

High Spatial-resolution Assessment of Diagenesis and Primary Isotopic Variability in Maastrichtian Molluscan Carbonates from Antarctica

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The history of Earth's surface environmental conditions is commonly reconstructed from bulk sample analysis of biogenic carbonate archives. These carbonate materials grow within the finite lifespans of individual organisms and record ambient conditions when shell precipitation occurs. Subsequent processes – including dissolution and reprecipitation, recrystallization, and precipitation of secondary domains of carbonate – can alter the original carbonate material and therefore the interpretation of the geochemical proxy (Immenhauser et al., 2016). Commonly, bulk proxy measurements integrate volumes of material ($>10\ \mu\text{g}$ or $\sim 0.004\ \text{mm}^3$) that not only might represent a considerable length of time during the growth of the organism but may also include altered domains. Recent developments in secondary ion mass spectrometry (SIMS) of carbonates allows for the precise measurement of much smaller ng-scale domains ($\sim 10\ \mu\text{m}$ diameter x $1\ \mu\text{m}$ deep pits, Valley & Kita, 2009), which can assist attempts to disentangle the effects of diagenesis and time averaging (e.g. Denny et al., 2020; Linzmeier et al., 2016).

A large temperature increase ($\sim 7^\circ\text{C}$) interpreted from bulk analysis of mollusk carbonates collected in the upper Maastrichtian (Upper Cretaceous) López de Bertodano Formation (Seymour Island, Antarctica) has led to the hypothesis that this interval may be an analogue for understanding high-latitude extinction during global warming events (Tobin et al., 2012). To assess this hypothesis and deconvolve the combined signals of diagenesis, seasonality, and behavior from the stable isotopic composition of mollusk shells, we used a variety of scanning electron microscope (SEM) imaging techniques, electron microprobe elemental mapping, and a CAMECA IMS 1280 SIMS to measure high-resolution ($< 10\ \mu\text{m}$) *in situ* $\delta^{18}\text{O}$ in two ammonites (Maorites), six foraminifera, and one bivalve from the López de Bertodano Formation.

We find that elemental and $\delta^{18}\text{O}$ alteration is confined to areas close to cracks within ammonite shells and shifts of approximately -1‰ are confined to these zones (arrows, Fig. 1). Extensive elemental and isotope exchange with adjacent sediments is not observed, although in some places nacreous microstructure appears degraded. The average $\delta^{18}\text{O}$ of Maorites ammonite shell from all analyses ($-1.1\ \text{‰}$ VPDB) is closer to average benthic $\delta^{18}\text{O}$ values ($-0.7\ \text{‰}$ VPDB, bivalve and foraminifera) than co-occurring planktic ($-3.18\ \text{‰}$ VPDB, foraminifera) $\delta^{18}\text{O}$ values, suggesting that Maorites was generally nekto-benthic in habitat. Variation of 1 to 2‰ across $\delta^{18}\text{O}$ transects within Maorites, however, suggests occasional swimming into shallow water with warmer temperature or lower salinity. Our results support the hypothesis of a high latitude late Maastrichtian warming event because $\delta^{18}\text{O}$ alteration is minimal in these mollusks and, therefore, the warming detected by bulk $\delta^{18}\text{O}$ analysis is likely representative of environmental change. This study highlights the power of *in situ* methods to provide robust tests for the

preservation of primary geochemical signals in mollusk shell material and reveals new environmental and behavioral signals.

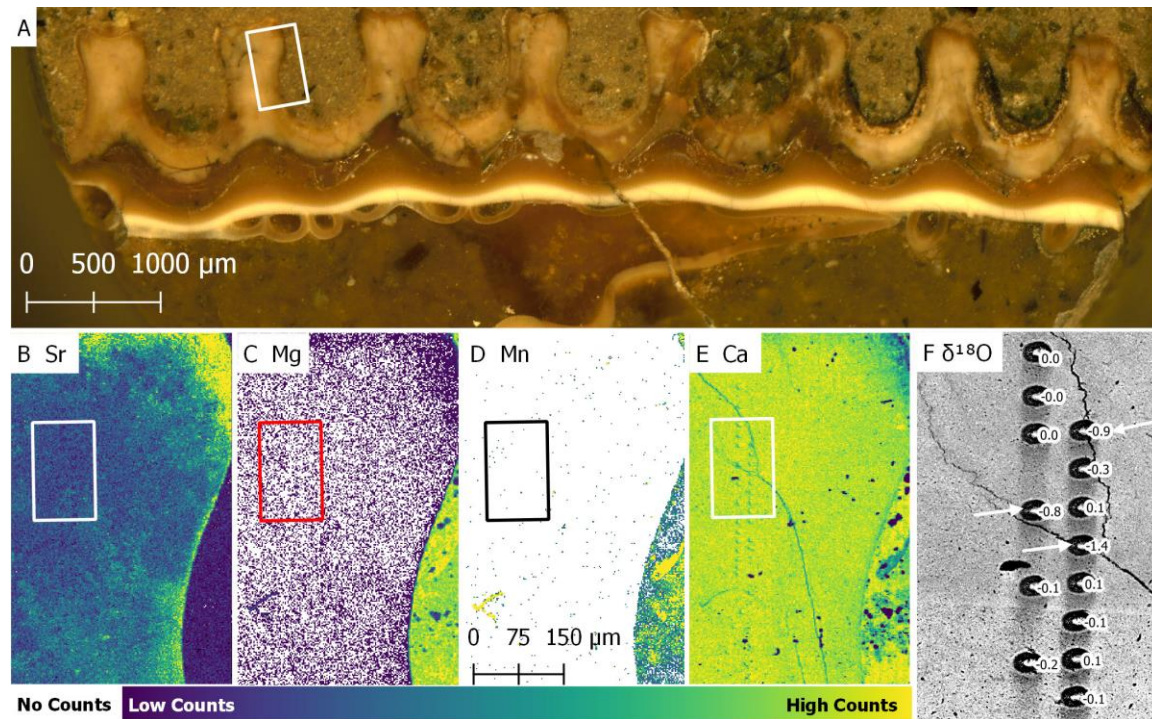


Figure 1. Figure 1. Overview of analyses on a single shell rib of *Maorites ammonite*. A) Overview image of ribs, septum, and sediment around ammonite shell showing area of interest (white box). B–E) EPMA maps of elemental distributions showing difference between shell (majority of image) and sediment (lower right) for most elements. F) BSE image of shell rib and SIMS $\delta^{18}\text{O}$ (‰, VPDB) pit transect. Note anomalous altered values near cracks (arrows). Figure created using QGIS (QGIS Development Team, 2020; Linzmeier et al., 2018).

References

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