



# Effects of sample pretreatment and external contamination on bivalve shell and Carrara marble $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures



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## ABSTRACT

Stable isotope signatures of bivalve shells serve as important paleoclimate proxies. However, such data can be biased as a consequence of physical and chemical sample pretreatment and contamination during sampling. As yet, the potential isotope error induced by paleontological preservation techniques and specific methods used in bivalve sclerochronology have not been systematically assessed. To address these issues, homogenized powder of a well-preserved, aragonitic fossil shell, *Glycymeris obovata* (ca. 30 Ma old) as well as Carrara marble powder (calcite) were exposed to ultrasound, a set of different staining solutions and cleaning agents. In addition, these reference materials were artificially contaminated with increasing proportions of powder prepared from periostracum, Alcian Blue and cured adhesives. Whereas some treatments (rinsing with Milli-Q water, immersion in Alizarin Red S solution and possibly Mutvei's solution) did not affect the isotope values of the carbonate samples, severe isotope shifts were observed after immersing shell powder in Feigl's solution ( $\Delta\delta^{18}\text{O} = -0.62\%$ ) and mixing Carrara marble powder with Gluetec Metal Epoxy (a contamination level of 41.7 wt% shifted  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values by  $-2.12\%$  and  $-1.74\%$ , respectively). Increasing levels of Metal Epoxy in the sample resulted in a sharp, non-linear decrease of the isotope values. The majority of tested treatments conducted with the carbonate powders and contaminants added to them caused minor to moderate, mainly statistically significant isotope offsets (bleaching with NaOCl and  $\text{H}_2\text{O}_2$ ; exposure to ethyl alcohol and Rewoquat W 3690 PG, a surfactant; ultrasonic cleaning; contamination with powder of Alcian Blue, cured superglue, several different polyepoxies, methacrylates and polyvinyl butyral resins as well as periostracum). In conclusion, pretreatment of bivalve shells with an intended use for isotope analysis should be kept at an absolute minimum and contamination with adhesives etc. should be avoided. Specimens from museum collections that underwent special conservation methods may be of limited value for isotope studies, unless the history of sample treatment is known. Although only a few of the tested substances and methods strongly biased the isotope signatures, even small changes can accumulate to levels that are unacceptable for high-resolution paleoclimatology.

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## 1. Introduction

The stable carbon and oxygen isotope composition of bivalve shells can provide important information on past seasonal to inter-annual climate variability. For example, changes in ambient water temperature are encoded in  $\delta^{18}\text{O}_{\text{shell}}$  values (Williams et al., 1982; Arthur et al., 1983; Wanamaker et al., 2008) and carbon dynamics in  $\delta^{13}\text{C}_{\text{shell}}$  (Mook, 1971; Chauvaud et al., 2011; Schöne et al., 2011). A major prerequisite for isotope-based reconstructions of environmental variables is that pristine isotope signals can be recovered from the shell carbonate, and sample pretreatment, preparation methods and sampling itself do not introduce any bias to the isotope data.

As demonstrated for different carbonates, cleaning procedures, contact with certain organic substances and treatment with dyes can significantly modify the original isotope signatures. To name just a few examples, immersion in formalin, a tissue fixative, shifted the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of foraminifera by up to  $+0.62\%$  and  $+0.80\%$ , respectively, and both isotope values of crushed Solnhofen limestone by ca.  $+0.15\%$  (Ganssen, 1981). In benthic foraminifera, the stain Sudan Black B modified  $\delta^{13}\text{C}$  values by  $+0.24\%$ , whereas hydrogen peroxide and ultrasonic cleaning resulted in a  $\delta^{18}\text{O}$  change of  $-0.18\%$  (Serrano et al., 2008). Furthermore, Grottoli et al. (2005) observed a negative shift of  $\delta^{13}\text{C}$  values of three different coral species after treatment with sodium hypochlorite and hydrogen peroxide. Similar pretreatment-related isotope effects in bivalve shells are much less well studied. In particular, it remains unknown if specimens from museum collections that underwent preservation procedures can still serve as reliable climate archives. For example, partly solidified argillaceous or marly sediments

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