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Clino core data table

Boron during meteoric diagenesis and its potential implications for Marinoan Snowball Earth δ^{11}B-pH excursions

Joseph A. Stewart[1]*, Marcus Gutjahr[2], Fay Pearce[1], Peter K. Swart[3], and Gavin L. Foster[1]

Clino Core lithology

The sedimentology, stratigraphy, diagenesis, and chronostratigraphy of the Clino core has been extensively described in a series of papers (Eberli, 2000; Ginsburg, 2001; Kenter et al., 2001; Manfrino and Ginsburg, 2001; McNeill et al., 2001; Melim et al., 2001; Swart et al., 2001a; Swart et al., 2001b; Melim et al., 2002). The Clino core was drilled in 1990 on the western margin of Great Bahama Bank (24°36.07' N, 79°10.41' W) in 7.63 m of water (Ginsburg, 2001) penetrating 641.42 m with a recovery of 85%. The core penetrated a series of shallow water carbonates consisting of coralline framestones and boundstones, skeletal grainstones and packstones, peloidal grainstones, and alteration of mudstone to grainstones. These sediments represent deposition in increasing deeper water depths extending from the shallow to deep slope (Kenter et al., 2001) grading into mixed pelagic and carbonate sediments (periplatform sediments). The upper 100 m of the core was punctuated by a series of 10 exposure surfaces, each believed to represent a fall in sea-level (Kievman, 1998) during the late-Pleistocene (note that sampling for this study avoided these exposure surfaces). As a result of such exposure, the upper 120 meters has been pervasively altered by meteoric fluids as evidenced by rapid disappearance of aragonite, the abundance of freshwater cements and dissolved allochems, and highly negative C and O isotope values (Melim et al., 2001). In fact this sequence shows the characteristic stable isotope zones as described by Allan and Matthews (1982). In this interval the δ^{13}C values of the inorganic and organic components are correlated as a result of the colonization of the exposed sediments by terrestrial plants (with negative δ^{13}C values) during sea level lowstands. During these same time periods the carbonate rocks were altered by freshwaters and acquired negative δ^{13}C values as a result of the input of CO_2 derived from the oxidation of organic material (Oehlert, 2014). Between 130 and 220 meters below mud pit (mbmp) the δ^{13}C and δ^{18}O values of the carbonates transition from negative values, characteristic of freshwater alteration, to positive

values typical of those found in unaltered marine sediments or in sediments which have been cemented in the marine phreatic zone (Melim et al., 2004). These sediments contain abundant cements which based on classic petrographic paradigms appear to have formed in freshwater. However, they have positive $\delta^{13}C$ and $\delta^{18}O$ values indicating that formed in the marine phreatic zone (Melim et al., 1995). Below 140 mbmp dolomite becomes a pervasive component of the sediments. In some intervals associated with non-depositional surfaces it rises to concentrations greater than 50% of the sediment (Swart and Melim, 2000).

Analytical techniques

All analytical techniques used in this study were carried out at the University of Southampton and follow the protocols of Foster (2008) and Henehan et al., (2013).

Auxiliary Al/Ca measurements were made during trace element analysis (Thermo Scientific Element 2 ICP-MS) to screen samples of clay contamination. Only samples with Al/Ca ratios less than 200 μmol/mol post-cleaning are considered to be suitably unaffected by clay contamination to be included in discussion (see below).

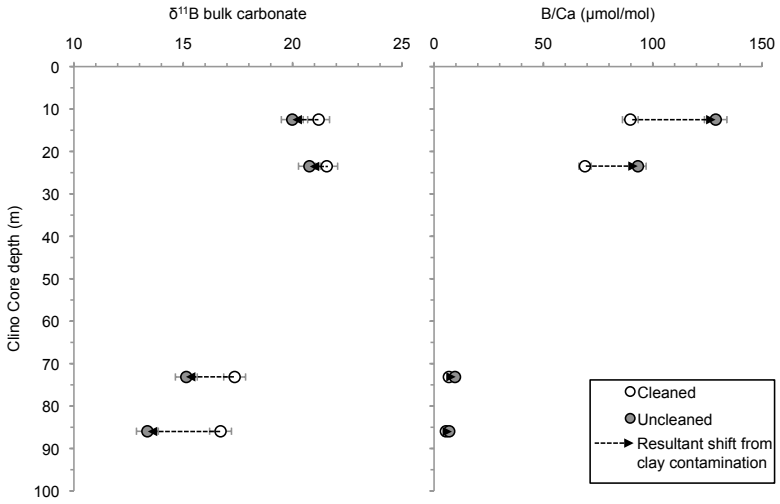
Amberlite IRA 743 boron-specific anionic exchange resin was used to separate sample-boron from matrix elements. All boron must be recovered from columns to avoid fractionation of samples, therefore the elution tails were checked with an extra acid rinse to ensure >99% of sample boron was returned from the columns. The $\delta^{11}B$ of purified boron samples was analysed using Thermo Finnigan Neptune multi-collector (MC)-ICPMS against NIST SRM 951. Following Rae et al., (2011), uncertainty on samples is boron concentration dependant (estimated using from voltage measured on ^{11}B cup) and is calculated as,

$$2\sigma = 2.25e^{-23.01[^{11}B]} + 0.28e^{-0.64[^{11}B]}$$

The total procedural blank measured alongside samples in this study revealed a small blank contribution of ~60 pg of B with a relatively low $\delta^{11}B$ of −1.0‰. A total procedural blank adjustment was not applied to the Clino Core samples because in this case the impact on $\delta^{11}B$ results was minimal (i.e. less than analytical uncertainty).

Detrital clay removal from samples

Clay minerals are relatively enriched in boron (>100 ppm), and often exhibit light isotopic signatures compared to associated with marine carbonates (Palmer et al., 1987; Ishikawa and Nakamura, 1993). Therefore the presence of even minor clay mineral contamination can be extremely detrimental to boron isotope measurements of sedimentary carbonates (e.g. Deyhle and Kopf, 2004). We demonstrate the impact of clay mineral contamination on samples by analyzing split bulk carbonate samples from Clino Core, applying standard mechanical cleaning (detailed above) to remove clay from one powder aliquot and leaving another sub-sample uncleaned. The results of this cleaning experiment are shown in Figure DR1. Samples for which the clay cleaning protocol was omitted yield $\delta^{11}B$ values that are on average 1.9‰ lighter and are associated with B/Ca ratios elevated by >30% compared to corresponding cleaned samples. The absolute magnitudes of these contaminant shifts in boron data are variable between samples and are likely a result of changes in initial clay content of the sample and/or clay mineralogy. The extent to which boron data are influenced by clay contamination highlights the need for diligence during sample cleaning and careful screening of data using Al/Ca ratios to identify samples with clay association.



Supplement: Stewart et al., Boron and meteoric diagenesis…

Figure DR1: $\delta^{11}B$ of carbonate samples cleaned and uncleaned of clay contaminants. Arrows highlight the potential shift in $\delta^{11}B$ and B/Ca caused by inadequate clay removal from samples.

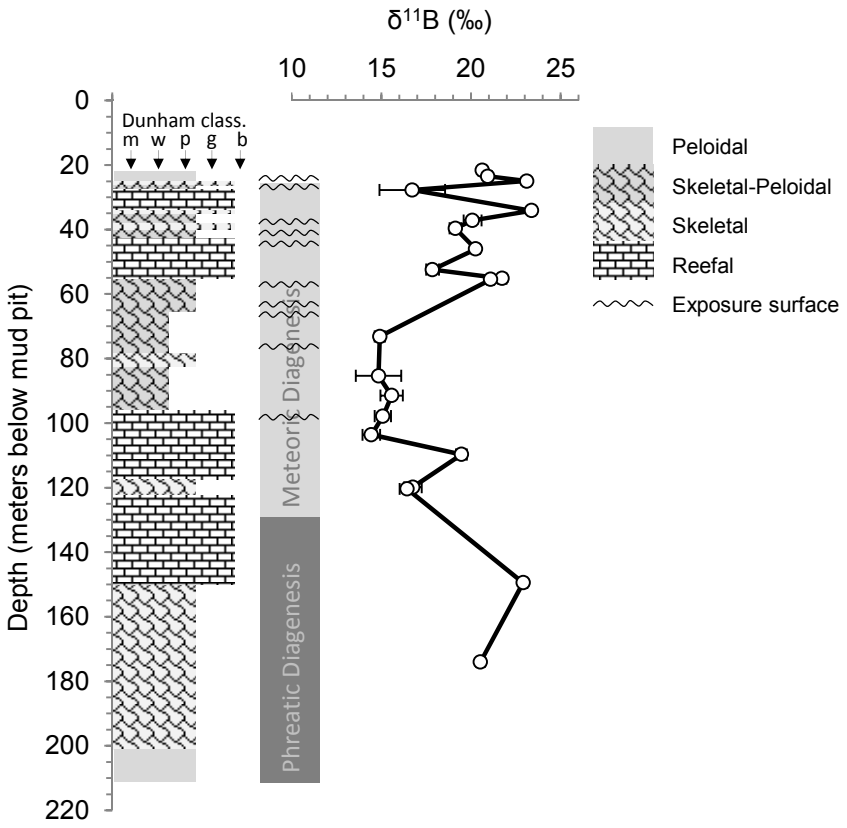

δ11B (‰)
10
15
20
25
0
20
40
60
80
100
120
140
160
180
200
220
Depth (meters below mud pit)
Dunham class.
m w p g b
Meteoric Diagenesis
Phreatic Diagenesis
Peloidal
Skeletal-Peloidal
Skeletal
Reefal
Exposure surface

Table DR1: Bulk carbonate $\delta^{13}C$ (Melim et al., 1995), and paired $\delta^{11}B$ and trace element data (This study) from Clino Core (24°36.07' N, 79°10.41' W; Great Bahama Bank).

Sample Depth (m)	$\delta^{13}C$ (‰)	$\delta^{11}B$ (‰)	±2σ	B/Ca (μmol/mol)	Na/Ca (mmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μmol/mol)	Sr/Ca (mmol/mol)	Mn/Sr (mmol/mol)
12.5	3.79	20.64	0.22	101.2	6.02	5.90	1.56	7.41	0.21
23.5	2.16	20.94	0.22	63.3	3.51	6.55	1.94	4.93	0.39
25.0	-0.79	23.11	0.20	28.4	1.48	22.40	5.11	1.97	2.59
27.7	-0.57	16.72	1.83	2.5	0.25	18.73	21.73	1.57	13.88
34.1	0.46	23.39	0.20	32.0	1.58	17.73	5.42	2.39	2.27
37.2	-0.23	20.09	0.50	11.2	0.70	19.85	5.11	1.84	2.77
39.6	-1.15	19.13	0.32	9.3	0.85	18.31	8.53	1.56	5.48
46.0	-0.46	20.27	0.24	11.4	0.62	9.97	4.26	1.73	2.46
52.4	-0.69	17.86	0.35	6.6	0.44	12.94	6.01	2.07	2.90
55.2	-0.22	21.75	0.23	15.8	0.62	10.44	4.20	2.49	1.69
55.5	-0.86	21.10	0.19	18.0	0.80	10.53	1.72	3.09	0.56
73.2	0.36	14.92	0.29	6.0	0.47	12.15	6.71	1.50	4.47
85.3	-0.09	14.85	1.27	3.8	0.36	15.06	8.31	1.61	5.17
91.4	0.99	15.58	0.62	3.7	0.37	13.99	6.31	1.34	4.71
97.8	0.49	15.09	0.46	4.6	0.29	16.75	11.04	1.20	9.17
103.6	-0.12	14.45	0.49	6.6	0.36	20.97	13.36	1.59	8.43
109.7	-0.27	19.47	0.30	2.8	0.37	17.00	4.68	2.24	2.09
119.9	-0.38	16.76	0.49	5.1	0.47	24.56	13.35	1.71	7.80
120.4	0.67	16.45	0.43	5.1	0.38	22.71	12.67	1.72	7.39
149.5	2.09	22.91	0.23	54.4	1.81	52.08	14.30	2.40	5.96
174.0	2.54	20.53	0.23	43.7	1.54	79.30	14.76	1.33	11.09

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