



Differential effects of cleaning procedures on the trace element chemistry of planktonic foraminifera



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ABSTRACT

We have investigated the effects of different sample cleaning procedures on six trace element/Ca ratios in *Globigerina bulloides*, a planktonic species widely used in palaeoenvironmental reconstructions. Foraminifera from core-top and down-core sediments were cleaned using seven different methods. Individual foraminifera were analysed before and after cleaning using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). We present a comparison between oxidative and reductive cleaning, and an analysis of the effect of using laser ablation versus solution-based ICPMS methods. Measurements of Mg/Ca and Sr/Ca values were identical whether samples were subjected to oxidative, reductive treatments, two-four acid leach treatments or a combination thereof. However, ultra trace element ratios Al/Ca, Mn/Ca, Zn/Ca and Ba/Ca are much more sensitive to the cleaning method, with up to an order of magnitude difference between techniques. Al/Ca was progressively removed with more intensive cleaning, but six or more acid leach treatments were required for full removal of this contaminant phase. Mn/Ca and Ba/Ca required a combination of oxidative and reductive and/or acid leaching for contaminant phase removal. By contrast, Zn/Ca values increased after acid leaching cleaning procedures. This may be a reflection of preferential dissolution of low-Zn calcite. Accurate measurement of Zn/Ca in planktonic foraminifera by solution methods requires oxidative and reductive treatment without acid leaching or alternatively, the use of an in situ method such as laser ablation ICPMS. Careful data processing following laser ablation ICPMS analysis appears to be the most effective method to ensure elimination of ultra trace metal TE/Ca contaminant phases.

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1. Introduction

The use of the Mg/Ca compositions of planktonic foraminifera test calcite as a palaeothermometer is now well-established (e.g. Anand et al., 2003; Pahnke et al., 2003; Cléroux et al., 2008) and has stimulated further interest in the use of other trace metals such as Zn and Ba as geochemical proxies to track palaeo-productivity, nutrient, fluvial input and ocean front migration through time (Lea and Boyle, 1991; Marchitto et al., 2000; Hall and Chan, 2004; Hönisch et al., 2011; Marr et al., in press). However, while our understanding of how foraminiferal trace elements reflect the natural environment is rapidly developing and these elements are more commonly being measured, there has not yet been a clear study on the effects of pre-cleaning protocols, especially pertinent as different analytical methods commonly employ different cleaning techniques. This is especially critical for elements such as Zn or Mn, for example, which have much lower concentrations in the test calcite than Mg or Sr,

and are highly susceptible to contamination from organic matter, clays and ferromanganese oxide coatings.

Three main methods of analysing foraminiferal calcite have been established for determining trace element/Ca (TE/Ca) values. Two involve test calcite dissolution; either the complete dissolution prior to analysis (e.g. Barker et al., 2003; Rosenthal et al., 2004) or progressive dissolution during analysis ('flow-through' method) (Haley and Klinkhammer, 2002; Klinkhammer et al., 2004). The third approach employs in situ analyses to target individual tests using electron microprobe, secondary ion mass spectrometry, or laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Such techniques enable repeat analyses of individual tests at a high spatial resolution (2–35 μm) with minimal sample destruction (e.g. Eggins et al., 2003a; Sadekov et al., 2010). Due to the nature of the different techniques, a range of strategies are employed for mitigating the potential impact of contamination. Pre-cleaning procedures vary for dissolution-based analyses depending on the trace element ratio(s) being targeted and level of test calcite contamination (e.g. Boyle, 1981; Barker et al., 2003). The suite of chemicals used may affect the trace element chemistry of the primary calcite, depending on how the solution and its constituents interact with test calcite. It is now well established that partial test dissolution can

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artificially lower Mg/Ca values of test calcite both in the natural and laboratory environments in response to preferential dissolution of Mg-rich portions of the calcite (Dekens et al., 2002; Rosenthal and Lohmann, 2002; Barker et al., 2003; Benway et al., 2003). For example, Barker et al. (2003) showed that the combined effect of chemical-based cleaning techniques can reduce Mg/Ca values by as much as 25%. The most affected elements however, are likely to be those that occur in ultra-low concentrations in foraminiferal calcite and are most susceptible to contamination and the inefficient removal of contaminant phases. As an example, Lea and Boyle (1991) found that levels of Ba/Ca were reduced by up to 53% when different pre-cleaning methods were employed. In addition, there has been recent speculation that the early loss of the fragile final chamber of planktonic foraminifera during cleaning may produce offsets between the results of laser ablation and solution based methods (Marr et al., 2011). However, as traditional solution-based methods require complete dissolution of the tests prior to analysis, the mechanism(s) by which these cleaning techniques reduce sample TE/Ca cannot be readily resolved.

The more recently developed in situ LA-ICPMS technique takes a different approach, initially removing test surface contamination via ablation and later discriminating between contaminated or primary TE/Ca values during data processing (e.g. Eggins et al., 2003a, 2003b). As in situ methods have the ability to discriminate between foraminiferal samples after analysis it has been assumed that extensive pre-treatment is not required (Sadekov et al., 2009).

In this study we examine the differential effects of various cleaning methods on the measurement of trace element ratios in the planktonic foraminifera, *Globigerina bulloides*. The key benefit to using laser ablation for this study is that we are able to undergo one particular treatment on an individual foraminifera, analyse by LA-ICPMS, then chemically treat the same specimen before geochemical reanalysis and imaging. Using this technique we are able to build a progressive

picture of how the different cleaning methods affect the test through different stages of the cleaning process.

2. Methods

2.1. Samples and sample preparation

G. bulloides is a shallow dwelling (~60 m water depth) spinose, planktonic foraminifera that calcifies multiple chambers, progressively adding calcite layers to older chambers with each new chamber addition (Fig. 1) (e.g. Wilke et al., 2009). The *G. bulloides* examined here were picked from sieved core-top sediment samples (size fraction 250–400 μm) from site D178, Southwest Pacific Ocean at 51.72°S, 169.83°E and water depth 629 m (Marr et al., 2011) with the antepenultimate or chamber *f-2* targeted for analysis. Surface waters overlying D178 are characterised as cold, micronutrient-depleted, Subantarctic Water (Boyd et al., 2001; Bowie et al., 2009) and the radiocarbon age of the sediment is 4835 ± 33 yrs (Marr et al., 2011). The core top was collected from the Campbell Plateau, an area dominated by pelagic carbonate ooze, with CaCO_3 content >70% during the Holocene (Weaver et al., 1998; Carter et al., 2000). *G. bulloides* samples previously investigated from this site (Marr et al., 2011) were determined to have experienced negligible post-depositional alteration, including the absence of blackish-brownish hydroxide crusts as informed by examination under scanning electron microscopy (SEM).

A summary of the sample preparation procedures is given in Fig. 2, with further detail in Supplementary information 1–3. All foraminifera were first treated with cleaning procedures typically used in LA-ICPMS analytical studies (e.g. Eggins et al., 2003a, 2003b; Sadekov et al., 2005). These are designed to remove clay contaminants and involve three ultrasonication washes in ultrapure water for 2–3 s, replacing the water after each ultrasonication. This was followed by two rinses

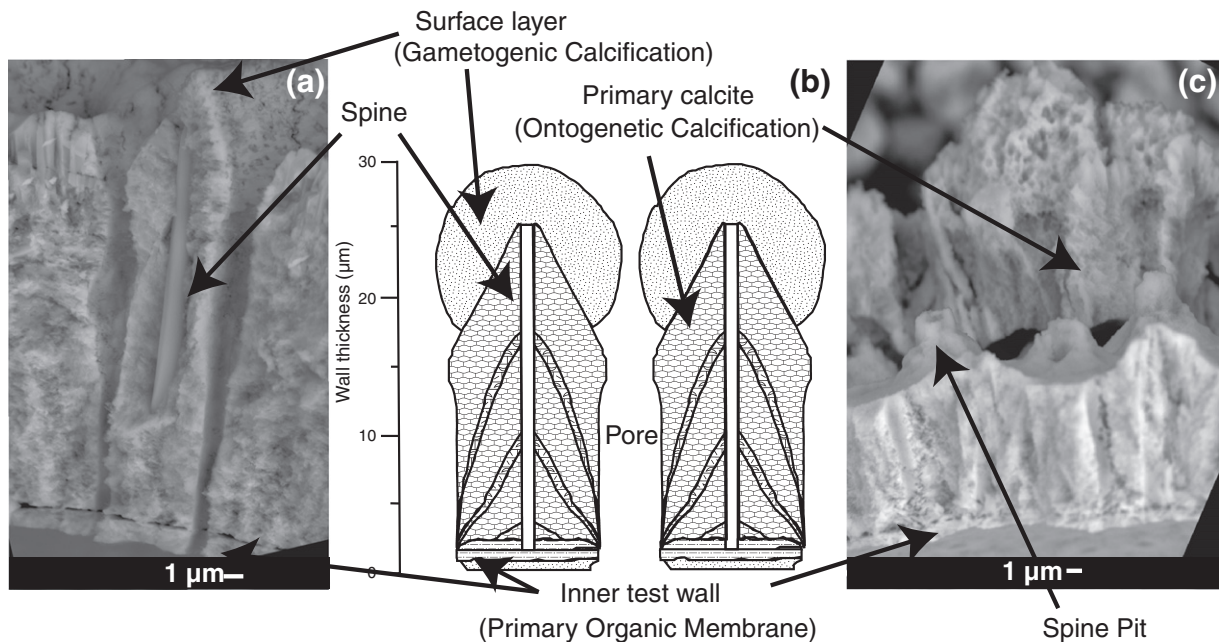


Fig. 1. Calcification of the foraminifera test wall. (a) Electron backscattered image of foraminifera-29 chamber *f-1*, which has undergone oxidative and $1 \times$ acid leach cleaning. Spines of the foraminifera have had incomplete resorption, leaving the remnant spine in the test wall the top of which was subsequently covered with gametogenic calcite (Bé, 1980; Erez, 2003; Sadekov et al., 2005). (b) Schematic diagram illustrating wall and pore structure of an adult *G. bulloides* showing successive growth stages of ontogenetic calcification. Successive primary calcite/ontogenetic calcification layers are indicated by 'bricks' with the thin layers between chamber formation indicated by blocks with 'crescents', inner test wall/primary organic membrane is indicated by dashed lines. Gametogenic calcification/surface layer is indicated by stippling. (c) Cross-section through the test wall of foraminifera-18, chamber *f-1* which has undergone oxidative and reductive treatments. Complete resorption of spines has occurred, with remnants of the outer spine wall clearly visible after primary calcite layer separation. Also illustrated is the relationship between stronger calcite formed in the inner test wall and immediately around the spines, and primary calcite layers. No distinctive dark or light banding was observed in these or other samples to indicate the presence of organic layers (Erez, 2003).

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