Supplementary Information:

Marine cements reveal the structure of a ferruginous anoxic Neoproterozoic ocean

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Detailed Methods

Sedimentological analysis and sampling of the Oodnaminta Reef Complex was undertaken in the northern Flinders Ranges, South Australia. Petrologic analysis was undertaken using several hundred polished thin sections. Cathodoluminescence microscopy was carried out on thin sections using a Nuclide ELM2B Cathodoluminoscope attached to a Wild M400 Photomacroscope operating at approximately 8 kilovolts with a 0.6 milliamp beam current. The petrology and cathodoluminescence character of cements was used as a first step in sample selection. Only marine cement samples with sharp, well-preserved cathodoluminescent zonations were selected for LA-ICP-MS analysis. Samples with diffuse zonation, areas of recrystallization, thin carbonate-filled fractures, or non-carbonate inclusions were rejected.

Trace element concentrations were determined via LA-ICP-MS on polished, 100 μm thick sections. LA-ICP-MS analyses were carried out on a Helex 193 nm ArF excimer laser ablation system connected to an Agilent 7700x quadrupole ICP-MS at the School of Earth Sciences, the University of Melbourne. This laser ablation system has been previously, with the ICP-MS tuned to give low oxide levels (ThO/Th <0.25%). (Woodhead et al., 2007). An ablation spot size of 93 μm was used, with a laser repetition rate of 10Hz and 60 seconds ablation time. Samples were analysed in blocks of ~50 analyses, with a NIST SRM612 standard analysed every ~7 samples. Data was reduced by Iolite Software (Paton et al., 2011) using the Trace_Elements Data Reduction Scheme (Woodhead et al., 2007). Outliers were rejected at the ±2 sd level. Calcium was used as an internal standard element, measured by electron microprobe, or assuming stoichiometric concentrations in dolomite. Limits of detection (LOD) for the trace metals (excluding Fe and Cr) range from 10 to 50 ppb, while for the rare earth elements, the LOD are typically in the sub-ppb range. For Cr, LOD is approximately 0.08 ppm or less.

There was some contribution of BaO to Eu in the LA-ICP-MS analyses, contributing slightly to a positive Eu anomaly. However the Ba/Eu levels in the samples are less than ~3000, meaning an overestimate of far less than 5%. As there is no correlation between Eu/Ba and the Eu anomaly in marine cements, Eu anomalies do not appear to be significantly affected by oxide interference (Figure S1.).

Additionally, Ce anomalies are defined as true anomalies using the cross plot developed by Bau and Dulski (1996), (e.g. adapted by Kamber and Webb, 2001)(Figure S2).

Iron analyses were repeated on the same samples using a Cameca SX50 Electron Microprobe at the University of Melbourne with an 80s count time, an accelerating voltage of 15kV, and a beam current of 35nA. The LOD for Fe was around 200 ppm.

Measured Fe concentrations using LA-ICP-MS may be unreliable due to mass interference caused by CaO and ArO. Iron values were systematically lower in the LA-ICP-MS results, than the microprobe. However, relative Fe concentrations co-vary between the two analyses. As electron microprobe Fe values have no analytical problems (other than much higher LOD) these values have been used for the total Fe concentrations stated in this study. Iron values from LA-ICPMS have only been used to compare other matching geochemical data from LA-ICPMS spots.

Error margins for rare earth elements and yttrium are as follows:

Element	2 σ error
Y	0.015687273
La	0.012372727
Ce	0.022758182
Pr	0.004074545
Nd	0.019087273
Sm	0.007710909
Eu	0.001916000
Gd	0.007314545
Tb	0.001062000
Dy	0.005761818
Ho	0.001222364
Er	0.003407273
Tm	0.000615491
Yb	0.003085818
Lu	0.000522747

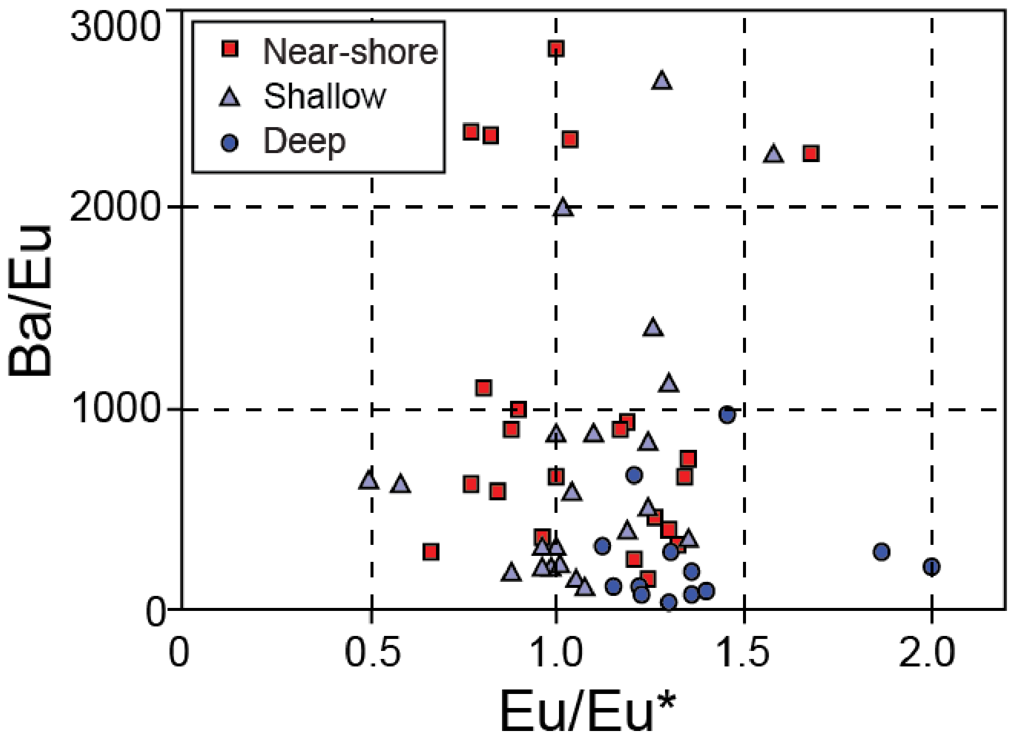

Figure S1. Plot of Eu anomaly vs. Eu/Ba to determine analytical contribution to Eu anomalies (i.e. to define true Eu anomalies). The lack of correlation between the Eu anomaly and Eu/Ba, indicates that there is negligible analytical contribution to positive Eu anomalies, suggesting that they are true anomalies.

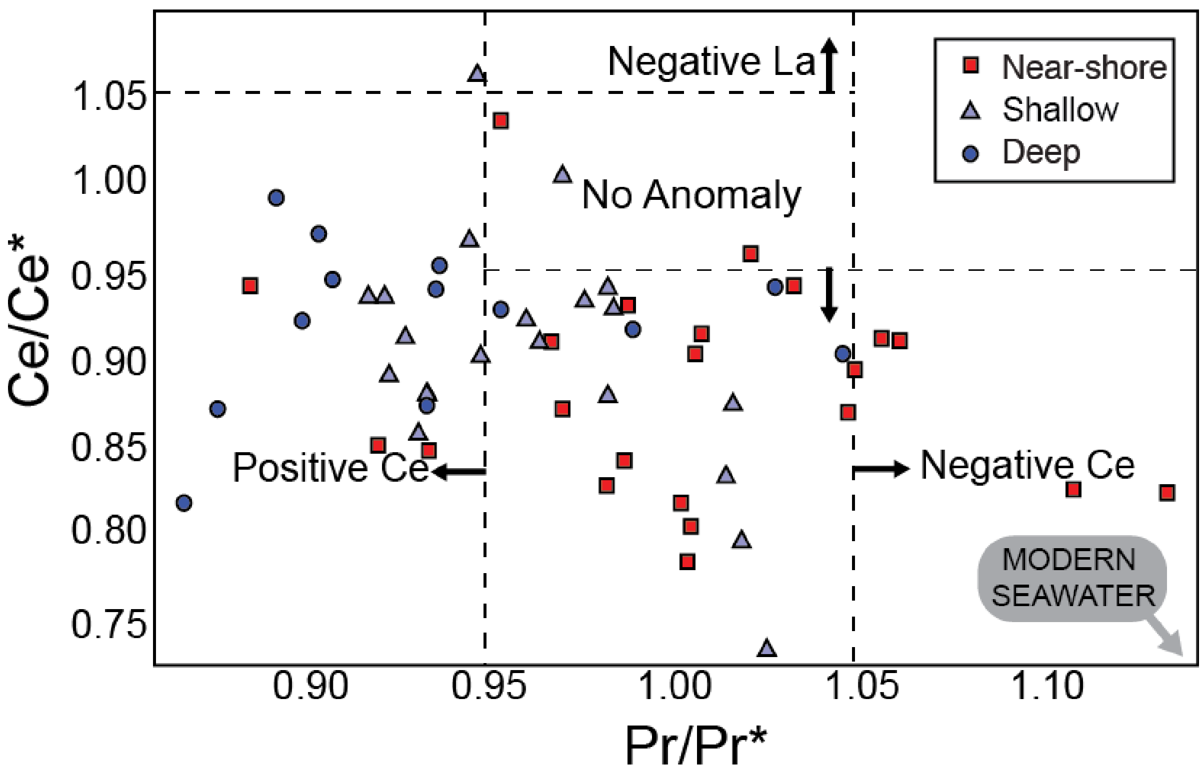

Figure S2. Cross plot of Pr anomalies vs. Ce anomalies, to determine true Ce and La anomalies (adapted after Bau and Dulski, 1996; Kamber and Webb, 2001). Dolomite cements of all depths generally plot in the positive or negligible Ce anomaly fields, with a positive or negligible La anomaly. Modern (carbonate) microbialites and modern seawater plot as indicated in the negative Ce anomaly, positive La anomaly field (Webb and Kamber, 2001).

References

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