

GEOCHEMICAL AND PETROGRAPHICAL ANALYSES FOR SELECTING QUATERNARY MARINE SHELLS FOR RADIOMETRIC DATING AND PALEOCLIMATE RECONSTRUCTIONS: EXAMPLES FROM PATAGONIA

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ABSTRACT: Consoloni I. *et al.*, *Geochemical and petrographical analyses for selecting Quaternary marine shells for radiometric dating and paleoclimate reconstructions: examples from Patagonia*. (IT ISSN 0394-3356, 2011)

The selection of suitable samples is a fundamental target in order to obtain reliable results in the field of radiometric dating and paleoclimate. Marine molluscs are particularly interesting in this respect in what different radiometric methods (e.g. U/Th, ESR) can be applied coupled with chemical analyses to reconstruct past environment. For this kind of material is imperative that the samples have not undergone any alteration. We present, as example, the study of marine molluscs from Quaternary beach ridges from the Atlantic Patagonian coast. Multiproxy analyses show that the degree of weathering is quite variable but not enough for undermining the paleoclimatic values of the stable isotopes content and of some trace element, but enough severe to make problematic the application of U/Th dating methods. However, the careful petrographic observation and trace element analyses can support the selection of suitable samples for U/Th dating.

RIASSUNTO: Consoloni I. *et al.*, *Analisi geochemiche e petrografiche per la selezione di conchiglie marine quaternarie per datazioni radiometriche e ricostruzioni paleoclimatiche: esempi dalla Patagonia*. (IT ISSN 0394-3356, 2011)

La scelta di campioni rappresentativi è fondamentale per ottenere risultati affidabili nel campo delle datazioni radiometriche e ricostruzioni paleoclimatiche. Questo è particolarmente rilevante quando si vogliono analizzare i resti di molluschi marini che potenzialmente possono essere direttamente datati (per esempio U/Th, ESR) e sugli stessi campioni possono essere effettuate analisi per ricostruzioni paleoambientali. È indispensabile, quindi, che i campioni non abbiano subito alcuna alterazione. In questo lavoro è discusso, a titolo di esempio, lo studio effettuato su dei molluschi marini provenienti dalle formazioni quaternarie marine affioranti sul margine atlantico della Patagonia. Lo studio comparato di molti proxy geochemici permette di concludere che alcune informazioni paleoambientali non sembrano aver subito particolarmente gli effetti dei processi di alterazione subaerea, come la composizione degli isotopi stabili, mentre anche piccoli gradi alterazione rendono difficoltosa l'applicazione del metodo di datazione dell'U/Th. Tuttavia, l'attenta selezione, attraverso lo studio petrografico e geochemico, dei campioni ha permesso di ottenere risultati oltremodo incoraggianti.

Key words: marine Molluscs, geochemistry, Quaternary, paleoclimate, Patagonia, radiometric datings

Parole chiave: Molluschi marini, geochemica, Quaternario, paleoclima, Patagonia, datazioni radiometriche

1. INTRODUCTION

The isotopic and trace element compositions of biogenic carbonates have been used for paleo-environmental and paleoclimate reconstruction for a while for reconstructing temperature, salinity and productivity (e.g. DODD, 1965; MOOK, 1971; KLEIN *et al.*, 1996).

Despite Late Quaternary marine molluscs can be potentially dated with U/Th, so offering a robust chronological support to geochemical proxies, the

applicability of this method is still a challenge owing to the postmortem migration of uranium into mollusc shells (KAUFMAN *et al.*, 1971; 1996).

The selection of well-preserved samples is of paramount importance for obtaining reliable result both in chronology and paleoproxy interpretation.

This work investigates the application of trace elements and petrographical analyses as indicator of preservation state for marine shells collected in the Quaternary coastal marine deposit of the Patagonia Atlantic margin.

2. SAMPLING AND METHODS

Specimens of Upper Pleistocene, Holocene and modern *Protothaca antiqua* (KING, 1832) bivalve shells were selected from S. Jorge gulf (Patagonia, Argentina). *Protothaca antiqua* represents the dominant molluscan species in these deposits. Articulated shells were preferred for the analyses to decrease the possibility to collect reworked shells from older beds. One to six whole shells were analysed for each layer.

After a careful cleaning, one half valve was powdered for geochemical analyses and the other was used for radiometric dating.

The bulk carbonate stable isotopic analyses ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were performed at S.U.E.R.C. (East Kilbride, Scotland) with the AP2003 mass spectrometer equipped with a separate acid injector system, and at I.G.G. – C.N.R. (Pisa) by manual CO_2 extraction after purification with cryogenic traps. Isotopic results were reported using the conventional $\delta\text{‰}$ notation relative to V-PDB.

Shells mineralogy was determined by X-Ray Diffraction (XRD) calibrated with mixture of known quantity of aragonite/calcite ratio.

Inductively coupled plasma mass spectrometry (ICP-MS) was used for trace element measurements.

The U/Th ages were determined using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the School of Earth Sciences at the University of Melbourne (HELLSTROM, 2003).

3. DISCUSSION AND CONCLUSION

Aragonite, forming the shell of these Bivalves, is the least-stable calcium carbonate phase at the Earth's surface and is diagenetically easily

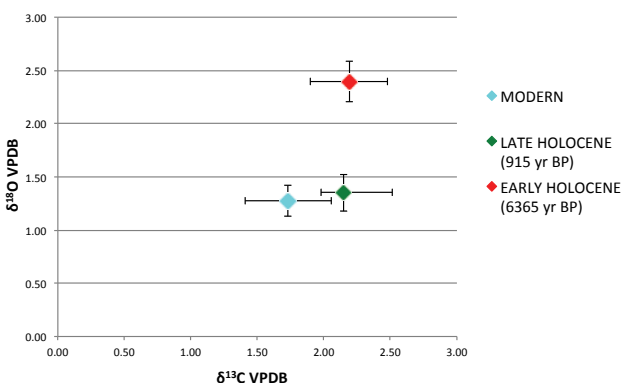


Fig. 1, Isotopic composition of shells of different ages from the same area (Camarones North). The bars represent the variability found on many shells.

Composizione isotopica di bivalvi di età differente provenienti dalla stessa area (Camarones Nord).

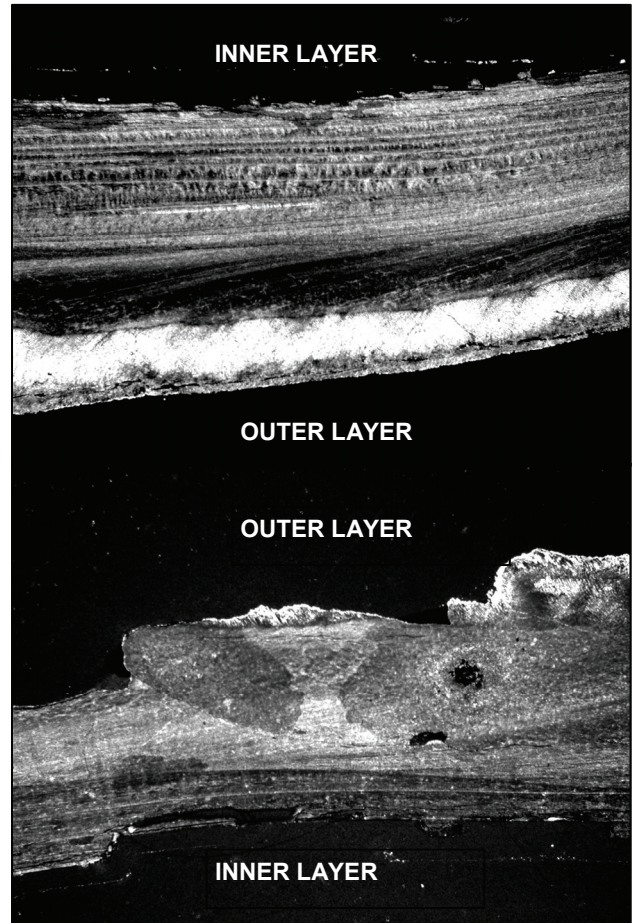


Fig. 2, Thin section of a modern unaltered shells (a) and a Pleistocene altered one (b) (2.5 X Magnification) *Sezione sottile di un bivalve attuale inalterato (a) e uno pleistocenico alterato (b) (Ingrandimento 2.5 X)*

transformed into low-Mg calcite (LAND, 1967; BRAND & VEIZER, 1980; TAKESUE & VAN GEEN; 2004). Mineralogical results from XRD indicate that the pristine aragonite composition was substantially preserved for all the samples analysed, without any calcite alteration.

Manganese content in fossil shells is within the variability of modern specimens concentrations. As the continental waters usually contain about 40 time Mn than seawater (DREVER, 1997), this support the nothing of no shell alternations.

Large variability of isotopic composition of modern shells from different sites of San Jorge gulf suggest that variable in salinity and variable dissolved inorganic carbon sources are responsible of this variability. Samples of different age collected in different places, suggest different trends in isotopic composition, which can be interpreted as substantial different paleoceanographic conditions. Figure 1 illustrates the variation in isotopic composition of shells of different ages from the same area (as examples). This probably can be interpreted as the changes in the relative front position between the warm and

saline Brazilian current and the cold and fresher Malvinas current.

However, other trace elements (including U) indicate that subtle diagenesis can have occurred for some specimens. In particular U concentration shows values higher in older samples (up to 4 ppm) above the values measured on modern specimens. These data suggest that not all the trace elements can be used as palaeoenvironmental tools and specifically U seems to indicate which samples cannot be selected for U/Th. Thin sections of the shells analysed (Fig. 2) show that *P. antiqua* is composed by two well distinct layers, with the outer layer showing the major degree of alteration.

Several samples of *P. antiqua* were then prepared for U/Th dating in a new manner: the inner and the outer surfaces of the shell are abraded and kept only the core of the inner layer.

The comparison between our U/Th from already dated outcrops obtained with others methods (SCHELLMANN & RADTKE, 2000 and refs therein) shows that this approach is particularly promising.

The data discussed stress the fact that the definition of the concept of alteration is related to the proxy we intend to analyse, and for dating (independently of the methods) careful selection of samples is vital.

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