Marine bivalve mollusc shell Δ_{47}–temperature calibration using the MIRA mass spectrometer

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A bivalve mollusc shell Δ_{47}–temperature calibration is presented for measurements made on the bespoke MIRA (Multiple Isotopologue Ratio Analyser) mass spectrometer at the University of East Anglia. MIRA is essentially linear, with respect to bulk isotope composition, across a 120‰ range in $\delta^{47}CO_2$ values and does not require application of any pressure baseline (i.e. PBL) correction (e.g. [1]). Δ_{47} values are calculated simply from raw Faraday cup signals, with normalisation onto the absolute reference frame [2], to compensate for scale compression, using an empirical transfer function based on measurements of CO_2 equilibrated with water at 25ºC and CO_2 heated at 1000ºC. Sample gases were prepared by 25ºC offline phosphoric acid reaction, with CO_2 clean-up completed manually via cryogenic transfer through an offline vacuum line consisting of two ca. -115ºC ethanol/liquid nitrogen mix spiral traps and a U-shaped porapak trap held between -20ºC and -30ºC. The porapak trap was heated to ca. 145ºC *in vacuo* between all samples.

Bivalve specimens measured are those investigated by two published studies [3, 4], allowing for comparison of Δ_{47} values between three clumped-isotope laboratories, as well as between sample preparation and mass spectrometric measurement techniques. Δ_{47} data also are presented for an osterich egg shell, with assessment of the veracity of the assumption that such calcite material is precipitated at 38ºC [5]. The MIRA bivalve shell Δ_{47} values and Δ_{47}–temperature calibration also are compared to theoretical predictions for calcium carbonate Δ_{47} dependency on temperature [6].

[1] He *et al*. (2012) *RCMS* **26**, 2837–2853. [2] Dennis *et al*. (2011) *GCA* **75**, 7117–7131. [3] Petrizzo *et al*. (2014) *GCA* **142**, 400–410. [4] Henkes *et al*. (2013) *GCA* **106**, 307–325. [5] Wacker *et al*. (2014) *GCA* **141**, 127–144. [5] Guo *et al*. (2009) *GCA* **73**, 7203–7225.