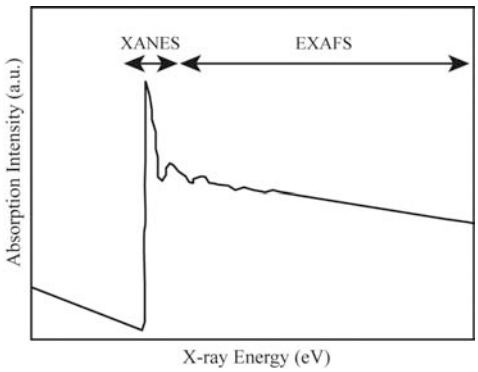


*fig. 2. Diagram illustrating the different regions, XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure), in an idealized synthetic spectrum of X-ray absorption spectroscopy (XAS).*

proteins, involved in biomineralization *(e.g., Tao et al., 2009)*. In addition, magnesium is known to be associated to amorphous calcium carbonate (ACC) as part of its stabilization process (see for example *Addadi et al., 2003; Politi et al., 2010*). On the other hand, testing whether $Mg^{2+}$ substitutes $Ca^{2+}$ in the crystal lattice has been technically challenging until recently. The fundamental understanding of the magnesium chemical environment can be currently resolved with synchrotron radiation sources using X-ray absorption spectroscopy (XAS). Spectra of XAS data can be divided in three regions although the most common used are XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) at higher energies *(Fig. 2)*. For example, a combination of both at the Mg-K-edge has been successfully used to study magnesium in ACC *(Politi et al., 2010)*. In contrast, Mg *K*-edge XANES has been mainly applied for biogenic carbonates. High resolution in situ analyses provide two sources of information for magnesium in terms of the concentration, based on fluorescence maps, and its chemical environment *(Fig. 3)*. Resulting biogenic carbonate Mg *K*-edge XANES spectra are compared with spectra from standards in which the magnesium chemical environment is known *(Fig. 4)*. This fingerprinting approach allows the use of XANES data to detect whether magnesium is likely to be hosted in the crystal lattice. Although this method could prove the validity of Mg/Ca data from biogenic calcite for thermometry, Mg *K*-edge XANES has only been applied to brachiopods and red coralline algae. Previous studies showed that low-Mg calcite shells of brachiopods and high-Mg skeletons of red coralline algae can record ambient seawater temperatures via Mg/Ca ratios *(Pérez-Huerta et al., 2008a; Kamenos et al., 2008)*. Mg *K*-edge XANES analyses in species of both marine invertebrates indicates that the magnesium chemical environment is similar to that of inorganic calcite from limestones indicating the likely $Mg^{2+}$ to $Ca^{2+}$ substitution in the calcite lattice, independently of magnesium

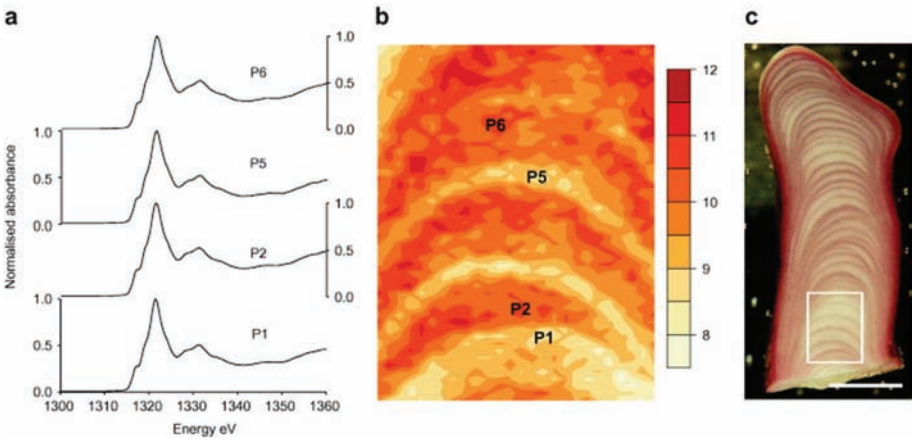


*fig. 3. Mg K-edge XANES data for different regions, corresponding to summer (P2, P6) and winter (P1, P5) growth bands, in the contemporary red coralline alga Lithothamnion glaciale. (a) XANES spectra; (b) magnesium fluorescence map; and (c) region of sample mapped/analyzed (Scale bar = 1 mm). Reprinted from Geochimica et Cosmochimica Acta, Vol. 73, N.A. Kamenos, M. Cusack, T. Huthwelker, P. Lagarde, R.E. Scheibling, Mg-lattice associations in red coralline algae, pp. 1901-1907, Copyright (2009), with permission from Elsevier.*

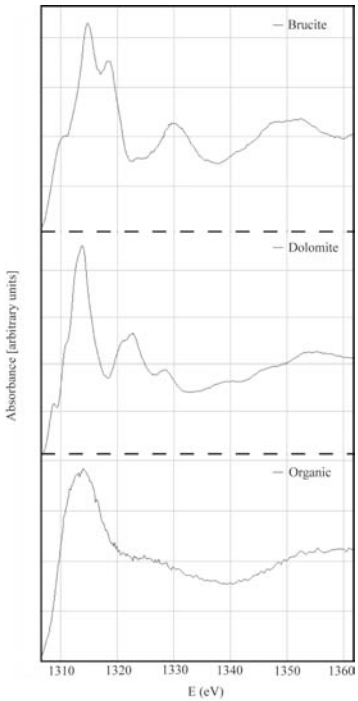


*fig. 4. Example of XANES spectra at Mg K-edge of powdered Mg-bearing standards for brucite (Mg $(OH)_2$), dolomite ($CaMg(CO_3)_2$) and organic material (Mytilus edulis tissue).*

concentrations *(Cusack et al., 2008a; Kamenos et al., 2009)*. A similar approach has been used to determine magnesium chemical environment in aragonitic shell of the bivalve Arctica islandica (*Foster et al., 2008)*. In contrast to findings for biogenic calcite in brachiopods and coralline algae, XANES data indicate that Mg is not hosted in aragonite, but the organic standard was the best fit *(Foster et al. 2008) (Fig. 5)*. Subsequent XAFS analyses showed that $Sr^{2+}$ substitutes $Ca^{2+}$ in aragonite for this bivalve species *(Foster et al. 2009)*. These examples demonstrate how useful synchrotron data can be applied for a correct application of Mg/Ca (paleo-) thermometry in biogenic calcite and aragonite, as well as Sr/Ca. In addition, synchrotron analyses can be carried out to determine the chemical environment of other trace elements, such as manganese and phosphorous, frequently used as (paleo-) environmental proxies *(e.g. Soldati et al., 2010)*. In summary, there is a necessity to develop synchrotron-based studies, and understand their correct application *(e.g. Pérez-Huerta et al., 2008b)*, for a better understanding of biogeochemistry in biominerals.

## 3. Stable Isotopes

### 3. 1 The Oxygen Isotope Fractionation Puzzle

For more than half century it is known that the oxygen isotope composition of carbonate shells ($\delta^{18}O_{shell}$) reflects temperature and oxygen isotopic composition of ambient water ($\delta^{18}O_w$) in which they formed *(Urey et al., 1951; Epstein & Mayeda, 1953; Epstein et al., 1953)*. If $\delta^{18}O_w$ is known,$\delta^{18}O_{shell}$ can be use as a temperature (paleo-) proxy. Based on this principle, several equations have been developed to extract temperature estimates from carbonate shells based on whether calcite or aragonite is the constituent mineral. For example, *Grossman & Ku (1986)* developed an equation to correlate $\delta^{18}O_{shell}$ and temperature that is widely used, including some modifications to its original definition, for aragonitic shells. As a result, high resolution records from carbonate shells can be obtained *(Fig. 6)*, with deviations in $\delta^{18}O_{shell}$ from predicted equilibrium values frequently attributed to vital effects. Related to biomineral structures, the only aspect usually under consideration is whether analyses are preformed in calcite or aragonite in order to apply the corresponding temperature equation. The possibility of having an isotope fractionation related crystal habit, size, and even to different crystallographic planes within the same mineralogy is not usually discussed. *Cusack et al. (2008b)* clearly showed in the mollusk species *Modiolus modiolus* that there is about a 0.4‰ difference in oxygen isotopic composition between aragonite nacre and prisms in the same specimen *(Fig. 7)*. This difference represents approximately 2°C without the involvement of any vital effect. In contrast, some mollusk shells contain several structural layers of the same mineralogical composition, but with some differences that could influence the oxygen isotope composition. For example, the mussel species *Choromytilus chorus* has two outer calcite layers with calcite prisms of different dimensions, and slightly dissimilar morpho-

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logy *(Fig. 8)*. Preliminary oxygen isotope analyses from each layer in the same shell region give average values of -0.3‰ (± 0.1; n = 10) for the outermost layer and -0.59‰ (± 0.1; n = 10) for the inner layer. These results reflect a nearly 0.3‰ difference that represents more than 1ºC using any available equation for calcite, as for example in *Epstein et al. (1953)*. In both examples for two different mussel species, there is an

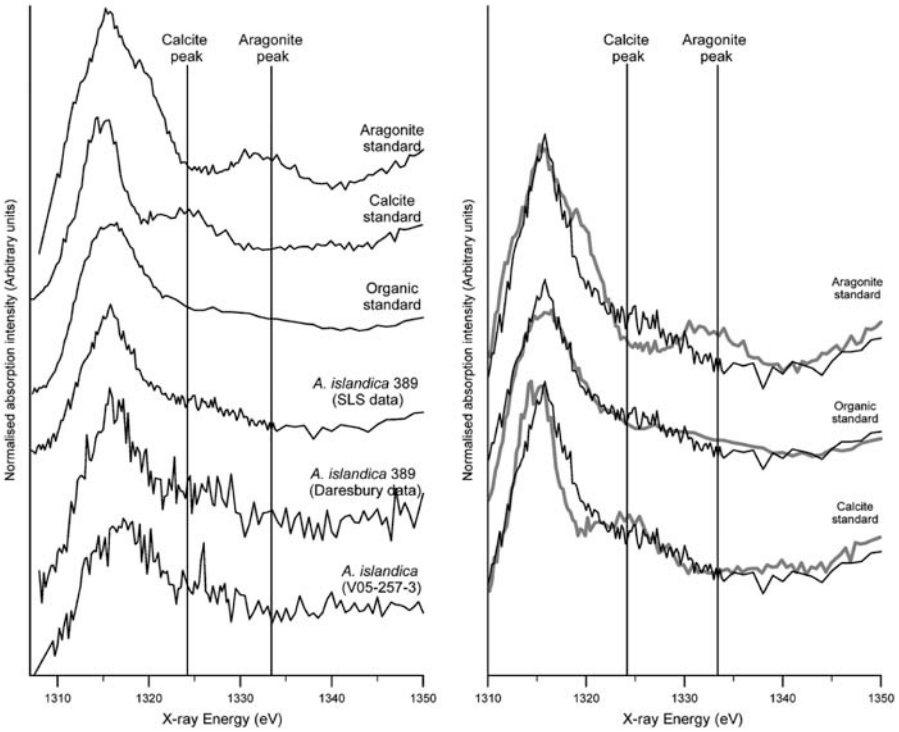


*fig. 5. Left – 'XANES of Mg from two A. islandica samples; V05-257-3, and 389 (data from SLS and Daresbury) together with organic, aragonite and calcite standard (standards from Finch and Allison, 2007). Note that V05-257-3 and 389 show similar spectrum, however the higher signal to noise in 389 measured at SLS reflects the higher beam energy available. Lines are added to identify the characteristic peaks of calcite (1323 eV) and aragonite (1332 eV).' Right – 'XANES of Mg from A. islandica sample 389 collected at SLS compared to organic, aragonite and calcite standard (shown in grey) (standards from Finch and Allison, 2007). Lines are added to identify the characteristic peaks of calcite (1323 eV) and aragonite (1332 eV).' Reprinted from Chemical Geology, Vol. 254, L.C. Foster, A.A. Finch, N. Allison, C. Andersson, L.J. Clarke, Mg in aragonitic bivalve shells: Seasonal variations and mode of incorporation in Arctica islandica, pp. 113-119, Copyright (2008), with permission from Elsevier.*

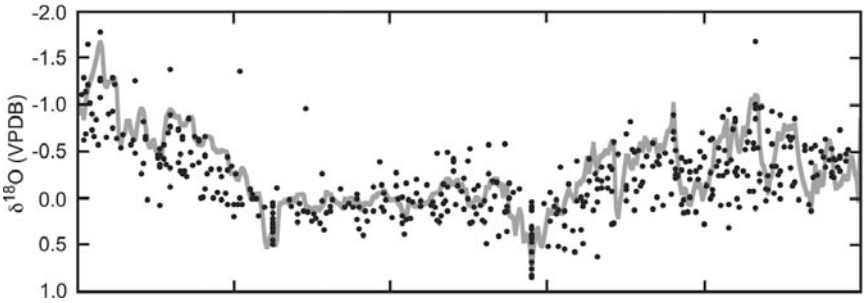


*fig. 6. Example of a high resolution $\delta^{18}O$ record, throughout the ontogeny of specimens of the bivalve mollusk Mytilus californianus. Black points indicate observed $\delta^{18}O_{shell}$ values compared with predicted $\delta^{18}O_{equilibrium\ calcite}$ (gray curve) for almost a complete year. Figure modified and adapted from Fig. 5 (p. 5) in Ford et al. (2010).*

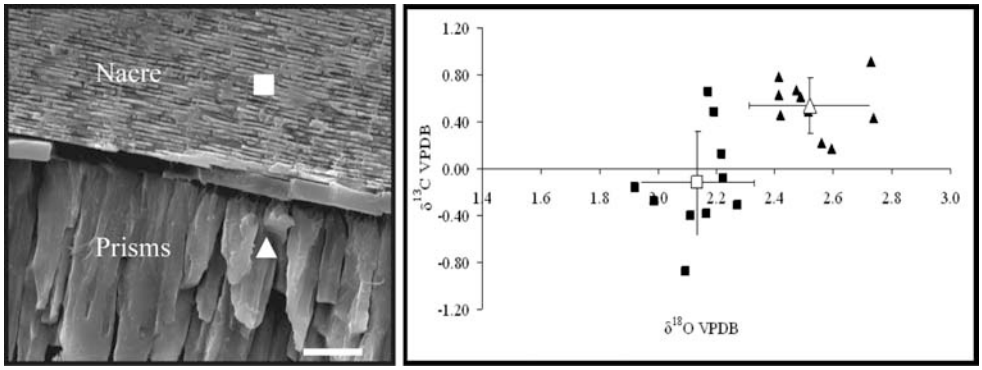


*fig. 7. Left – SEM image of the interface between aragonite nacre (top) and prisms (bottom) [Scale bar = 10 µm] in the shell of Modiolus modiolus; Right - Cross-plot of $\delta^{18}O$ and $\delta^{13}C$ values of nacreous and prismatic aragonite. Filled triangles represent values for prismatic aragonite and the large open triangle indicates the overall mean and standard deviation (1σ) for the prism data. Filled squares represent values for nacreous aragonite and the large open square indicates the overall mean and standard deviation (1σ) for the nacre data. Figure modified and adapted from Figs. 1 and 5 in Cusack et al. (2008b).*

approximate 0.3‰ oxygen isotopic fractionation related to crystal habit or size within the same mineralogy. Available knowledge from experiments on inorganic carbonates is not sufficient to explain these observations. *Tarutani et al. (1969)* proposed that the incorporation of different concentrations of trace elements, such as magnesium, can induce some oxygen isotopic fractionation, although some recent studies for aragonite neglect such an effect *(Kim et al., 2007)*. On the other hand, these experiments are usually carried out with constant pH and ionic concentrations, which could influence fractionation, differing from conditions during biomineralization processes. However, few studies indicate that changes in pH at high values (> 7.5) do not influence the equilibrium aragoni-

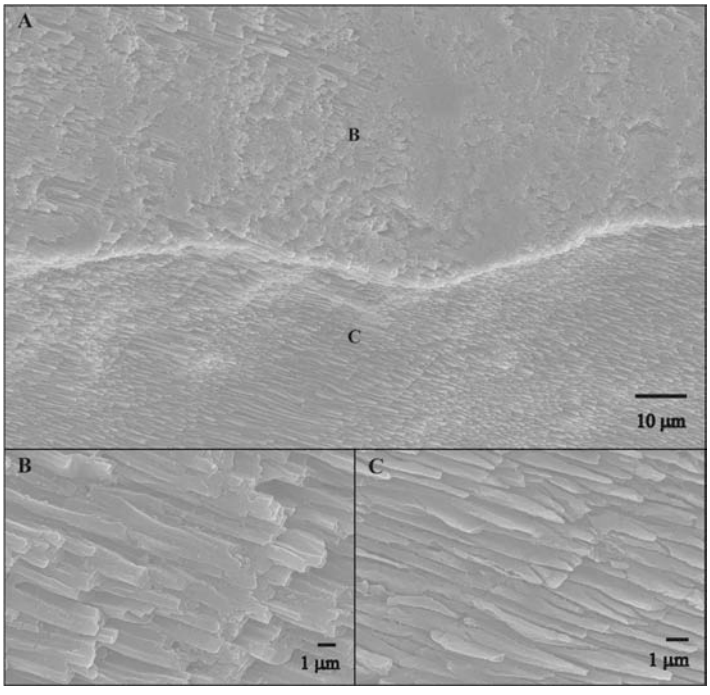


*fig. 8. SEM image of the interface between the two calcite layers in the shell of Choromytilus chorus, showing calcite prisms of different dimensions. Figure courtesy of Christie Jones.*

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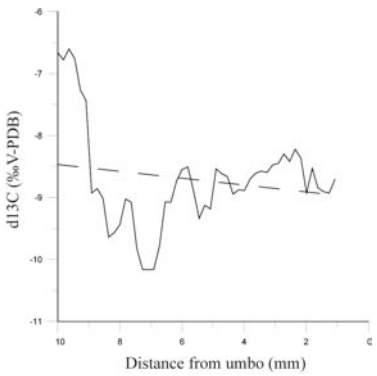


*fig. 9. Example of a negative $\delta^{13}C$ trend throughout the ontogeny of one specimen of the bivalve mollusk Rangia cuneata.*

te – water fractionation *(Kim et al., 2006; 2007)*, but there are not comparable analyses at lower pH and for calcite. Another aspect is that many carbonate biominerals have amorphous calcium carbonate (ACC) as a precursor phase for their formation. This mechanism does not correspond well with a classic carbonate inorganic precipitation and therefore, it is not known whether ACC can contribute to isotope fractionation.

### 3.2. Trends in ontogenetic mollusk $\delta^{13}C$: An example of a 'true' vital effect?

Mollusk shell $\delta^{13}C$ data can provide significant environmental information and important data to understand calcification physiology (see review in McConnaughey & Gillikin, 2008). Recent studies have been focused in understanding how much of $\delta^{13}C$ data reflects environmental dissolved inorganic carbon (DIC), and indirectly its correlation to salinity *(Gillikin et al., 2006)*, in contrast to metabolic carbon (CM) *(e.g., Lorrain et al., 2004; Geist et al., 2005; Poulain et al., 2010)*. Although the exact contribution of metabolic carbon is difficult to estimate, new data suggests a variable contribution of about 10% *(Poulain et al., 2010)*. Such an understanding is a good example of assessing a 'true' vital effect, associated to metabolism. Besides this aspect, trends in $\delta^{13}C$ throughout the ontogeny of mollusk species have been also attributed to vital effects (see *Lorrain et al., 2004)*. Most of the studied species present a negative trend with more negative values in $\delta^{13}C$ correlating with an increase in age *(Fig. 9)*. The presence of a negative trend has been explained in terms of the metabolic effect, although this is independent of apparent seasonal variations in $\delta^{13}C$ (see explanation in *Lorrain et al., 2004*). In contrast, some species present a positive trend throughout the ontogeny. This finding has been attributed to kinetic effects related to growth rates with depletion in $\delta^{13}C$ in shell regions of rapid growth *(McConnaughey 1989; Klein et al., 1996)*. The current understanding of trends in ontogenetic mollusk

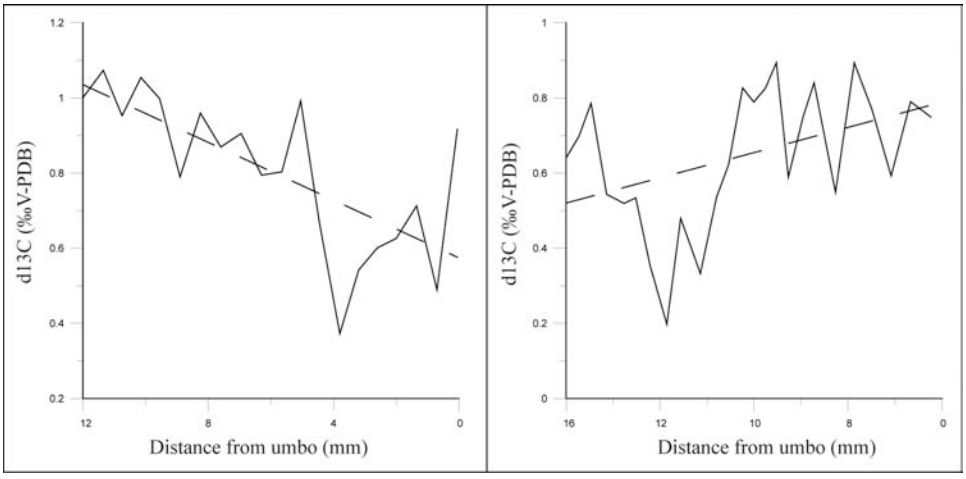


*fig. 10. – Example of two opposite $\delta^{13}C$ trends, negative and positive, throughout the ontogeny of two similar specimens of the bivalve mollusk Donax obesulus, collected from the same locality. Data courtesy of Miguel Etayo-Cadavid.*

$\delta^{13}C$, based on kinetic and metabolic vital effects, do not explain all available data, particularly for sub-fossil shell samples. *Watanabe et al. (2004)* show that there is no $\delta^{13}C$ ontogenetic trend in the giant clam *Tridacna gigas* (6216 years BP), confirming previous results in Recent specimens (Aharon, 1991), and carbon isotope data cannot be explained based on shell growth rate. In addition, new data from archeological samples, collected in Trujillo, northern Peru (± 1400 years BP; 475-539 AD $^{14}C$-dated) of *Donax obesulus* give surprising results. As an example, two shells collected from the same location, and with similar dimensions and age (~14 months), provide opposite trends (negative and positive) in shell $\delta^{13}C$ *(Fig. 10)*. Results in both mollusk sub-fossil species may be indicative of an alteration of shell $\delta^{13}C$ values with diagenesis or differences in specific past environmental DIC. However, further analyses are required to acquire a reliable knowledge of $\delta^{13}C$ distribution and content in mollusks and other organisms.

## 4. Concluding Remarks

The understanding of vital effects in the context of biomineralization is still a relatively unexplored field of study *(Weiner & Dove, 2003)*. This review article provides a first glance at some problems in the current interpretation of geochemical signals extracted from biogenic carbonate minerals. The emphasis is placed on aspects traditionally ascribed to the influence of vital effects but which are not related to biological processes. Few selected examples have been provided for carbonate biominerals, although the same ideas could apply to other biomineral systems used in biogeochemistry, such as silica. In addition to the provided examples, some other biogeochemical questions related to carbonate biogenic minerals are summarized as follows:

• Is $Mg^{2+}$ always hosted in the crystal lattice in biogenic calcite and in organic phases in biogenic aragonite? Does $Sr^{2+}$ represent a true lattice component in biogenic calcite and aragonite?

• To what extend do other trace elements *(e.g. Ba and Mn)* provide reliable environmental information? Are they affected by 'true' vital effects?

• What is the influence of ACC in the recorded biomineral geochemical signal and its relationship to environmental parameters?

• Is sector zoning (see *Reeder & Paquette, 1989*) important in biogenic minerals?

• To what extent can the incorporation of different concentrations of trace elements induce some oxygen isotopic fractionation and influence carbon isotope composition (see *Jiménez-López et al., 2006*)? Is there isotopic fractionation in relation to non-equivalent crystallographic planes of biogenic calcite and aragonite crystals?

• How important is oxygen and carbon isotopic fractionation related to crystal habit and size within the same mineralogy?

• Does oxygen isotope fractionation related to polymorphs in abiogenic carbonates (see *Zheng, 1999*) apply to biogenic counterparts?

• How much of carbonate shell $\delta^{13}C$ distribution and concentration relate to vital effects?

• To what extend are geochemical findings from experiments in abiogenic mineralization applicable to biominerals?

The answer to some of these questions, and in general improving our knowledge of vital effects in the context of biomineralization, will greatly contribute to a better interpretation of biogeochemical proxies for paleoenvironmental and paleoclimatic reconstructions. Furthermore, this knowledge will add important information for the fundamental understanding of biomineralization itself *(Lowenstam & Weiner, 1989; Weiner & Dove, 2003)*.

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