

Analytical Methods

Sample preparation and analysis strategy

Sample preparation follows the procedures outlined in the supporting on-line material of Trotter et al (2008). Conodonts extracted from 18 rock samples by conventional acetic acid processing were mounted for SHRIMP analysis. Each mount contained 5 conodonts from each of 7 rock samples, arranged in 5 groups of 7, each around a piece of an in-house gem-quality Durango (#3) reference apatite. This randomised any possible isotope fractionation effects related to sample geometry. The samples were cast in epoxy resin (Struers Epofix) as 35 mm “Megamounts”, then cut and polished to section the specimens using first 1200 grade SiC paper, then 1 μm diamond paste. After cleaning with petroleum spirit and warm detergent solution, the mounts were rinsed in Millipore water, then dried in an oven at 60°C for a minimum of 24 hours before being coated with 12 nm of high purity Al and positioned into the SHRIMP vacuum lock at least 12 hours prior to analysis.

Each sample mount was analysed during a single 24-hour analytical session. Each session consisted of repeated analyses of the Durango 3 standard until stable operating conditions were achieved. The Durango 3 composition of 9.81 ± 0.25 permil is based on bulk analyses of 6 aliquots by Christophe Lécuyer at the Université Claude Bernard (Lyon 1, France) using techniques described by Lécuyer et al. (1998). Then an analysis of each conodont element in each group, analysing the nearest piece of Durango 3 standard after every 4 conodont analyses. When all elements had been analysed once, the cycle was repeated twice resulting in a total of 3 analyses of each element throughout the session. This procedure ensured that, if there was a time-dependent drift in isotope fractionation, the analyses of all elements were equally affected. Both hyaline and albid crown tissues were analysed but no systematic differences were determined.

Three of the samples were represented by only a single species, fourteen by two species, and one by 4 species. Sixteen species in all were analysed, most from two or three different samples, but some from up to four samples. This not only allowed comparison of the compositions measured on different species from the same sample, but also comparison between the compositions measured on the same species from different samples. No species-related differences in isotope composition were evident.

Sensitive High-Resolution Ion Microprobe (SHRIMP) analysis

The samples were analysed using an instrumental configuration and procedures described in detail by Ickert *et al.* (2008). In brief, the RSES *SHRIMP II* was operated in multi-collector negative ion mode. A 15 kV, ~3 nA Cs⁺ primary ion beam was focused to a ~30 µm diameter spot on the target, producing 200–250 pA of secondary ¹⁶O⁻, ¹⁶O⁻ and ¹⁸O⁻ were extracted at 10 kV and measured simultaneously at ~R3000 on Faraday cups in current mode using ANU-built Iflex electrometers. Typical count rates were 3 GHz for ¹⁶O⁻ and 6 MHz for ¹⁸O⁻. Target charging was neutralised using a focused beam of ~350 eV electrons from an oblique-incidence, high-energy electron gun. Analyses were corrected for a small amount of isotopically fractionated electron-induced secondary ion emission (EISIE). Each analysis consisted of a pre-burn of 90 seconds to allow the secondary ion isotopic composition to stabilise and during which baselines were measured, followed by automatic tuning of the secondary ion beam, then 12 10-second estimates of the ¹⁸O/¹⁶O ratio. The beam was retuned after the first 6 estimates, thereby generating two blocks of data measured under slightly different conditions that could be compared for consistency. EISIE was measured before and after each data block.

The data were processed off line using POXI software that took account of any long-term drift in baselines and/or isotopic fractionation. Isotope compositions were calculated by difference relative to the measured composition of the Durango 3 standard assumed, from multiple conventional GIRMS analyses, to have an absolute δ¹⁸O relative to V-SMOW of 9.8 ‰. The standard error of any one analysis, calculated from the reproducibility of the 12 individual estimates of ¹⁸O/¹⁶O, was commonly better than 0.1‰. The standard deviation of the multiple analyses of Durango 3 for a single session (29 to 32 estimates) was, with one exception, 0.20–0.28‰. The exception was the first session, with a standard deviation of 0.42‰.

The mean composition of each element was calculated as the unweighted mean of the three analyses of that element. In very rare cases where one estimate was aberrant, the mean of two analyses was used. The uncertainty assigned to the mean value was the observed standard error of the three estimates, unless it was less than the expected standard error calculated from the standard deviation of the Durango 3 analyses, in which case the latter was used. The five measurements on conodonts from the same sample were then combined to calculate a weighted mean composition for that species from that sample. In the great majority of cases, the five measurements were the same within analytical uncertainty, so the precision of the mean value was that calculated from the individual uncertainties. In the few cases where there was significant scatter, the precision of the mean was calculated

from the standard deviation of the 5 analyses, thereby reflecting the higher uncertainty introduced by the scatter. A final estimate of the accuracy of each weighted mean was obtained by combining the standard error of the 5 analyses with the standard error of the Durango 3 analyses for the session in quadrature and multiplying by 't' to calculate 95% confidence limits.

Possible sensitivity of the calculated $\delta^{18}\text{O}_{\text{apatite}}$ to the mismatch in matrix between Durango apatite and conodont fluorapatite has previously been tested in two ways (Trotter et al., 2008). Firstly, analyses of the two tissue types in individual conodont elements, hyaline (containing CO_3 and PO_4) and albid (containing only PO_4), were compared. No systematic difference between the $^{18}\text{O}/^{16}\text{O}$ ratios measured on the contrasting tissue types was found. Secondly, tooth enameloid from a modern great white shark, *Caracharodon carcharias*, caught offshore South Australia (Cape Jaffa) was analysed as an unknown. The mean composition determined relative to Durango apatite was $23.0 \pm 0.3\text{‰}$, essentially the same as $22.3 \pm 0.3\text{‰}$ measured on the same tooth by conventional GIRMS techniques, and compositions of teeth from the same shark species caught near Durban, South Africa, $22.3\text{--}22.7 \pm 0.2\text{‰}$.

References:

- Ickert, R.B., Hiess, J., Williams, I.S., Holden, P., Ireland, T.R., Lanc, P., Schram, N., Foster, J.J., and Clement, S.W., 2008, Determining high precision, in situ, oxygen isotope ratios with a SHRIMP II: Analyses of MPI-DING silicate-glass reference materials and zircon from contrasting granites: *Chemical Geology*, v. 257, p. 114-128.
- Lécuyer, C., Grandjean, P., Barrat, J-A., Nolvak, J., Emig, C., Paris, F. and Robardet, M. 1998, $\delta^{18}\text{O}$ and REE contents of phosphatic brachiopods: A comparison between modern and lower Paleozoic populations: *Geochimica et Cosmochimica Acta*, v. 62, n. 14, p. 2429-2436.
- Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C., and Nicoll, R.S. 2008, Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry: *Science*, v. 32, p. 550–554.

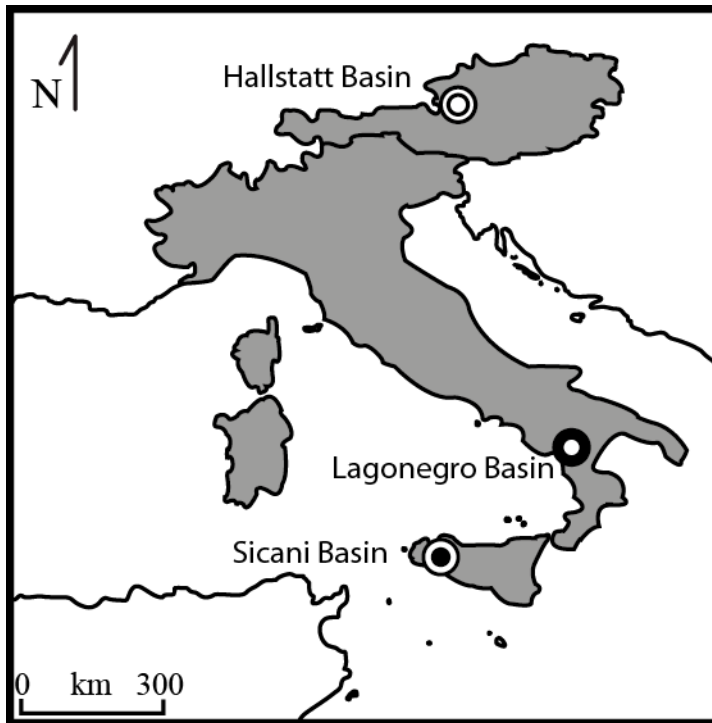


Figure DR1. Location of the study site, the Sicani Basin, and nearby Hallstatt and Lagonegro basins discussed in the text

Geological Facies of the Sicani Basin with Reference to the Hallstatt and Lagonegro Basins Discussed in the Text

While the upper Carnian-Norian cherty limestone facies of the Pizzo Mondello section in the Sicani Basin clearly belongs to a open marine environment (e.g. pelagic radiolarians), the uppermost lower Carnian facies of the Mufara Formation at Pizzo Mondello indicate a shelf environment with high hydraulic energy and intense reworking of shallow water grains (e.g., ooids). This indicates that the Sicani Basin was closer to the continental margin and comparatively shallower than the Lagonegro Basin, where banded chert and siliceous clay were deposited below the Carbonate Compensation Depth (Rigo et al., 2007) during the same period. The sedimentary environment of the Halstatt Basin has been described as a starved periplatform domain with seafloor highs, with the formation of black shales during the latest early Carnian (Hornung and Brandner, 2005).

Microfacies and components of Carnian-lower Norian limestones of the Pizzo Mondello section in the Sicani Basin

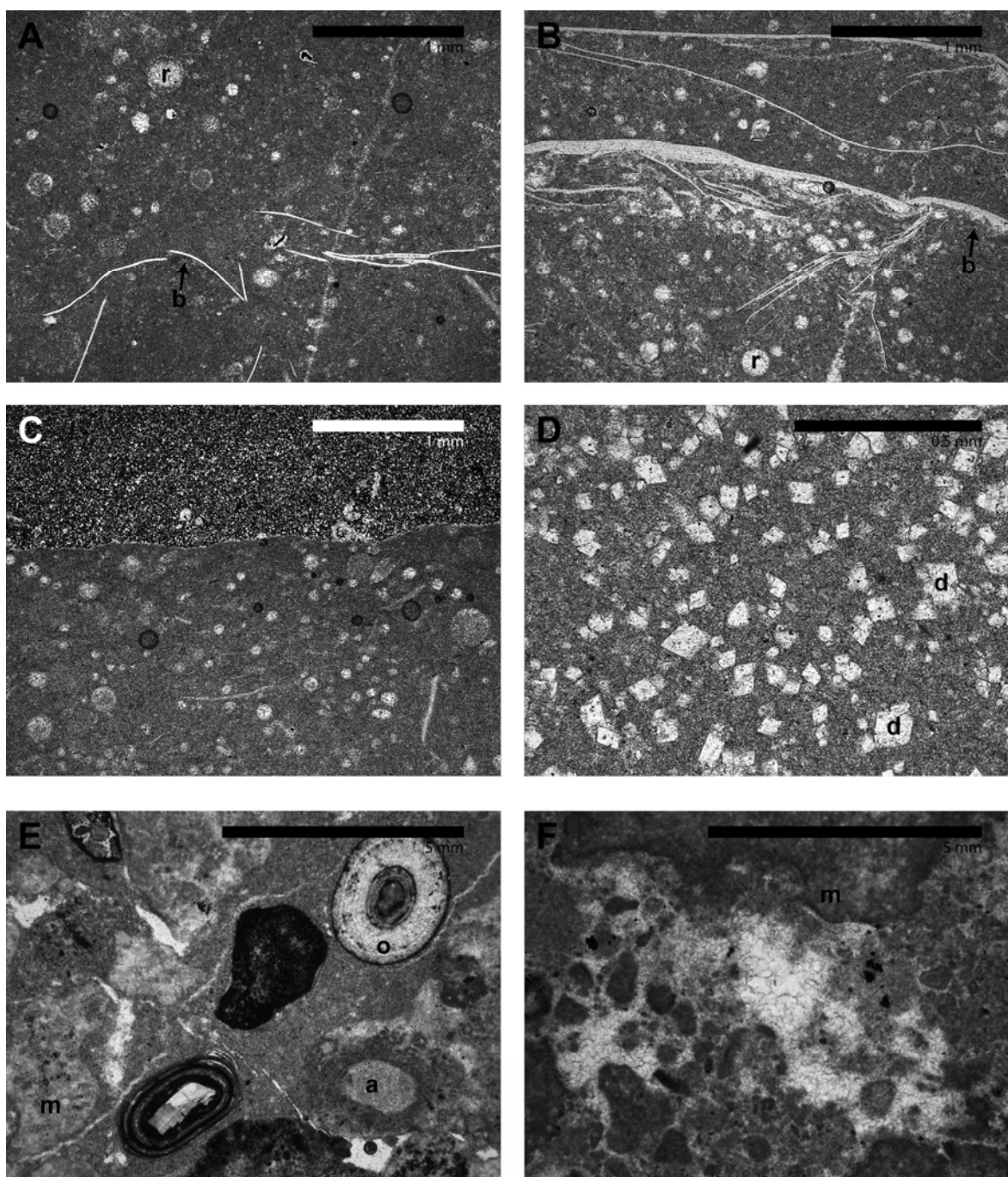


Figure DR2. Microfacies and components of Carnian-lower Norian limestones of the Pizzo Mondello section in the Sicani Basin. From A to D: microfacies of hemipelagic cherty limestones, yielding conodonts; E-F: microfacies of the Mufara Formation, uppermost lower Carnian, cropping out at the base of the Pizzo Mondello section. A: Wackestone with

calcified radiolarians (r) and thin-shelled bivalves (b). **B:** Wackestone-packstone with calcified radiolarians (r) and thin shelled-bivalves, concentrated by mechanical compaction. **C:** Wackestone with abundant calcified radiolarians, part of a chert nodule is visible in the upper part. **D:** Sparse isolated dolomite rhombs (d). Dolomite crystals are common in the cherty limestones of Pizzo Mondello, but do not usually achieve these dimensions and are clearly visible only at high magnification or at SEM. **E:** Rudstone with ooids (o), agglutinated tubes (a) and intraclasts of microbial boundstone with clotted peloidal fabric (m). Blackened grains reflect a high degree of reworking. **F:** Microbial boundstone (m) with primary cavity partially infilled by an internal sediment composed of fragments of microbial boundstone and peloids.

References:

- Hornung, T., and Brandner, R., 2005, Biostratigraphy of the Reingraben Turnover (Hallstatt Facies Belt): local black shale events controlled by the regional tectonics, climatic change and plate tectonics: *Facies*, v. 51, p. 460–479.
- Rigo, M., Preto, N., Roghi, G., Tateo, F., and Mietto, P., 2007, A CCD rise in the Carnian (Upper Triassic) of western Tethys, deep-water equivalent of the Carnian Pluvial Event: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 246, p. 188-205.

Table DR1.

| Species | Sample | d18O | s.e. | Weighted mean d18O | 95% c.i. | Mount |
|-------------------------|--------|------------------|-----------------|-----------------------|----------|-------|
| <i>P. noah</i> | NA19 | 20.69 | 0.19 | 20.96 | 0.29 | 5 |
| | | 21.22 | 0.44 | | | |
| | | 20.93 | 0.16 | | | |
| | | 20.89 | 0.40 | | | |
| | | 21.14 | 0.16 | | | |
| <i>C. pseudodiebeli</i> | NA19 | 21.44 | 0.25 | 21.18 | 0.31 | 5 |
| | | 20.77 | 0.26 | | | |
| | | 21.06 | 0.41 | | | |
| | | 21.16 | 0.16 | | | |
| | | 21.36 | 0.22 | | | |
| <i>C. orchardi</i> | FNP53 | 21.17 | 0.28 | 20.98 | 0.34 | 5 |
| | | 20.56 | 0.16 | | | |
| | | 20.71 | 0.23 | | | |
| | | 21.29 | 0.16 | | | |
| | | 20.74 | 0.16 | | | |
| <i>E. vialovi</i> | NA30 | 21.28 | 0.19 | 21.23 | 0.32 | 5 |
| | | 21.42 | 0.35 | | | |
| | | 21.14 | 0.38 | | | |
| | | 21.28 | 0.19 | | | |
| | | 21.07 | 0.21 | | | |
| <i>P. noah</i> | NA16 | 21.28 | 0.16 | 21.13 | 0.26 | 5 |
| | | 21.00 | 0.16 | | | |
| | | 20.94 | 0.32 | | | |
| | | 21.18 | 0.20 | | | |
| | | 21.13 | 0.16 | | | |
| <i>C. gulloae</i> | NA43 | 20.75 | 0.35 | 21.42 | 0.30 | 5 |
| | | 21.38 | 0.16 | | | |
| | | 21.33 | 0.19 | | | |
| | | 21.59 | 0.20 | | | |
| | | 21.92 | 0.30 | | | |
| <i>N. trinacriae</i> | NA42 | 21.06 | 0.19 | 21.30 | 0.28 | 5 |
| | | 21.03 | 0.23 | | | |
| | | 21.45 | 0.17 | | | |
| | | 21.24 | 0.21 | | | |
| | | 21.59 | 0.19 | | | |