

## Appendix 2:

### SEM, XRD, isotope and Pyrolysis measurement methodologies

#### SEM

Scanning Electron Microscopy was carried out at TNO Environment and Geosciences (Utrecht, the Netherlands) on a MIRA TESCAN electron microscope. We visualized the shell structure by using secondary electron (SE) images. For SEM analysis preparation, a fragment was broken from the shell, fixed in wax and subsequently polished in order to get a smooth cross-sectional surface. Subsequently the samples were coated with gold. The SEM analysis was combined with X-ray-microanalysis allowing simultaneous element analysis.

In order to identify possible internal carbonate transformations (Mangerud, 1972), carbonate compositions was determined using X-ray powder diffraction (XRD). The measurements were carried out at the Department of Inorganic Chemistry and Catalysis, Utrecht University (Utrecht, the Netherlands). All samples were gently ground into powder under ethanol using an agate mortar and pestle to avoid inducing kinetic transformations of aragonite into calcite (Gammage and Glasson, 1976; Dandurand *et al.*, 1982). Pesenti *et al.* (2008) suggested that kinetic transformation could be induced by the grinding period. We tested this for several samples and found only minimal variations in the XRD outcomes (Tab. S1). We therefore used a standard grinding period of 4 minutes in the remainder of the preparations.

#### XRD

XRD analysis was performed on an D8 XRD machine (Bruker AXS, Delft, the Netherlands). The measurements utilised Co-K $\alpha_{1,2}$  radiation ( $d = 1.79026 \text{ \AA}$ ), operated at 30 kV, 45 mA) and a Vântec detector. The scan rate was 366.0 seconds per degree and approximately 50mg of powdered shell was used for each test. The machine detection limit was about 1%. Post processing of the measurement results was done using Rietveld analysis (Rietveld, 1969; Bish & Post, 1993). This procedure involved minimizing the sum of the weighted, squared differences between observed and calculated intensities at every 20 step in a digital powder diffraction pattern.

#### Isotope analysis

$\delta^{13}\text{C}/\delta^{18}$  isotope ratios of all samples were measured on an Isocarb-SIRA-24 combination at the Department of Earth Sciences, Utrecht University (Utrecht, the Netherlands). Sequential acid (102% H<sub>3</sub>PO<sub>4</sub>) digestion in a single acid bath (90°C) was performed on 0.5 to 1.5 mg grinded samples. The produced CO<sub>2</sub> was frozen through a water trap (-85°C melting acetone) and lead into the inlet system of the mass spectrometer and measured versus CO<sub>2</sub> reference gas (dual inlet method). The samples were normalised (drift-corrected) according to laboratory standard Naxos and reported with reference to VPDB.

#### Pyrolysis-gas chromatography-mass spectrometry

The shells were decalcified prior to pyrolysis by shaking the samples with 1 M HCl twice (4 and 12 h). The samples were then rinsed twice with demineralized water, and freeze-dried. Tests showed that the amount of organic C hydrolysed by the HCl treatment was negligible (Van Santvoort *et al.*, 2002). Pyrolysis was carried out on a Horizon Instruments Curie-Point pyrolyser. Samples were heated for 5 s at 600°C. The pyrolysis unit was connected to a Carlo Erba GC8060 gas chromatograph and the products were separated by a fused silica column (Varian, 25 m, 0.25 mm i.d.) coated with CP-Sil5 (film thickness 0.40  $\mu\text{m}$ ). Helium was used as carrier gas. The oven was initially kept at 40°C for 1 min, next it was heated at a rate of 7°C/min to 320°C and maintained at that temperature for 15 min. The column was coupled to a Fisons MD800 mass spectrometer (mass range  $m/z$  45-650, ionization energy 70 eV, cycle time 0.7 s). Identification of the compounds was carried out by their mass spectra using a NIST library or by interpretation of the spectra, by their retention times and/or by comparison with literature data.