

## ECORD Research Grant Final Report

### Ocean temperature and pH estimates from the enigmatic late Paleocene greenhouse; new data from the Indian Ocean

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#### Introduction

Generating paired sea-surface temperature (SST) and marine pH records from past greenhouse worlds, is vitally important if we are to better understand the sensitivity of climate and the carbon-cycle to changes in internal and external forcing in high pCO<sub>2</sub> regimes. In recent years, many studies have attempted to reconstruct the greenhouse climate and oceanic chemistry of the mid-late Paleocene (~59–55.5 Ma) using novel trace metal proxies (e.g. Babila et al., 2016; Penman et al., 2014; Zachos et al., 2003); however, much of this effort has focused on the flagship “hyperthermal” events, such as the Paleocene-Eocene Thermal Maximum (PETM), leaving a distinct lack of absolute temperature or pH estimates for the background greenhouse climate of the Paleocene–Eocene (Fig. 1). This project aims to address this gap in our knowledge by applying the Mg/Ca paleothermometer and B/Ca proxy to exceptionally well-preserved planktic, thermocline-dwelling and benthic foraminifera from the recently drilled (January 2015) International Ocean Discovery Program (IODP) Expedition 353 Site U1443, to generate the first long-term orbital-resolution, absolute SSTs, vertical temperature profile and carbonate chemistry changes of the background climate for this time period from the Indian Ocean.

The Mg/Ca paleothermometer has emerged as one of the most promising techniques for determining absolute temperatures in the deep past and is based on the strong temperature dependence on the substitution of Mg<sup>2+</sup> into biogenic calcite, with secondary effects exerted by salinity and pH of the ocean waters. An exponential positive relationship between Mg/Ca ratios and calcification temperature in foraminiferal calcite has become well established from multiple cultivation experiments, sediment trap and core-top analyses (e.g. Elderfield & Ganssen, 2000; Rosenthal & Linsley, 2006). When applying this proxy to estimate longer term temperature trends in the deep past using extinct species, a number of problems must be overcome, including: species-specific variations in trace metal ratios due to marked vital effects and depth migration through the water column, the preferential dissolution of high-Mg calcite in undersaturated waters, and the evolving Mg/Ca ratio of ocean waters on million year timescales. These problems can be overcome by using a single species from a very narrow size fraction which is known to only occupy one part of the water column during its lifespan, selecting well preserved specimens with minimal recrystallization and no visible diagenetic overgrowths, and selecting a fossil species which has a closely related extant species with an established Mg/Ca-temperature calibration.

B/Ca ratios represent a novel method of estimating changes in ocean chemistry, closely related to pH. Empirical studies have revealed that abundance of the aqueous borate ion (B(OH)<sub>4</sub><sup>-</sup>) correlates positively with seawater pH (Kakahana et al., 1977), and that boron uptake into planktic foraminiferal carbonate is dependent on the concentration of (B(OH)<sub>4</sub><sup>-</sup>), dissolved inorganic carbon and/or bicarbonate (HCO<sub>3</sub><sup>-</sup>), therefore dissolved CO<sub>2</sub> in the oceans (Allen & Hönisch, 2012). Therefore, B/Ca ratios in foraminiferal carbonate should correlate positively with pH of the ocean water. As with all new proxies, there are significant unknowns including the effects of ocean temperature, salinity and carbonate dissolution on foraminiferal B/Ca ratios (Henehan et al., 2015; Coadic et al., 2013).

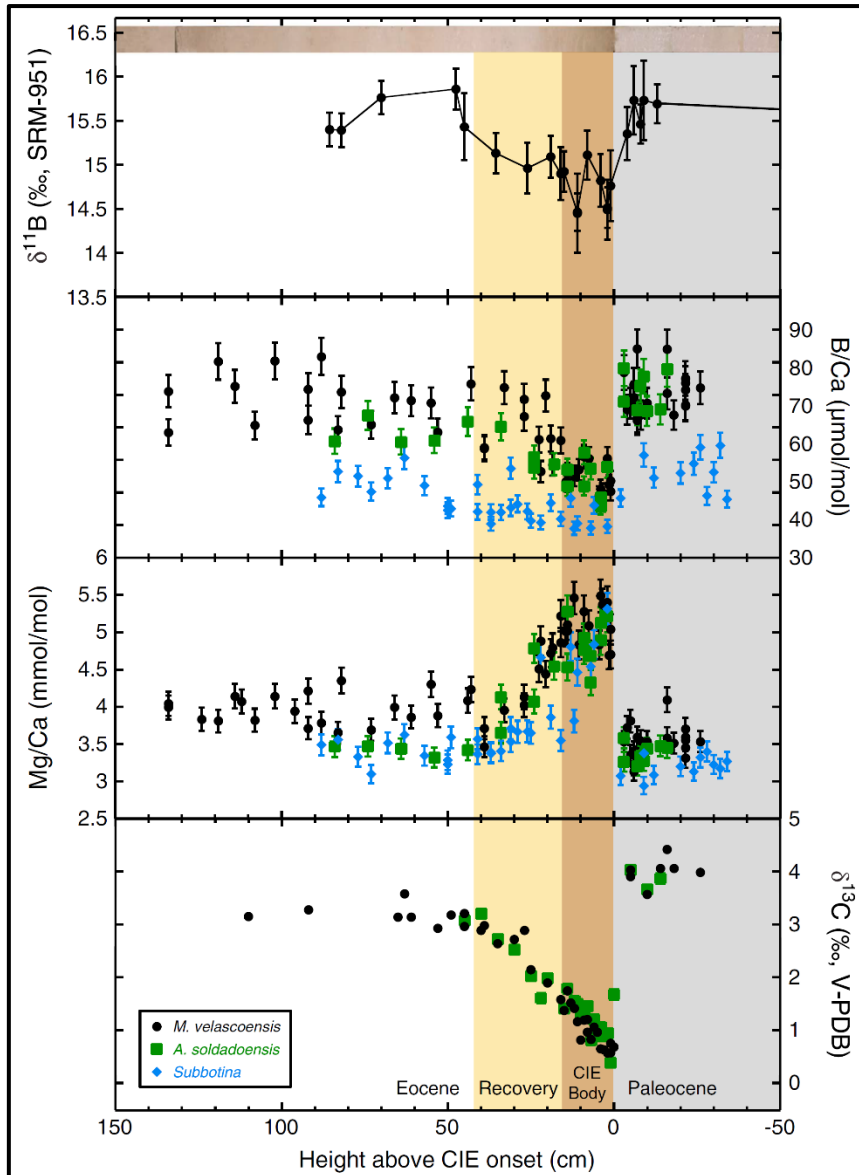


Fig. 1. Application of the Mg/Ca and B/Ca proxies to suggest warming and acidification in the surface waters and at thermocline depths during the PETM (brown shaded interval) from the central Pacific ODP Site 1209 (Penman et al., 2014)

IODP Site U1443 (Ninetyeast Ridge, Indian Ocean) represents an excellent opportunity to test these novel trace metal proxies, where the foraminifera were deposited at a shallow paleo-depth of ~2000m, well above the Paleocene lysocline and Calcite Compensation Depth, and are therefore exceptionally preserved (Fig. 2). The initial plan involved examining temperature and ocean chemistry on orbital (100 kyr and 400 kyr) timescales, however due to a coarser than anticipated sample resolution of 2-11 cm (~5-27 kyr) obtained from the biscuited Paleocene section of the U1443 core, only the 400 kyr cycles are clearly resolvable throughout the record. Once this issue was identified, the primary aim of the project migrated to identifying the longer term trends in temperature and chemistry of the Indian Ocean during the late Paleocene, from the peak of the Paleocene Carbon Isotope Maximum (PCIM, ~57.5 Ma) to the end of the Paleocene, providing a unique insight into how the temperature and chemistry of the oceans evolved in the run up to the PETM (Fig. 3).

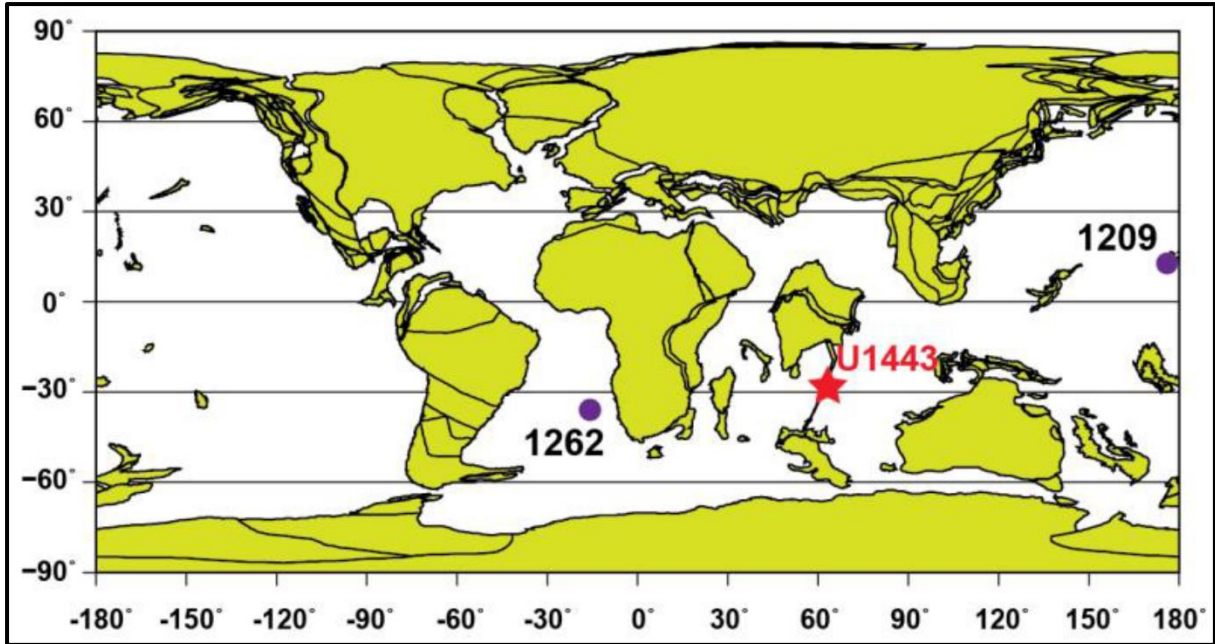


Fig. 2. Location of IODP Site U1443 (Ninetyeast Ridge, Indian Ocean) on a late Paleocene (57 Ma) paleogeographic reconstruction (<http://www.odsn.de/odsn/services/paleomap/paleomap.html>). Locations of ODP Site 1209 and 1262 are also illustrated for reference.

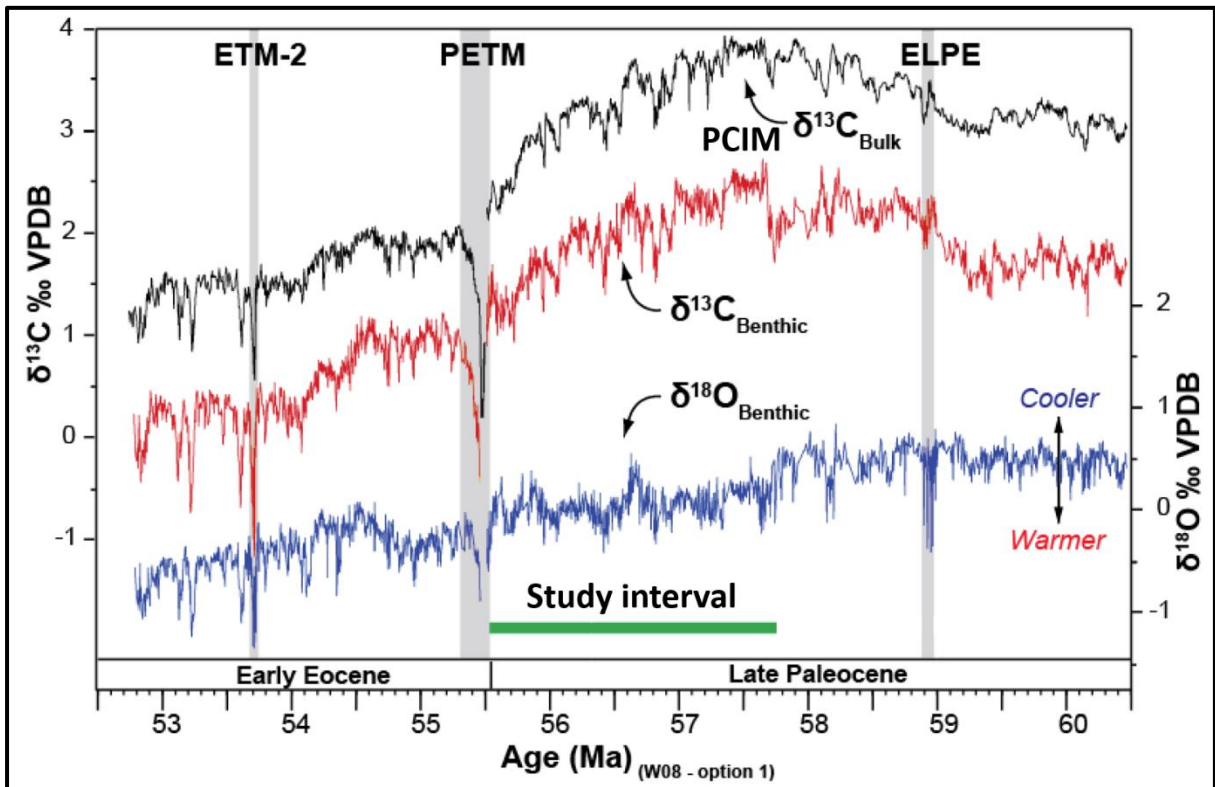


Fig. 3. Benthic and bulk isotope data from ODP Site 1262, plotted against age (Westerhold et al., 2008; Option 1), illustrating the long-term trends in climate and the carbon cycle during the late Paleocene to early Eocene (Littler et al., 2014)

## 2.0. Methodology

165 samples (at 2-11 cm resolution) were collected from the Kochi Core Centre in October 2015 by Dr. Kate Littler and arrived at the Camborne School of Mines, University of Exeter in December 2015.

Firstly,  $\delta^{13}\text{C}$  analyses were performed on the entire sample batch at the NERC Isotope Geosciences Laboratory (NIGL), to determine the orbital stratigraphy and identify where the sample batch sits with respect to the “reference” high-resolution  $\delta^{13}\text{C}$  curve for the late Paleocene from ODP Site 1262 (Littler et al., 2014; Fig. 3).

38 samples were then selected at each major peak and trough in the bulk  $\delta^{13}\text{C}$  record for trace metal analyses. These samples were firstly freeze-dried and then disaggregated in a cold Calgon solution, before being washed through a 63  $\mu\text{m}$  sieve to isolate the >63  $\mu\text{m}$  coarse fraction, containing the foraminifera species of interest. The following species were picked at the Camborne School of Mines under the supervision of Dr. Kate Littler and Dr. Kirsty Edgar (illustrated in Fig. 4):

- The symbiont-bearing, mixed layer dwelling species *Morozovella velascoensis* was picked from the 250-300  $\mu\text{m}$  fraction for sea surface Mg/Ca and B/Ca data. In the younger part of the dataset, *M. velascoensis* became scarce and was replaced by closely related 4-chambered species from the *M. subbotinae-marginodentata* plexus, with some overlap samples
- The thermocline dwelling species *Subbotina velascoensis* was picked from the 212-250  $\mu\text{m}$  fraction for thermocline Mg/Ca and B/Ca data. In the younger part of the dataset, *S. velascoensis* became scarce and was replaced by the closely related coarsely-cancellate species *S. hornibrooki*, with some overlap samples
- The epifaunal benthic species *Nuttallides truempyi* was picked from the >150  $\mu\text{m}$  fraction for bottom water B/Ca data
- The infaunal benthic species *Oridorsalis umbonatus* was picked from the >150  $\mu\text{m}$  fraction for bottom water Mg/Ca data

Foraminifera crushing and strict cleaning protocol were carried out in the trace metal clean lab at the Department of Earth and Planetary Sciences, University of California Santa Cruz (UCSC), under the supervision of Mr. Dustin Harper and Prof. James Zachos during late April-May 2016. The specific cleaning protocol employed at UCSC follows a modified version of the Boyle & Keigwin (1985/86) method, involving: ultrasonic cleaning in boron-clean MilliQ water and methanol to remove clays and fine-grained carbonates, a reductive cleaning procedure in a hot hydrazine/ammonium citrate solution to remove surface ferromanganese contaminants, and a subsequent oxidative cleaning procedure in hot hydrogen peroxide to remove surface organics.

200-800  $\mu\text{g}$  of samples were then dissolved in 350  $\mu\text{l}$  of nitric acid ( $\text{HNO}_3$ ) and run on a Thermo Finnigan Element XR Inductively-Coupled Plasma-Mass Spectrometer at the University of California, Santa Cruz, using the methods of Brown et al. 2011. Larger *Morozovella sp.* samples (>600  $\mu\text{g}$ ) were divided into two and replicate runs were performed. The masses analysed for B/Ca were  $^{11}\text{B}$  and  $^{43}\text{Ca}$ , and for Mg/Ca were  $^{24}\text{Mg}$ , and  $^{43}\text{Ca}$ . Samples containing <40 ppm calcium were considered too small and excluded from the final results, whilst samples with Mn/Ca & Fe/Ca ratios of >100  $\mu\text{mol/mol}$  and Ti/Ca & Zn/Ca ratios of >50  $\mu\text{mol/mol}$  were excluded due to the likelihood of contamination from adsorbed clays, overgrowths or gloves. Solution standards with known elemental composition and blanks were routinely run between samples to check instrument precision, accuracy and consistency.

### 3.0. Results and discussion

Mg/Ca ratios within the tests of the *Morozovella sp.*, *Subbotina sp.* and *Oridorsalis umbonatus* all increase from the PCIM towards the end of the Paleocene on the order of  $\sim 1$  mmol/mol, suggesting a long-term warming trend within the surface waters, at thermocline depths and within the bottom waters respectively. These results are in agreement with high-resolution long-term stable oxygen isotope records for this period, which suggest an overall trend towards progressively lighter isotopic values (e.g. Littler et al., 2014). The long 405 kyr eccentricity cycles, identified as the dominant forcing mechanism of the late Paleocene climate by Littler et al. (2014), can also be identified within the Mg/Ca record, along with a few of the more prominent short 100 kyr eccentricity cycles. Interestingly, there also appears to be a decoupling in the magnitude of warming recorded by the mixed layer and thermocline dwelling species, suggesting a shifting depth of the thermocline during the late Paleocene, changes in the source of thermocline waters towards the end of the Paleocene, or a previously unidentified depth migration of the species analysed.

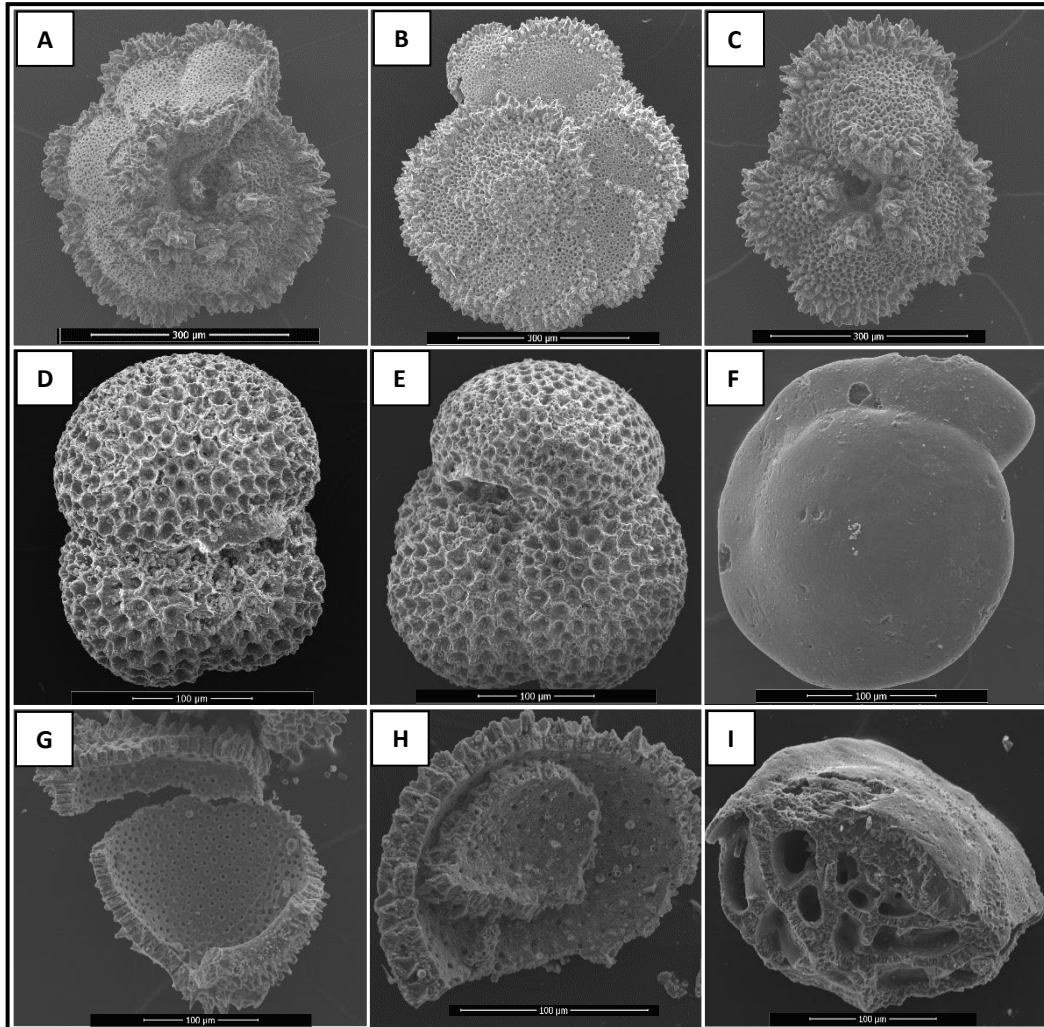


Fig. 4. Scanning electron micrographs of representative specimens of the foraminifera species used in this study. *Morozovella velascoensis*, umbilical view (A) and spiral view (B), *Morozovella subbotinae-marginodentata* plexus (C), *Subbotina velascoensis* (D), *Subbotina hornibrooki* (E), *Oridorsalis umbonatus* (F), *Morozovella subbotinae-marginodentata* plexus cross section (G), *Subbotina velascoensis* cross section (H) and *Nuttallides truempyi* cross section (I)

B/Ca ratios within the tests of the *Morozovella sp.*, and *Nuttallides truempyi* all decrease from the PCIM towards the end of the Paleocene on the order of ~25%, suggesting a relative decrease in pH of the water column over this period, although the magnitude of unit pH change cannot be quantified by this method. This is in agreement with long-term stable carbon isotope ( $\delta^{13}\text{C}$ ) records across the late Paleocene, which display decreasing values interpreted to reflect increasing atmospheric  $\text{CO}_2$  concentrations. The second major episode of volcanism within the North Atlantic Igneous Province across east Greenland and the Rockall Plateau represents the most likely source of this increasing atmospheric  $\text{CO}_2$ , a significant portion of which was subsequently absorbed into the oceans (Westerhold et al., 2011).

This data therefore provides valuable new constraints on the evolution of temperature and pH of the Indian Ocean during the late Paleocene, in the build-up to being pushed over equilibrium states during the PETM.

#### 4.0. Budget

Date	Item	Cost (€)
15/03/2016	ESTA for travel to the United States (\$14)	12.35
19/04/2016	Travel to Heathrow Airport (£23)	29.38
19/04/2016	<b>**Return flight from London Heathrow to San Francisco (£598.15)</b>	<b>764.12</b>
19/04/2016	Travel from San Francisco airport to Santa Cruz (\$7.75)	6.85
19/04/2016	Accommodation for 33 nights in Santa Cruz (£1034)	1320.91
20/04/2016	Subsistence in Santa Cruz (\$33.06)	29.18
03/06/2016	Return travel from Heathrow airport (£31)	39.60
08/06/2016	<b>*Lab analyses – 147 samples equivalent to 22.25 hours on ICP-MS @ \$23/hour for non-UCSC student (\$511.75)</b>	<b>452.04</b>
09/06/2016	Electronic transfer fee for lab analyses payment (£20)	25.54
<b>Total from ECORD</b>		<b>1679.97</b>

Costs in € calculated using the appropriate exchange rate on the date of purchase

\*Covered in full by a grant from the International Association of Sedimentologists (IAS) Postgraduate Grant Scheme (€1000)

\*\*€547.96 of the flight costs are covered by the IAS grant

#### 5.0. Acknowledgements

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#### 6.0. References

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