LAWRENCE LIVERMORE NATIONAL LABORATORY

LLNL-JRNL-835235

Examining the effects of chemical cleaning, leaching, and partial dissolution on zinc and cadmium isotope fractionation in marine carbonates

J. M. Rolison

May 12, 2022

Chemical Geology

Examining the effects of chemical cleaning, leaching, and partial dissolution on zinc and cadmium isotope fractionation in marine carbonates

Matthew **Druce** (1,2), Claudine H. **Stirling*** (1,2), Helen C. **Bostock** (3) and John M. **Rolison** (4)

Affiliations:

(1) Department of Geology, University of Otago, PO Box 56, Dunedin, NZ

(2) Centre for Trace Element Analysis, University of Otago, PO Box 56, Dunedin, NZ

(3) National Institute for Water and Atmospheric Research, Wellington, 6021, NZ; Now at: School of Earth and Environmental Sciences, University of Queensland, Brisbane, Australia.

(4) Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551-0808, U.S.A.

*Corresponding author. E-mail: claudine.stirling@otago.ac.nz

Manuscript submitted to *Chemical Geology*

Main text word count: ca. 7,315 (excluding abstract, references, Table and Figure captions)

Keywords: zinc isotopes; cadmium isotopes; carbonate sediment; foraminifera; chemical cleaning; reductive step; Cd-cleaning; Mg/Ca cleaning; MC-ICPMS.

Abstract

The application of zinc (Zn) and cadmium (Cd) isotopes as palaeo-proxies in carbonate sediment is rapidly expanding due to their potential for tracing changes in biological productivity in the modern and past oceans. However, there are limited investigations into the chemical cleaning methods required to produce the most consistent and accurate data for these novel isotope systems. This could impact their use as palaeo-proxies to reconstruct ocean-atmosphere-climate interactions throughout Earth's history.

To address this concern and expand the utility of the Zn and Cd stable isotope systems as palaeo-productivity tracers, the performance of two standard chemical cleaning protocols for acquiring robust and reliable Zn and Cd isotope datasets were assessed. These include (i) the *Cd-cleaning* method that uses a reductive step to selectively leach contaminating secondary iron (Fe)-manganese (Mn) (oxyhydr)oxide coatings from the carbonate surface, and an oxidative step that is used to remove post-depositional organic matter and sulphide precipitates; and (ii) the *magnesium/calcium cleaning* protocol that includes an oxidative step only, leaving secondary Fe-Mn (oxyhydr)oxide coatings largely intact. Well-preserved Holocene-, and Mesozoic-aged carbonate sediments were used to test the reliability of these two chemical cleaning methods. The Holocene samples comprised not only aliquots of bulk sediment, but also individual species of planktic and benthic foraminifera.

Our results show that the best practice chemical cleaning method for retrieving consistent and accurate Zn and Cd isotope, and Zn/Ca and Cd/Ca datasets for carbonate sediments, requires both reductive and oxidative cleaning following the Cd-cleaning method. This differs from most methodological approaches applied to date that remove the reductive step from the chemical cleaning protocol and apply an oxidative step only, or no chemical cleaning at all. Inclusion of the reductive step in the chemical cleaning method typically shifts

$\delta^{66}Zn$ by ~0.1 ‰ lower and $\delta^{114}Cd$ by 0.3 ‰ higher in the solid phase, while Zn/Ca and Cd/Ca typically decrease 2-fold. The benthic foraminifera, *C. wuellerstorfi*, that live in ocean bottom waters where the seawater Zn and Cd isotope composition is homogeneous display evidence of Zn and Cd isotope fractionation between seawater and carbonate on the order of 0.08 ± 0.08 ‰ (1SD, n=4) and -0.25 ± 0.13 ‰ (1SD, n=4), respectively, in agreement with experimental constraints. Furthermore, evidence of Zn isotope fractionation effects are recorded in a naturally-dissolved carbonate sediment, together with laboratory-controlled carbonate dissolution experiments. Based on these results we recommend the Cd-cleaning method and the application of Zn and Cd isotope fractionation factors to accurately reconstruct past seawater Zn and Cd isotope compositions of carbonate sediments.

1 Introduction

The zinc (Zn) and cadmium (Cd) isotope composition of ocean sediments, including sedimentary carbonates, are highly sought after as palaeo-productivity proxies, providing important information on marine primary production and its role in modulating key ocean-atmosphere and climate reorganisations throughout Earth's geological past (Horner et al., 2020; Little et al., 2021; Pichat et al., 2003). This emanates from the biological importance of Zn and Cd as micronutrients necessary for carbon fixation by phytoplankton, marine primary producers that exist in the upper ocean (Morel et al., 1994; Price and Morel, 1990; Xu et al., 2008) and draw-down carbon dioxide (CO_2) from the atmosphere. Zinc and Cd isotopes have superior resolving power compared with using elemental ratios alone. This is because biological processes can induce isotope fractionation in seawater that is ultimately recorded in sedimentary archives. This is directly linked to micronutrient demand and supply, which effects the efficiency of the ocean's biological pump that transfers carbon from the surface to the deep ocean controlling carbon drawdown from the atmosphere (John et al., 2007; Lacan et al., 2006).

The uptake of Zn and Cd by phytoplankton induces isotope fractionation between seawater and the organic cell that is on the order of ~0.3 permil (‰) for the Zn isotope ($^{66}Zn/^{64}Zn$) system and up to 0.9 ‰ for the Cd isotope ($^{114}Cd/^{110}Cd$) system (John and Conway, 2014; Köbberich and Vance, 2019; Lacan et al., 2006). For both Zn and Cd, biological uptake typically favours the preferential incorporation of lighter isotopes into the organic biomass due to their lower energy requirements (Urey, 1947), leaving the residual seawater enriched in heavy isotopes (John et al., 2007; Lacan et al., 2006). However, seawater can also record light Zn isotope signatures due to the additional complexation of heavy Zn isotopes with organic matter (Köbberich and Vance, 2019), and Zn adsorption onto particulates (John and Conway, 2014; Gélabert et al., 2006). Increasing evidence also demonstrates that both Zn and Cd isotopes are fractionated at the permil (‰)-level during the formation of sulphide minerals in oxygen-depleted, euxinic (anoxic and sulfidic) marine environments, typically involving low oxygen bottom waters or interstitial porewaters (Guinoiseau et al., 2018; Janssen et al., 2014; Schmitt et al., 2009; Vance et al., 2016). The unique Zn and Cd isotope signatures in the residual seawater are transferred to biogenic carbonate and authigenic minerals during co-precipitation. These materials accumulate as marine sediments recording a time-series of changing productivity, particle flux and bottom water/porewater conditions (Andersen et al., 2011; Hendry and Andersen, 2013; Hohl et al., 2017; Horner et al., 2010; Horner et al., 2011; John et al., 2017; Kunzmann et al., 2013; Little et al., 2014b; Maréchal et al., 2000; Pichat et al., 2003; Schmitt et al., 2009; Sweere et al., 2018).

Efforts to apply Zn and Cd isotope compositions of marine carbonates to document modern and past environmental processes are increasing (Bryan et al., 2021; Hohl et al., 2017; John et al., 2017; Kunzmann et al., 2013; Little et al., 2021; Pichat et al., 2003; Sweere et al., 2018; Xiao et al., 2020; Zhao et al., 2021). However, the accurate reconstruction of past oceanic productivity using Zn and Cd isotopes requires improved understanding of the isotope systematics in carbonate sediments, including from post-formation processes that perturb the isotope signatures. A robust assessment of the most effective carbonate cleaning and digestion methods for carbonate sediments is therefore needed. Current cleaning methods rely on the effective physical or chemical removal of post-depositional Zn- and Cd-rich secondary deposits that can skew the Zn and Cd isotopes as well as the calcium (Ca)-normalised Zn and Cd concentrations (Zn/Ca and Cd/Ca) towards anomalous values, leading to inaccurate reconstructions (Boyle, 1981). These secondary phases typically include hydro-soluble metals weakly bound to the primary mineral surfaces, finely dispersed clay particles, residual biogenic organic matter, sulphides, and iron (Fe)- and manganese (Mn)-bearing (oxyhydr)oxide phases (Boyle, 1981; Rosenthal et al., 1995).

Of particular concern is the entrapment of secondary Zn and Cd (mg g^{-1} and µg g^{-1} concentrations, each) in Fe-Mn (oxyhydr)oxides (Boyle, 1981), which precipitate on the carbonate (µg g^{-1} and ng g^{-1} Zn and Cd content, respectively) mineral surface in high-Zn and high-Cd oceanic bottom waters and porewaters (Boyle, 1983). Under these conditions, Zn and Cd concentrations are two to three orders of magnitude higher than in the upper ocean where phytoplankton and planktic foraminiferal carbonate typically forms (Boyle et al., 1976; Bruland et al., 1978). These secondary Fe-Mn (oxyhydr)oxides can therefore contaminate the Zn and Cd isotope composition of the primary carbonate sediment if they are not effectively removed.

Two commonly used carbonate cleaning protocols have been developed and used in previous studies to selectively remove contaminating non-carbonate phases surrounding the primary carbonate of the sediment for the purpose of obtaining reliable Zn/Ca and Cd/Ca stratigraphies. These are the '*Cd-cleaning*' and '*Mg/Ca cleaning*' procedures. The Cd-cleaning method (Boyle and Keigwin, 1985; Boyle, 1981) specifically targets the effective removal of Fe-Mn (oxyhydr)oxide coatings from the primary carbonate sediment using a '*reductive step*', and also removes sulphides (Rosenthal et al., 1997) and residual organic matter using an '*oxidative step*'. The reductive step of the Cd-cleaning method uses the reducing agent citrate that is capable of binding divalent metal cations, such as Mn^{2+}, Fe^{2+}, Zn^{2+} and Cd^{2+}, which are present in high concentrations within Fe-Mn (oxyhydr)oxide phases (Wyrzykowski and Chmurzyński, 2010). The limitations of this method originate from the corrosive properties of citrate that partially dissolves the carbonate phase (Yu *et al*., 2007) and could preferentially leach Zn and Cd from the primary carbonate leading to isotope fractionation effects. In contrast, the Mg/Ca cleaning protocol retains the oxidative step, but removes the reductive step of the Cd-cleaning method to prevent the occurrence of secondary dissolution effects. However, application of the Mg/Ca cleaning method accepts that some contamination from Fe-Mn (oxyhydr)oxide coatings may still skew the Zn and Cd concentrations towards higher values, and potentially affect the Zn and Cd isotope compositions.

The effectiveness of the Cd-cleaning method has been demonstrated for Cd/Ca in foraminifera carbonates, as highly consistent data are attained for replicate analysis of individually prepared sample aliquots (Boyle and Keigwin, 1985; Boyle, 1981; Bryan and Marchitto, 2010; Marchitto et al., 2000; Marchitto et al., 2002; Ripperger et al., 2008; Yu et al., 2007). However, the efficacy of Cd-cleaning remains untested for Cd isotope analysis. For Zn/Ca, the effectiveness of the Cd-cleaning method has not been reliably demonstrated (Marr et al., 2013a; Yu et al., 2007). Moreover, Zn isotope investigations report reduced consistency in the results when the reductive step that is integral to the Cd-cleaning method is implemented, compared to datasets obtained using the Mg/Ca cleaning method without the reductive step (Pichat et al., 2003). This has led to inconsistent chemical cleaning methods being applied to isotope-based investigations using carbonate sediments. Some studies selectively leach Fe-Mn (oxyhydr)oxide phases from the primary carbonate using the reductive-oxidative steps of the Cd-cleaning protocol (Little et al. 2021), while others apply the Mg/Ca cleaning method that omits the reductive step (Pichat et al. 2003; Maréchal et al. 2000; Kunzmann et al. 2013; John et al. 2017; Little et al. 2021; Zhang et al. 2021; Zhao et al. 2021), and several studies imply that no carbonate cleaning also achieves accurate results (Clarkson et al., 2020; Xiao et al. 2020; Zhao et al. 2021; Hohl et al. 2017).

In this study, the performance of the Cd-cleaning and Mg/Ca carbonate chemical cleaning protocols, and sediment sub-samples processed without chemical cleaning are evaluated for the Zn and Cd isotope systems using well-preserved carbonate Holocene and Mesozoic sediments. Bulk sediments, aided by measurements of individual foraminifera species are used to assess the consistency and accuracy of Zn and Cd isotope observations and account for sample heterogeneity, and identify best practice laboratory protocols and digestion methods for obtaining reliable Zn and Cd isotope compositions of the primary carbonate within sediments. Standardised best practice chemical cleaning methods for Zn and Cd isotope signatures are proposed to obtain consistent, reliable and accurate palaeo-productivity reconstructions.

2 Sample materials

2.1 Holocene sediments

Eight Holocene-aged (<11 thousand year old, ka) carbonate sediments were retrieved from the SW Pacific (offshore from New Zealand) and Indian (offshore from southeast Africa) Oceans and establish a north-south transect across the Subtropical Front of the Southern Ocean

(Table 1, Figure 1). Fresh samples were air dried under laminar flow at the University of Otago, New Zealand, and all samples were then stored dry in acid clean glass vials.

All sediments are well preserved and show minimal evidence of post-depositional dissolution, with the exception of P937 that was retrieved from a depth of 3,253 meters below sea level (mbsl). Locally, the lysocline at P937 is 3,100 mbsl (Bostock et al., 2011), and carbonate from this location shows evidence of dissolution, with foraminifera chamber walls typically displaying rounded-smoothed and partially corroded tests.

Each sediment sample was physically processed under laminar flow, gently broken up and transferred to acid cleaned glass vials for storage. For each sample, 0.4-5.0 g of material was sub-sampled to obtain the bulk sediment fraction. A sub-sample of sediment from each site was physically washed through a <63 μm nylon mesh using high-purity H_2O supplied by a Milli-Q Element purification system (Millipore, USA). The >63 um size fraction was air-dried under laminar flow before being dry sieved with a stainless-steel mesh to obtain the 500-250 μm particle size fraction. Individual species of planktic and benthic foraminifera tests were hand-picked (n>100) using a fine-tipped paintbrush from the 500-250 μm size fraction using binocular light microscopy techniques to obtain a mass of ~0.1 g.

2.2 Mesozoic sediment

The Mesozoic (~94 Ma) sediment PM680 was obtained from the Cretaceous Plenus Marl sequence spanning 'Ocean Anoxic Event 2' (Hancock, 1975) within the chalk outcrop at Eastbourne, England, and was housed within archives at the University of Oxford, UK. Sample PM680 predominantly comprises phytoplankton carbonate with a low organic carbon content (Linnert et al., 2011; Tsikos et al., 2004), and was deposited on a shallow continental shelf setting from a water depth of <600 mbsl during the ‘Plenus Cold Event’. The Eastbourne carbonate sequence is well preserved, displaying minimal evidence of dissolution and low rates of diagenesis from sulphate reduction in porewaters (Clarkson et al., 2018; Owens et al., 2013; Owens et al., 2012; Sweere et al., 2018).

The Mesozoic carbonate was received as a solid limestone weighing ~40 g. The outer surface of lithified marl was removed using a micro-rotary tool (Dremel, USA) fitted with a diamond coated disk. The sediment was sequentially washed with high-purity H_2O and ethanol under laminar flow to remove surface contaminants, then dried and powdered using an agate pestle and mortar pre-cleaned with SiO_2 (99.995 %) sand and ethanol. The powdered sample was then transferred to a glass vial for storage.

3 Chemical cleaning and digestion

All chemical preparation took place within a Class 10 (ISO 4) laminar flow workstation within a Class 100 (ISO 5) clean laboratory housed in the Centre for Trace Element Analysis at the University of Otago, New Zealand, using high-purity reagents throughout.

All sediment samples and individual species of foraminifera were sequentially washed with H_2O and ethanol to remove hydro-soluble contaminants and fine grained clays from the primary carbonate prior to each chemical cleaning step (Figure 2). Aliquots corresponding to 0.1-5 g of material were then chemically cleaned to remove contaminating phases following the (i) Cd-cleaning (Boyle and Keigwin, 1985; Boyle, 1981; Rosenthal et al., 1997; Tessier et al., 1979; Yu et al., 2007) and (ii) Mg/Ca cleaning (Barker *et al*., 2003) methods. For comparative purposes, bulk sediment aliquots weighing ~0.3 g were also taken that did not undergo any chemical cleaning.

3.1 Cd-cleaning method

Selected sub-samples were chemically prepared using the Cd-cleaning method. This involves the selective removal of contaminating Fe-Mn (oxyhydr)oxide secondary phases from the carbonate surfaces by using a reductive step. The chemical cleaning solution used in the reductive step comprised 1 M hydrous hydrazine in 0.25 M citric acid within a 16 M ammonia (NH_4) solution that is combined with the solid carbonate sample, before being agitated in an ultrasonic water bath at 25 °C for 30 minutes. Select samples were processed without the use of hydrous hydrazine because it is not a fundamental component in the reductive cleaning solution (Yu et al., 2007), and it is also toxic, carcinogenic, corrosive and explosive. Following reductive cleaning, the sample was rinsed with H_2O. Organic matter and sulphide precipitates were then selectively removed through oxidative cleaning using a solution of ammonium buffered 1 % hydrogen peroxide (H_2O_2) at pH 5.5, which is heated and intermittently ultrasonicated.

3.2 Mg/Ca cleaning method

Selected sub-samples were chemically processed using the Mg/Ca method. This applies an oxidative cleaning step only, as outlined for the Cd-cleaning method.

3.3 Digestion

Following chemical cleaning, the primary carbonate phase of each sample was selectively digested with 1 M acetic acid at 25 °C using one of two methods:

i) *Total digestion*. Aliquots of 0.1-0.5 g of the bulk carbonate sediment, and all samples of individual species of foraminifera with a mass of ~0.1 g, were leached to completion until no further carbonate remained. The bulk sediment was combined with 5-10 ml of 1 M acetic solution, while the foraminifera samples were admixed with 1-2 ml of 1 M acetic solution until no further carbonate remained, and no additional CO_2 was evolved. Each sample was then centrifuged to separate the insoluble silicate residue from the carbonate digest.

ii) *Partial digestion*. Bulk carbonate sediment aliquots corresponding to 2-5 g were partially digested to selectively dissolve the carbonate phase using 1-2 ml of 1 M acetic acid solution. The reaction between the carbonate phase and acetic acid proceeded until the solution reached saturation and no further CO_2 was released. The carbonate digest was then isolated from the residual undigested carbonate and siliceous residues by centrifugation. Partial digestion was sequentially conducted a further two times, ensuring that progressively more carbonate was dissolved following each digestion step. This provided a total of three partially digested sample aliquots from each cleaned bulk sediment aliquot.

4 Analysis of Zn and Cd isotopes and elemental concentrations

All elemental concentration analyses, as well as the Zn and Cd isotope measurements were performed at the Centre for Trace Element Analysis, University of Otago using methods detailed in the Supplementary Material (SM).

Analysis of Zn and Cd isotope composition was performed using a Nu Plasma HR MC-ICPMS (Ametek, UK) with high-precision double spike methods to reliably account for mass-dependent isotope fractionation effects during processing and instrumental analysis (Druce et al., 2020; Gault-Ringold et al., 2012; Gault-Ringold and Stirling, 2012; George et al., 2019). Zinc and Cd were first extracted from the sample matrix and purified using double-pass anion exchange chromatography with BioRad AG-MP1 resin (200-400 mesh size, Bio-Rad Laboratories, USA). Zinc and Cd isotope compositions are reported as the $^{66}Zn/^{64}Zn$ and $^{114}Cd/^{110}Cd$, respectively reformulated into delta notation as $\delta^{66}Zn$ and $\delta^{114}Cd$ relative to the average of the two bracketing measurements of the primary reference standard as described in (1) and (2) below.

$$\delta^{66}\mathrm{Zn} = \left(\frac{(^{66}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{sample}}}{(^{66}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{IRMM-3702}}} - 1\right) \quad (1)$$

$$\delta^{114}Cd = \left(\frac{(^{114}Cd/^{110}Cd)_{sample}}{(^{114}Cd/^{110}Cd)_{NIST-3108}} - 1\right) \quad (2)$$

The primary standard is IRMM-3702 (sourced from the Institute for Reference Materials and Measurements; IRMM, Belgium) for Zn and NIST-3108 (sourced from the National Institute of Standards and Technology; NIST, USA) for Cd. In (1) and (2), the $^{66}Zn/^{64}Zn$ and $^{114}Cd/^{110}Cd$ of the sample is referred to as $(^{66}Zn/^{64}Zn)_{sample}$ and $(^{114}Cd/^{110}Cd)_{sample}$, respectively, while $(^{66}Zn/^{64}Zn)_{IRMM-3702}$ refers to the $^{66}Zn/^{64}Zn$ of IRMM-3702, and $(^{114}Cd/^{110}Cd)_{NIST-3108}$ denotes the $^{114}Cd/^{110}Cd$ of NIST-3108. The $\delta^{66}Zn$ and $\delta^{114}Cd$ are then reported in permil (‰) by multiplying the delta value by 10^3. The Zn isotope composition is reported relative to the JMC Lyon-Zn standard via the addition of +0.30 ‰ (Archer et al., 2017). The 2SE reported for each sample is typically better than ±0.02 ‰ for

$\delta^{66}Zn$ and ±0.05 ‰ for $\delta^{114}Cd$, and includes the contributions from the sample and the two bracketing standards. Accuracy is confirmed through repeat $\delta^{66}Zn$ and $\delta^{114}Cd$ measurements of standards and certified reference materials (see SM; Table S1-S3, Figure S1).

Elemental concentrations were determined using quadrupole – ICPMS (Q-ICP-MS) using a 7900 instrument (Agilent Technologies, USA) to determine the concentrations of aluminium (Al), Ca, Mn, Fe, Zn and Cd. Further details of the methodology and analytical performance are provided in the SM.

5 Results

The Zn and Cd isotope compositions, as well as the elemental concentrations normalised to Ca (Al/Ca, Mn/Ca, Fe/Ca, Zn/Ca, Cd/Ca) following chemical cleaning and carbonate dissolution, and with no chemical cleaning applied are reported in Table S2-S5. The results represent independently processed sub-samples of Holocene (SW Pacific and Indian Ocean) bulk sediments and individual species of foraminifera from sites G824, J21, H555 and F111, as well as a Mesozoic bulk sediment, further details are given in the SM.

5.1 Carbonate chemical cleaning and dissolution

Individual sub-samples of the Holocene-aged bulk carbonate sediment (G824, SW Pacific) and a Mesozoic-aged bulk sediment were processed using the Cd-cleaning (reductive-oxidative steps) and the Mg/Ca cleaning (oxidative step only) methods, and without any chemical cleaning applied. The results are consistent for the Holocene and Mesozoic sediments, with lower Zn/Ca and Cd/Ca displayed when the reductive step is included, compared with when this step is removed (Table S4 and Figure 3). Use of the reductive step typically decreases δ^{66}Zn and increases δ^{114}Cd, compared to when this step is not applied.

Experimentally-induced partial carbonate digestion of Holocene bulk sediment (G824, SW Pacific) displays no resolvable change in δ^{66}Zn, δ^{114}Cd and Zn/Ca as dissolution progresses from digest one to three, excluding the initial digest where Zn/Ca is lower. In contrast, Cd/Ca halves from digest one to three (Table S5, Figure 4). However, the partially digested aliquots consistently record higher δ^{66}Zn, Zn/Ca and Cd/Ca than the bulk sediment (G824) digested to completion, with the exception of the initial digest for Zn/Ca. The SW Pacific Holocene sediment (P937) that has been partially dissolved by natural processes yields a δ^{66}Zn that is ~0.2 ‰ lower than the value for well-preserved bulk sediment (G824) digested to completion. However, there is no resolvable difference in the mean Zn/Ca, δ^{114}Cd or Cd/Ca between P937 and G824.

Results are further supported by the sediments in the north-south transect (Figure 1), which also show Zn/Ca, Cd/Ca and δ^{66}Zn are typically lower and δ^{114}Cd increases when the reductive step is applied, compared with when the reductive step is omitted (Table S6, Figure 5).

Routine monitoring of potential non-carbonate Zn and Cd contaminating phases was assessed using trace metal ratios. In all samples, the Al/Ca content is typically <1 mmol/mol, indicating that the proportion of aluminosilicates in the digests is negligible. The Mn/Ca and Fe/Ca are used to monitor possible contamination from Fe-Mn (oxyhdr)oxide secondary phases and vary from 1.07-0.04 mmol/mol and 0.98-0.02 mmol/mol, respectively, for all samples.

5.2 Heterogeneity of zinc and cadmium systematics between sub-samples

An initial assessment of the extent to which fine-scale heterogeneity in the geochemistry of the primary carbonate influences the Zn and Cd systematics between different sub-samples was performed. This is in order to evaluate how well within-sample variability is captured by the analytical uncertainty associated with the Zn and Cd isotope compositions and the elemental concentration signatures. To access the primary carbonate signatures, compositional variations in sub-samples that had been chemically cleaned using the Cd-cleaning method were considered.

When sequential reductive and oxidative chemical cleaning is applied, the δ^{66}Zn of different, independently processed sub-samples of Holocene bulk sediment (G824) (Table S7, Figure 6) and individual species of foraminifera (sites G824, J21, H555 and F111) do not always agree within their reported analytical 2SE. To this end, the measurement uncertainty must be expanded by approximately a factor of two, to ±0.05 ‰ for the bulk sediment and ±0.04 ‰ for the foraminifera, to obtain consistent results that fully account for variations arising from sample heterogeneity. The Zn/Ca of bulk sediment aliquots processed with both reductive and oxidative steps yield values that are in agreement within the analytical uncertainty limits of ±7 %. Replicate sub-samples of individual species of foraminifera provide Zn/Ca that are statistically identical when the analytical uncertainty is expanded two-fold to ±13 %, and is therefore applied to all sub-samples of bulk sediment and foraminifera.

Using both reductive and oxidative cleaning, the δ^{114}Cd of individual, independently processed aliquots of Holocene bulk sediment (G824) and individual species of foraminifera (sites G824, J21, H555 and F111) (Table S7, Figure 6) are all identical within their reported 2SE and no expansion of the uncertainties is therefore required. The Cd/Ca of the bulk sediment and foraminifera sub-samples processed with both reductive and oxidative cleaning are all identical when the uncertainty is expanded marginally from ±12 % to ±14 %.

This approach of expanding the uncertainties allows for geochemical variations between different sub-samples of the same carbonate material, and more reliably accounts for sample heterogeneity, as well as artefacts introduced during sample preparation and chemical processing, compared with using the analytical uncertainty alone. Expanding the uncertainty limits associated with Zn/Ca and Cd/Ca by two- to four-fold, depending on the chemical cleaning method used, is consistent with the degree of variability observed in other elemental studies where data for multiple sub-samples are reported (Boyle, 1992; Marchitto et al., 2000). Given these results, the expanded uncertainties determined here for sub-samples processed with the Cd-cleaning method are applied to all datasets presented herein.

6 Discussion

The results of the different carbonate chemical cleaning and dissolution procedures tested above provide the basis for evaluating the (i) accuracy of Zn and Cd isotope analysis, (ii) performance of carbonate chemical cleaning methods, and (iii) impact of dissolution procedures on the Zn and Cd isotope systematics of carbonate sediments, discussed in turn below.

6.1 Constraining the accuracy of zinc and cadmium systematics in carbonates

Dissolved seawater is relatively homogeneous with respect to δ^{66}Zn and δ^{114}Cd below depths of ~1000 m, giving respective values of 0.46 ± 0.11 ‰ (2SD, n=301) and 0.28 ± 0.15 ‰ (2SD, n=395) using available datasets from 0-50 ºS (GEOTRACES Intermediate Data Product 2017; Schlitzer et al., 2018) across latitudes spanning those of the study sites, and avoiding high latitude North Atlantic Deep Water and Circumpolar Deep Water endmember water masses that skew the mean (Conway and John, 2015; Zhao et al., 2014). The ability of chemically cleaned biogenic carbonates, processed using the reductive and oxidative steps (Cd-cleaning method) to accurately record seawater δ^{66}Zn and δ^{114}Cd can be assessed by comparing the known isotopically homogeneous deep seawater signature with those determined for the benthic foraminifera species *C. wuellerstorfi* that precipitates its carbonate test in oceanic bottom waters. This approach builds on previous carbon isotope studies demonstrating that *C. wuellerstorfi* tests provide accurate constraints on the seawater ^{13}C/^{12}C (δ^{13}C) composition (eg. Schmittner et al., 2017).

The mean δ^{66}Zn of *C. wuellerstorfi* (sites G824, J21, H555 and F111) is 0.53 ± 0.19 ‰ (2SD, n=4), and is comparable to the average deep seawater value of 0.46 ± 0.11 ‰ (2SD, n=301, >1000 m depth, latitude 0-50 ºS) (Figure 6). However, the retrieval depth of sediments from sites G824, J21 and F111 is above 1000 m where the δ^{66}Zn of seawater is not always homogeneous. This increases the variability in the carbonate δ^{66}Zn between sites. To account for this heterogeneity, each site is also assessed independently for Zn isotope fractionation effects that occur during the removal of Zn from seawater into the carbonate phase. The δ^{66}Zn of the seawater at similar water column depths as the sediment retrieval depth (taken as the approximate bottom water depth at each site) is subtracted from the δ^{66}Zn of *C. wuellerstorfi* at each site to determine the magnitude of Zn isotope fractionation (Table S8). The large associated uncertainty in the seawater δ^{66}Zn is due to the relative paucity of data when the depth range is restricted, which are also skewed towards spring-summer sampling and influenced by seasonal cycling that increases the spread in reported values (Samanta et al., 2017). However, the mean δ^{66}Zn is expected to remain accurate for seawater below 500 m depth because of the multi-millennial scale residence time for both Zn and Cd in the oceans and the centennial-millennial rate of overturning circulation (Black et al., 2019; Little et al., 2014b). Taken together, an average Zn isotope fractionation factor of 0.08 ± 0.08 ‰ (1SD, n=4) is obtained that generally favours the incorporation of heavy Zn isotopes into the solid phase from the seawater, but remains unfractionated within uncertainty. There is a smaller magnitude of net isotope fractionation determined in this study compared with values of up to 0.60 ‰ obtained from experimental and *ab initio* studies (Dong and Wasylenki, 2016; Ducher et al., 2016; Fujii et al., 2014; Fujii et al., 2011; Mavromatis et al., 2019; Veeramani et al., 2015). This could arise from competition between equilibrium and kinetic isotope fractionation effects associated with carbonate precipitation, Zn concentration in the dissolved phase, surface area effects and/or biological effects (eg. biomineralisation strategies) that may show variable isotopic shifts in opposing directions and are more complex in natural settings. Importantly, the value of 0.08 ± 0.08 ‰ (1SD, n=4) determined in this study is identical, within uncertainty (expressed as 1SD for consistency with Little et al., 2021), to the Zn isotope fractionation factor calculated for cold water corals of 0.03 ± 0.17 ‰ (1SD, n=20) (Little et al., 2021), demonstrating that accurate seawater δ^{66}Zn can be obtained using biogenic carbonates when the Cd cleaning method is used.

For δ^{114}Cd, *C. wuellerstorfi* record a mean δ^{114}Cd of 0.18 ± 0.15 ‰ (2SD, n=4) and is comparable to the deep seawater value of 0.28 ± 0.15 ‰ (2SD, n=395, >1000 m depth, latitude 0-50 ºS) (Figure 6). Comparing the δ^{114}Cd of *C. wuellerstorfi* with values for seawater at latitude 0-50 ºS and at a similar seawater depth to the sediment retrieval depth at each site (Table S8), in a similar manner as for δ^{66}Zn, yields a mean estimate for Cd isotope fractionation between the solid carbonate and dissolved seawater phase of -0.25 ± 0.13 ‰ (1SD, n=4). This distinct offset observed between the δ^{114}Cd of carbonate and seawater across a range of depths demonstrates that Cd isotope fractionation occurs at a quantifiable level during the incorporation of Cd from the aqueous phase into the solid during carbonate precipitation and preferentially favours light Cd isotopes. This isotopic shift is similar to the value of -0.45 ±

0.12 ‰ derived from experimentally-controlled calcite precipitation experiments using artificial high-ionic strength seawater (Horner et al., 2011; Xie et al., 2021), but is for a natural setting rather than a laboratory experiment. The consistent offset is possibly responsible for the lighter δ^{114}Cd observed in palaeo-environmental reconstructions using carbonate sediments that has previously been considered to be a function of salinity change between the modern and ancient oceans. For example, a salinity correction for δ^{114}Cd using yttrium/holmium has been developed (Hohl et al., 2017) due to an observed increase in the magnitude of Cd isotope fractionation between artificial low-and high-salinity solutions and solid carbonate during laboratory controlled calcite precipitation experiments (Horner et al., 2011), but may not be justified.

The accuracy of Zn/Ca and Cd/Ca in biogenic carbonates can be inferred by comparison with previously reported values. The Zn/Ca of *C. wuellerstorfi* typically spans a range from 1.2-5.8 µmol/mol (Marchitto et al., 2000), which is in good agreement with the values of 3.2-8.9 µmol/mol obtained in this study, with the exception of *C. wuellerstorfi* from site H555 that is higher than expected at 22.6 µmol/mol and represents the deepest study site (2738 mbsl). Reported Cd/Ca of *C. wuellerstorfi* vary from 0.03-0.38 µmol/mol (e.g. Boyle 1992), which also compares well with the values of 0.14-0.48 µmol/mol observed in this study. Furthermore, the highest Cd/Ca of 0.48 µmol/mol is obtained at site F111 in the Southern Ocean where Cd concentrations in modern seawater are typically higher than in the subtropical regions where the other study sites are located.

The Zn/Ca and Cd/Ca determined in this study are positioned in the upper range of previously reported values. These differences are likely to originate from the less intense carbonate chemical cleaning protocols applied in this investigation, compared with previous studies (Boyle, 1981, 1992; Marchitto et al., 2000; Ripperger and Rehkämper, 2007; Ripperger et al., 2008). Excessive chemical cleaning can cause elemental fractionation during partial carbonate dissolution that is capable of biasing Zn/Ca and Cd/Ca towards lower values (Marr et al., 2013a; McCorkle et al., 1995; Yu et al., 2007; Fritz-Endres and Fehrenbacher, 2021). This suggests that a revised partition coefficient may be required to accurately reconstruct local Zn and Cd concentrations in past seawater using the less aggressive chemical cleaning methods applied in this study and warrants further investigation. Nonetheless, the Zn/Ca and Cd/Ca of *C. wuellerstorfi* determined here remain comparable with previous investigations, which validates the accuracy of the data and further verifies the reliability of the chemical cleaning methods used.

6.2 The performance of chemical cleaning methods

The performance of the carbonate chemical cleaning methods used for Zn and Cd isotope analysis are assessed by comparing the consistency in results between individually prepared sub-samples using the same carbonate cleaning method, and without chemical cleaning applied. The effectiveness of each chemical cleaning approach is also considered through the observed lowering, or otherwise, in Fe/Ca and Mn/Ca. This would indicate the effective removal of secondary Fe and Mn present in Fe-Mn (oxyhydr)oxide coatings.

6.2.1 The performance of chemical cleaning for zinc and its isotopes

The δ^{66}Zn of the Holocene and Mesozoic bulk sediments processed without chemical cleaning, as well as using the Mg/Ca method, both show a general increase in the consistency between individually prepared sub-samples of the same sediment when compared with sub-samples processed using the Cd-cleaning method (Figure 3). The marginal decrease in consistency in δ^{66}Zn when Fe-Mn (oxyhydr)oxide coatings are selectively removed is a reoccurring feature in this investigation and is either the result of partial contamination from insufficiently cleaned Fe-Mn (oxyhydr)oxide coatings, or from carbonate dissolution or leaching effects. This observation has previously been used to support the exclusion of the reductive step that removes secondary Fe-Mn (oxyhydr)oxide coatings in palaeo-environmental reconstructions based on Zn isotope stratigraphy (Kunzmann et al., 2013; Pichat et al., 2003; Sweere et al., 2018).

In the Holocene sediments, there is a moderate correlation between δ^{66}Zn and Mn/Ca (r^2 =0.75, p =0.01), while no significant correlation occurs between δ^{66}Zn with Fe/Ca (Figure 7). In the Mesozoic carbonate, however, δ^{66}Zn weakly correlates with Fe/Ca (r^2 =0.55, p <0.01), but a correlation is not readily observed between δ^{66}Zn and Mn/Ca (Figure 7). This could indicate that the δ^{66}Zn of Fe-Mn (oxyhydr)oxide coatings is fractionated towards higher values compared with seawater through adsorption effects (Little et al., 2014a; Little et al., 2014b; Maréchal et al., 2000). This would lead to a deterioration in data consistency when the selective removal of Fe-Mn (oxyhydr)oxide coatings is inconsistently applied between different sub-samples.

The Zn/Ca of the Holocene and Mesozoic sediments typically decreases when the reductive step is used to remove Fe-Mn (oxyhydr)oxide coatings (Figure 3). For example, the Holocene sediment processed without reductive cleaning yields a Zn/Ca of 7.8 ± 1.0 µmol/mol, while the same sample processed using the reductive step gives a value of 4.9 ± 0.6 µmol/mol. The positive correlation between Zn/Ca and Mn/Ca in the Holocene sediment (r^2 =0.92, p =0.05), and between Zn/Ca and Fe/Ca in the Mesozoic sediment (r^2 =0.83, p =0.03) indicates the effective removal of secondary Fe (oxyhydr)oxides when reductive cleaning is applied (Figure S2). This could indicate that rapid scavenging of Zn from porewaters onto Fe (oxyhydr)oxides occurs, as Mn (oxyhydr)oxides dissolve at the Mn-redox boundary within the interstitial sediment porewaters during diagenesis, releasing their constituent elements back into the surrounding aqueous phase. Zinc scavenging onto Fe (oxyhydr)oxides could then serve as the major contaminating pathway for Zn concentrations in ancient deposits, making the monitoring of Fe/Ca an important quality control parameter during the derivation of Zn isotope records for carbonate sediments.

6.2.2 The performance of chemical cleaning for cadmium and its isotopes

For both the Holocene and Mesozoic sediments, the average $\delta^{114}Cd$ and Cd/Ca are identical, within uncertainty, when processed with and without the reductive step (Figure 3). This indicates that Fe-Mn (oxyhydr)oxides do not dominate the Cd mass balance in these carbonate sediments, consistent with previous studies showing that the Mesozoic sample (PM680) has not been significantly altered through diagenesis (Owens et al., 2013; Owens et al., 2012). However, the two-fold increase in consistency in $\delta^{114}Cd$ for the Mesozoic carbonate when the reductive step is used suggests the effective removal of secondary Fe-Mn (oxyhydr)oxide coatings remains an important protocol for obtaining reliable Cd isotope datasets for ancient carbonates. Further, the agreement in Cd/Ca obtained for each sample, irrespective of the chemical cleaning method used, could imply that cadmium sulphide precipitation removes mobilised Cd from porewaters (Framson and Leckie, 1978; Rosenthal et al., 1995) at a faster rate than adsorption onto Fe (oxyhydr)oxides occurs, or that alternative non-carbonate mineral phases form during sedimentary diagenesis. However, routine monitoring of Fe/Ca is important to verify that the Cd mass balance remains tied to the low-Cd primary carbonate rather than non-carbonate minerals.

6.2.3 Recommendation for best-practice chemical cleaning

The above findings for the Holocene and Mesozoic carbonate sediments indicate that the Cd cleaning method is recommended for the acquisition of accurate datasets of $\delta^{66}Zn$ and Zn/Ca, and $\delta^{114}Cd$ and Cd/Ca. The reductive step is necessary to remove secondary Fe-Mn (oxyhydr)oxide coatings, and an oxidative step to remove post-depositional organic material and sulphides. The inclusion of the reductive step yields robust and highly reproducible datasets for $\delta^{114}Cd$ and Cd/Ca, but may lead to anomalous Zn isotope results in some samples by fractionating $\delta^{66}Zn$ towards lower values, requiring the reported uncertainties to be expanded accordingly. In this study, expanding the uncertainties by a factor of two to ±0.05 ‰ (bulk sediment) and ±0.04 ‰ (foraminifera) was sufficient to overcome the influence of any potential isotope fractionation arising from reductive chemical cleaning, as well as fine-scale spatial heterogeneity, from the $\delta^{66}Zn$ results.

Our investigation also leads to the hypothesis that overly aggressive reductive-oxidative chemical cleaning protocols are not always necessary to obtain accurate Zn and Cd isotope analysis and could exacerbate the anomalous isotope effects. For example, the use of hydrazine in the reductive step may be unnecessary (Yu et al., 2007), because it serves as an oxidising agent that can bind protons from citric acid, shifting the chemical equilibrium towards the citrate product, and enhancing the availability of citrate within the reductive cleaning solution. The removal of hydrazine from the reductive cleaning solution could buffer the production of citrate, allowing the reaction between the Fe-Mn (oxyhydr)oxide phase and citrate to occur at a slower rate and with increased selectivity (refer to SM).

We therefore recommend that both reductive and oxidative cleaning steps are implemented, but with the removal of hydrazine from the reductive cleaning solution to reduce the intensity of leaching and dissolution effects during carbonate chemical cleaning.

6.3 Isotope fractionation during carbonate dissolution

Chemical cleaning aside, the effects of dissolution may potentially introduce systematic biases in Zn and Cd isotope composition during laboratory-controlled carbonate digestion following chemical cleaning. Therefore, a sequential partial dissolution experiment involving three successive leaching steps was undertaken using the Holocene bulk sediment G824 to assess the magnitude of these dissolution effects, if any (Figure 4).

Subtle, but resolvable, Zn isotope fractionation from the initial to the final digestion step of -0.13 ‰ was recorded in an individual sample aliquot. Additionally, the δ^{66}Zn of all six partially digested carbonate aliquots are ~0.3 ‰ higher than the bulk sediment digested to completion (Figure 4). Furthermore, four of the six partial sediment digests record higher Zn/Ca compared with the bulk sediment digested to completion. In contrast to Zn, no resolvable Cd isotope fractionation is observed, but Cd/Ca is up to five times higher in the initial digest compared with the bulk sediment digested to completion (Figure S3), supporting previous findings showing the sensitivity of Cd/Ca to dissolution effects (McCorkle et al., 1995). However, Cd/Ca and Mn/Ca are correlated (r^2 =0.80, p <0.01), which may indicate that the variable, incomplete removal of secondary contaminating phases is responsible for the observed variations (Figure S3) rather than elemental fractionation between Cd and Ca in the primary carbonate.

Sub-samples of the naturally dissolved bulk sediment (P937) support the findings from the partial dissolution experiment in that δ^{114}Cd remains identical, within uncertainty, and δ^{66}Zn yields values that are ca. 0.2 ‰ lower than the composition of well-preserved Holocene bulk sediment (G824), retrieved from a similar water mass and nutrient regime (Figure 4). This offset may reflect dissolution-induced Zn isotope fractionation, or instead relate to variability in the physical sedimentary characteristics (eg. phytoplankton/zooplankton assemblage and dissolution rates) between sites. In contrast, the Zn/Ca and Cd/Ca of the naturally dissolved bulk sediment (P937) are identical, within uncertainty, to their respective composition in the well-preserved sediment (G824), potentially due to physical sedimentary differences between P937 and G824. However, it remains well established that the Zn/Ca and Cd/Ca palaeo-environmental proxies are sensitive to partial dissolution effects and carbonate saturation (Marchitto et al., 2000; Marchitto et al., 2005; Marchitto et al., 2002; McCorkle et al., 1995; van Dijk et al., 2017). The results of this study demonstrate that the accuracy of δ^{66}Zn may also be hindered by partial dissolution, while δ^{114}Cd appears to remain relatively unaffected by dissolution.

6.4 Evaluating the best practice cleaning and dissolution procedures using a north-south sediment transect

Holocene-aged sediments from sites U1476, G824, J21, MD02-2588, U1475, H555 and F111 (Figure 1) span a 3,700 km long, north-south transect in both the Indian and SW Pacific distributed across the Subtropical Front. As such, this transect captures a wide range of upper ocean Zn and Cd nutrient regimes, recorded in carbonate sediments affected by variable levels of Fe and Mn (oxyhydr)oxides, sulphides and organic material, and terrigenous aluminosilicate inputs. This transect is therefore used to demonstrate the importance of applying the best practice Cd-cleaning method that includes both reductive (without hydrazine) and oxidative steps, to obtain robust datasets of δ^{66}Zn, δ^{114}Cd, Zn/Ca and Cd/Ca. Partial dissolution effects were avoided by digesting all bulk carbonate sediments to completion.

The $\delta^{66}Zn$ of sediments from the north-south transect processed using the Cd-cleaning method (reductive-oxidative steps) range from 0.41-1.03 ‰, while $\delta^{114}Cd$ varies from 0.19-1.01 ‰ (Figure 5 and S4). By comparison, when the Mg/Ca cleaning method (oxidative step only) is used, bulk carbonate $\delta^{66}Zn$ and $\delta^{114}Cd$ shift towards values that are higher by ~0.1 ‰ and lower by ~0.3 ‰, respectively, relative to samples processed with the reductive step included (see SM). These results support the findings of the chemical cleaning experiments, in that the use of the reductive step improves the accuracy of past seawater Zn and Cd isotope reconstructions using carbonate sediments. However, the north-south sediment transect across a wide range of nutrient regimes demonstrates that $\delta^{66}Zn$ and $\delta^{114}Cd$ can vary by up to ~1 ‰ (U1476) if Fe-Mn (oxyhydr)oxide phases are not sufficiently removed. Furthermore, the consistent 2-fold decrease in Zn/Ca and Cd/Ca recorded when the reductive step is applied, demonstrates that the effective removal of Fe-Mn (oxyhydr)oxide coatings using the Cd-cleaning method is necessary, and is particularly important at sites underlying water masses with ultra-low Zn and Cd and/or high Fe and Mn concentrations (eg. U1476). For example, a 0.1 ‰ and 0.3 ‰ inaccuracy in $\delta^{66}Zn$ and $\delta^{114}Cd$, respectively, is comparable to the difference between the Bulk Silicate Earth (BSE, $\delta^{66}Zn$ of 0.3 ‰, $\delta^{114}Cd$ of 0.0 ‰, eg. Little et al. 2014; Bridgestock et al. 2017) and the modern deep ocean ($\delta^{66}Zn$ of 0.5 ‰, $\delta^{114}Cd$ of 0.3 ‰, eg. Little et al. 2014; Ripperger et al. 2007). The implication is that variations in the sources and sinks of Zn and Cd isotopes in the past ocean cannot be quantitatively resolved unless the carbonate is initially leached of Zn and Cd contaminating Fe-Mn (oxyhydr)oxide coatings using the Cd-cleaning method, prior to carbonate digestion and analysis.

7 Conclusions

A scarcity of evidence-based investigations determining the most suitable chemical cleaning and carbonate dissolution protocols for accurate Zn and Cd isotope analysis of marine carbonates is hindering their applicability for tracing palaeo-productivity. Two commonly used carbonate chemical cleaning protocols, the Cd-cleaning and the Mg/Ca cleaning methods are applied in this study to Holocene (<11 ka) and Mesozoic (~94 Ma) bulk sediments, as well as individual species of foraminifera isolated from Holocene-aged bulk sediments, to determine the best practice chemical cleaning and carbonate dissolution methodology. We find that the Cd-cleaning method that includes both a reductive step (without hydrazine) to remove Fe-Mn (oxyhydr)oxide coatings without inducing appreciable isotope fractionation, and an oxidative step to remove organic matter and sulphide precipitates, is the best method for obtaining reliable Zn and Cd isotope signatures, as well as Zn/Ca and Cd/Ca compositions.

Holocene and Mesozoic bulk sediment $\delta^{66}Zn$ and $\delta^{114}Cd$ demonstrate that the inclusion of a reductive step increases the accuracy of, and consistency between, signatures for different sub-samples of the same sediment, particularly for the Cd isotope system. This is because contaminating Fe-Mn (oxyhydr)oxide coatings are selectively removed from the primary carbonate phase. Inclusion of the reductive step in the carbonate chemical cleaning method typically shifts $\delta^{66}Zn$ and $\delta^{114}Cd$ towards lower and higher values, respectively, in the solid phase, and closer to their primary compositions at the time of carbonate formation, while both Zn/Ca and Cd/Ca typically decrease by a factor of two in the same samples.

Reliable uncertainty estimates for replicate Zn and Cd isotope analysis of Holocene bulk sediment demonstrate that sample heterogeneity in the primary carbonate phase together with any residual secondary phases, and introduced during laboratory processing is accounted for when the reductive step is applied. For $\delta^{66}Zn$, the uncertainty requires expanding by a factor of two to ±0.05 ‰ for bulk sediment and ±0.04 ‰ for foraminifera to obtain consistent results between different, independently processed sub-samples of the same sediment. For the Cd isotope system, the analytical uncertainty alone fully accounts for the heterogeneity between replicate analyses of different sub-samples for all sample types. The expanded uncertainties required to obtain consistent datasets in Zn/Ca and Cd/Ca are ±13 % and ±14 %, respectively.

The accuracy in Zn and Cd isotope analysis of marine carbonates is verified using benthic foraminifera (*Cibicides wuellerstorfi*) that precipitate their carbonate tests at the sediment-water interface where the δ^{66}Zn and δ^{114}Cd of seawater is well known. The results show that the Zn isotope fractionation factor between the carbonate of *C. wuellerstorfi* and seawater is 0.08 ± 0.08 ‰ (1SD, n=4), while the δ^{114}Cd of the solid carbonate phase is consistently offset by -0.25 ± 0.13 ‰ (1SD, n=4) from seawater.

Isotopic and elemental Zn and Cd fractionation effects are evident from laboratory-controlled carbonate dissolution experiments and in a natural partially dissolved Holocene bulk sediment. Dissolution-induced isotope fractionation typically shifts δ^{66}Zn towards low values in the solid carbonate phase as heavy isotopes are preferentially removed, which indicates that partially dissolved carbonates may not reliably record environmental signatures. Therefore, laboratory carbonate dissolution should ensure sub-samples are digested to completion to guarantee that reliable results are obtained.

The findings of this study provide an evidence-based approach demonstrating the best practice carbonate chemical cleaning and digestion protocol for the Zn and Cd isotope analysis of marine carbonate sediments. This will improve the reliability of palaeo-productivity investigations using these stable isotope systems, expanding their utility in deconvolving the role of marine primary production in regulating carbon and climate cycling during past ocean-atmosphere reorganisations.

Acknowledgments

Funding for this research was provided by a Royal Society of New Zealand Marsden Grant (UOO1717) and University of Otago Research Grant to C.H.S., an International Ocean Discovery Programme Grant to J.M.R. and C.H.S., and a University of Otago Doctoral Scholarship to M.D. Surface sediments for the SW Pacific were provided from the National Institute of Water and Atmospheric Research archive. In addition, we are grateful to H. Jenkyns, University of Oxford, UK, for providing the Mesozoic sediment. We are also grateful to D. Barr and M. Reid at the Centre for Trace Element Analysis for providing instrumental and laboratory support, and elemental data. Finally, we also thank E. Fordyce, University of Otago, for access to the light microscopy equipment, and to S. Little, Imperial Collage London, UK and M. Ellwood, Australian National University, Australia, the Editor and two anonymous reviewers for their constructive and succinct comments.

References

Andersen, M.B., Vance, D., Archer, C., Anderson, R.F., Ellwood, M.J. and Allen, C.S. (2011) The Zn abundance and isotopic composition of diatom frustules, a proxy for Zn availability in ocean surface seawater. Earth and Planetary Science Letters 301, 137-145.

Archer, C., Andersen, M.B., Cloquet, C., Conway, T.M., Dong, S., Ellwood, M., Moore, R., Nelson, J., Rehkämper, M. and Rouxel, O. (2017) Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis. Journal of Analytical Atomic Spectrometry 32, 415-419.

Barker, S., Greaves, M. and Elderfield, H. (2003) A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochemistry, Geophysics, Geosystems 4.

Black, E., Lam, P., Lee, J.M. and Buesseler, K. (2019) Insights from the 238U-234Th method into the coupling of biological export and the cycling of cadmium, cobalt, and manganese in the Southeast Pacific Ocean. Global Biogeochemical Cycles 33, 15-36.

Black, J.R., Kavner, A. and Schauble, E.A. (2011) Calculation of equilibrium stable isotope partition function ratios for aqueous zinc complexes and metallic zinc. Geochimica et Cosmochimica Acta 75, 769-783.

Bostock, H.C., Hayward, B.W., Neil, H.L., Currie, K.I. and Dunbar, G.B. (2011) Deep-water carbonate concentrations in the southwest Pacific. Deep Sea Research Part I: Oceanographic Research Papers 58, 72-85.

Boyle, E. and Keigwin, L. (1985) Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. Earth and Planetary Science Letters 76, 135-150.

Boyle, E.A. (1981) Cadmium, zinc, copper, and barium in foraminifera tests. Earth and Planetary Science Letters 53, 11-35.

Boyle, E.A. (1983) Manganese carbonate overgrowths on foraminifera tests. Geochimica et Cosmochimica Acta 47, 1815-1819.

Boyle, E.A. (1992) Cadmium and δ13C paleochemical ocean distributions during the stage 2 glacial maximum. Annual Review of Earth and Planetary Sciences 20, 245-287.

Boyle, E.A., Sclater, F. and Edmond, J. (1976) On the marine geochemistry of cadmium. Nature 263, 42-44.

Bruland, K., Knauer, G. and Martin, J. (1978) Zinc in north-east Pacific water. Nature 271, 741-743.

Bryan, A.L., Dickson, A.J., Dowdall, F., Homoky, W.B., Porcelli, D. and Henderson, G.M. (2021) Controls on the cadmium isotope composition of modern marine sediments. Earth and Planetary Science Letters 565, 116946.

Bryan, S.P. and Marchitto, T.M. (2010) Testing the utility of paleonutrient proxies Cd/Ca and Zn/Ca in benthic foraminifera from thermocline waters. Geochemistry, Geophysics, Geosystems 11.

Clarkson, M.O., Stirling, C.H., Jenkyns, H.C., Dickson, A.J., Porcelli, D., Moy, C.M., von Strandmann, P.A.P., Cooke, I.R. and Lenton, T.M. (2018) Uranium isotope evidence for two episodes of deoxygenation during Oceanic Anoxic Event 2. Proceedings of the National Academy of Sciences 115, 2918-2923.

Conway, T.M. and John, S.G. (2015) Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. Geochimica et Cosmochimica Acta 148, 269-283.

Cortese, G. and Prebble, J. (2015) A radiolarian-based modern analogue dataset for palaeoenvironmental reconstructions in the southwest Pacific. Marine Micropaleontology 118, 34-49.

Dong, S. and Wasylenki, L.E. (2016) Zinc isotope fractionation during adsorption to calcite at high and low ionic strength. Chemical Geology 447, 70-78.

Druce, M., Stirling, C. and Rolison, J. (2020) High-precision zinc isotopic analysis of Certified Reference Materials relevant to the environmental, Earth and planetary sciences. Geostandards and Geoanalytical Research.

Ducher, M., Blanchard, M. and Balan, E. (2016) Equilibrium zinc isotope fractionation in Zn-bearing minerals from first-principles calculations. Chemical Geology 443, 87-96.

Ellwood, M.J. (2004) Zinc and cadmium speciation in subantarctic waters east of New Zealand. Marine Chemistry 87, 37-58.

Ellwood, M.J., Law, C.S., Hall, J., Woodward, E.M.S., Strzepek, R., Kuparinen, J., Thompson, K., Pickmere, S., Sutton, P. and Boyd, P.W. (2013) Relationships between nutrient stocks and inventories and phytoplankton physiological status along an oligotrophic meridional transect in the Tasman Sea. Deep Sea Research Part I: Oceanographic Research Papers 72, 102-120.

Framson, P.E. and Leckie, J.O. (1978) Limits of coprecipitation of cadmium and ferrous sulfides. Environmental Science & Technology 12, 465-469.

Frew, R.D. and Hunter, K.A. (1995) Cadmium-phosphorus cycling at the subtropical convergence south of New Zealand. Marine Chemistry 51, 223-237.

Fritz-Endres, T., and Fehrenbacher, J. (2021) Preferential loss of high trace element bearing inner calcite in foraminifera during physical and chemical cleaning. Geochemistry, Geophysics, Geosystems 22.1: e2020GC009419.

Fujii, T. and Albarede, F. (2012) Ab initio calculation of the Zn isotope effect in phosphates, citrates, and malates and applications to plants and soil. PLoS One 7.

Fujii, T., Moynier, F., Blichert-Toft, J. and Albarède, F. (2014) Density functional theory estimation of isotope fractionation of Fe, Ni, Cu, and Zn among species relevant to geochemical and biological environments. Geochimica et Cosmochimica Acta 140, 553-576.

Fujii, T., Moynier, F., Pons, M.-L. and Albarède, F. (2011) The origin of Zn isotope fractionation in sulfides. Geochimica et Cosmochimica Acta 75, 7632-7643.

Gault-Ringold, M., Adu, T., Stirling, C.H., Frew, R.D. and Hunter, K.A. (2012) Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: mechanistic constraints from cadmium isotopes. Earth and Planetary Science Letters 341, 94-103.

Gault-Ringold, M. and Stirling, C.H. (2012) Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS. Journal of Analytical Atomic Spectrometry 27, 449-459.

Gélabert, A., Pokrovsky, O.S., Viers, J., Schott, J., Boudou, A. and Feurtet-Mazel, A. (2006). Interaction between zinc and freshwater and marine diatom species: surface complexation and Zn isotope fractionation. Geochimica et Cosmochimica Acta, 70, 839-857.

George, E., Stirling, C.H., Gault-Ringold, M., Ellwood, M.J. and Middag, R. (2019) Marine biogeochemical cycling of cadmium and cadmium isotopes in the extreme nutrient-depleted subtropical gyre of the South West Pacific Ocean. Earth and Planetary Science Letters 514, 84-95.

Guinoiseau, D., Galer, S.J. and Abouchami, W. (2018) Effect of cadmium sulphide precipitation on the partitioning of Cd isotopes: Implications for the oceanic Cd cycle. Earth and Planetary Science Letters 498, 300-308.

Hancock, J.M. (1975) The petrology of the Chalk. Proceedings of the Geologists' Association 86, 499-535.

Hendry, K.R. and Andersen, M.B. (2013) The zinc isotopic composition of siliceous marine sponges: investigating nature's sediment traps. Chemical Geology 354, 33-41.

Hohl, S., Galer, S., Gamper, A. and Becker, H. (2017) Cadmium isotope variations in Neoproterozoic carbonates–A tracer of biologic production? Geochemical Perspectives Letters 3, 32-44.

Horner, T., Little, S., Conway, T., Farmer, J., Hertzberg, J., Janssen, D., Lough, A., McKay, J., Tessin, A. and Galer, S. (2020) Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data. Wiley Online Library.

Horner, T., Schönbächler, M., Rehkämper, M., Nielsen, S., Williams, H., Halliday, A., Xue, Z. and Hein, J. (2010) Ferromanganese crusts as archives of deep water Cd isotope compositions. Geochemistry, Geophysics, Geosystems 11.

Horner, T.J., Rickaby, R.E. and Henderson, G.M. (2011) Isotopic fractionation of cadmium into calcite. Earth and Planetary Science Letters 312, 243-253.

Hunter, K.A. and Ho, F.W. (1991) Phosphorus-cadmium cycling in the northeast Tasman Sea, 35–40° S. Marine Chemistry 33, 279-298.

Janssen, D.J., Conway, T.M., John, S.G., Christian, J.R., Kramer, D.I., Pedersen, T.F. and Cullen, J.T. (2014) Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. Proceedings of the National Academy of Sciences 111, 6888-6893.

John, S.G. and Conway, T.M. (2014) A role for scavenging in the marine biogeochemical cycling of zinc and zinc isotopes. Earth and Planetary Science Letters 394, 159-167.

John, S.G., Geis, R.W., Saito, M.A. and Boyle, E.A. (2007) Zinc isotope fractionation during high-affinity and low-affinity zinc transport by the marine diatom Thalassiosira oceanica. Limnology and Oceanography 52, 2710-2714.

John, S.G., Kunzmann, M., Townsend, E.J. and Rosenberg, A.D. (2017) Zinc and cadmium stable isotopes in the geological record: A case study from the post-snowball Earth Nuccaleena cap dolostone. Palaeogeography, Palaeoclimatology, Palaeoecology 466, 202-208.

Köbberich, M. and Vance, D. (2019) Zn isotope fractionation during uptake into marine phytoplankton: Implications for oceanic zinc isotopes. Chemical Geology 523, 154-161.

Kunzmann, M., Halverson, G.P., Sossi, P.A., Raub, T.D., Payne, J.L. and Kirby, J. (2013) Zn isotope evidence for immediate resumption of primary productivity after snowball Earth. Geology 41, 27-30.

Lacan, F., Francois, R., Ji, Y. and Sherrell, R.M. (2006) Cadmium isotopic composition in the ocean. Geochimica et cosmochimica acta 70, 5104-5118.

Linnert, C., Mutterlose, J. and Mortimore, R. (2011) Calcareous nannofossils from Eastbourne (southeastern England) and the paleoceanography of the Cenomanian–Turonian boundary interval. Palaios 26, 298-313.

Little, S., Sherman, D., Vance, D. and Hein, J. (2014a) Molecular controls on Cu and Zn isotopic fractionation in Fe–Mn crusts. Earth and Planetary Science Letters 396, 213-222.

Little, S., Vance, D., Walker-Brown, C. and Landing, W. (2014b) The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments. Geochimica et Cosmochimica Acta 125, 673-693.

Little, S.H., Wilson, D.J., Rehkämper, M., Adkins, J.F., Robinson, L.F. and van de Flierdt, T. (2021) Cold-water corals as archives of seawater Zn and Cu isotopes. Chemical Geology 578, 120304.

Marchitto, T.M., Curry, W.B. and Oppo, D.W. (1998) Millennial-scale changes in North Atlantic circulation since the last glaciation. Nature 393, 557-561.

Marchitto, T.M., Curry, W.B. and Oppo, D.W. (2000) Zinc concentrations in benthic foraminifera reflect seawater chemistry. Paleoceanography 15, 299-306.

Marchitto, T.M., Lynch-Stieglitz, J. and Hemming, S.R. (2005) Deep Pacific CaCO3 compensation and glacial–interglacial atmospheric CO2. Earth and Planetary Science Letters 231, 317-336.

Marchitto, T.M., Oppo, D.W. and Curry, W.B. (2002) Paired benthic foraminiferal Cd/Ca and Zn/Ca evidence for a greatly increased presence of Southern Ocean Water in the glacial North Atlantic. Paleoceanography 17, 10-11-10-18.

Maréchal, C.N., Nicolas, E., Douchet, C. and Albarède, F. (2000) Abundance of zinc isotopes as a marine biogeochemical tracer. Geochemistry, Geophysics, Geosystems 1.

Marr, J.P., Bostock, H.C., Carter, L., Bolton, A. and Smith, E. (2013a) Differential effects of cleaning procedures on the trace element chemistry of planktonic foraminifera. Chemical Geology 351, 310-323.

Marr, J.P., Carter, L., Bostock, H.C., Bolton, A. and Smith, E. (2013b) Southwest Pacific Ocean response to a warming world: Using Mg/Ca, Zn/Ca, and Mn/Ca in foraminifera to track surface ocean water masses during the last deglaciation. Paleoceanography 28, 347-362.

Mavromatis, V., González, A.G., Dietzel, M. and Schott, J. (2019) Zinc isotope fractionation during the inorganic precipitation of calcite–Towards a new pH proxy. Geochimica et Cosmochimica Acta 244, 99-112.

McCorkle, D.C., Martin, P.A., Lea, D.W. and Klinkhammer, G.P. (1995) Evidence of a dissolution effect on benthic foraminiferal shell chemistry: δ13C, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau. Paleoceanography 10, 699-714.

Morel, F., Reinfelder, J., Roberts, S., Chamberlain, C., Lee, J. and Yee, D. (1994) Zinc and carbon co-limitation of marine phytoplankton. Nature 369, 740-742.

Owens, J.D., Gill, B.C., Jenkyns, H.C., Bates, S.M., Severmann, S., Kuypers, M.M., Woodfine, R.G. and Lyons, T.W. (2013) Sulfur isotopes track the global extent and dynamics of euxinia during Cretaceous Oceanic Anoxic Event 2. Proceedings of the National Academy of Sciences 110, 18407-18412.

Owens, J.D., Lyons, T.W., Li, X., Macleod, K.G., Gordon, G., Kuypers, M.M., Anbar, A., Kuhnt, W. and Severmann, S. (2012) Iron isotope and trace metal records of iron cycling in the proto-North Atlantic during the Cenomanian-Turonian oceanic anoxic event (OAE-2). Paleoceanography 27.

Panfili, F., Schneider, A., Vives, A., Perrot, F., Hubert, P. and Pellerin, S. (2009) Cadmium uptake by durum wheat in presence of citrate. Plant and soil 316, 299-309.

Pichat, S., Douchet, C. and Albarède, F. (2003) Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. Earth and Planetary Science Letters 210, 167-178.

Prebble, J., Crouch, E., Carter, L., Cortese, G., Bostock, H. and Neil, H. (2013) An expanded modern dinoflagellate cyst dataset for the Southwest Pacific and Southern Hemisphere with environmental associations. Marine Micropaleontology 101, 33-48.

Price, N. and Morel, F. (1990) Cadmium and cobalt substitution for zinc in a marine diatom. Nature 344, 658-660.

Read, J., Lucas, M., Holley, S. and Pollard, R. (2000) Phytoplankton, nutrients and hydrography in the frontal zone between the Southwest Indian Subtropical gyre and the Southern Ocean. Deep Sea Research Part I: Oceanographic Research Papers 47, 2341-2367.

Rickaby, R. and Elderfield, H. (1999) Planktonic foraminiferal Cd/Ca: paleonutrients or paleotemperature? Paleoceanography 14, 293-303.

Ripperger, S. and Rehkämper, M. (2007) Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. Geochimica et cosmochimica acta 71, 631-642.

Ripperger, S., Schiebel, R., Rehkämper, M. and Halliday, A.N. (2008) Cd/Ca ratios of in situ collected planktonic foraminiferal tests. Paleoceanography 23.

Rolison, J.M., Stirling, C.H., Middag, R., Gault-Ringold, M., George, E. and Rijkenberg, M.J. (2018) Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue. Earth and Planetary Science Letters 488, 1-13.

Romero, O., Kim, J.H., Bárcena, M., Hall, I.R., Zahn, R. and Schneider, R. (2015) High-latitude forcing of diatom productivity in the southern Agulhas Plateau during the past 350 kyr. Paleoceanography 30, 118-132.

Rosenthal, Y., Boyle, E., Labeyrie, L. and Oppo, D. (1995) Glacial enrichments of authigenic Cd and U in Subantarctic sediments: A climatic control on the elements' oceanic budget? Paleoceanography 10, 395-413.

Rosenthal, Y., Boyle, E.A. and Labeyrie, L. (1997) Last glacial maximum paleochemistry and deepwater circulation in the Southern Ocean: Evidence from foraminiferal cadmium. Paleoceanography 12, 787-796.

Samanta, M., Ellwood, M.J., Sinoir, M. and Hassler, C.S. (2017) Dissolved zinc isotope cycling in the Tasman Sea, SW Pacific Ocean. Marine Chemistry 192, 1-12.

Schlitzer, R., Anderson, R.F., Dodas, E.M., Lohan, M., Geibert, W., Tagliabue, A., Bowie, A., Jeandel, C., Maldonado, M.T. and Landing, W.M. (2018) The GEOTRACES intermediate data product 2017. Chemical Geology 493, 210-223.

Schmitt, A.-D., Galer, S.J. and Abouchami, W. (2009) Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. Earth and Planetary Science Letters 277, 262-272.

Schmittner, A., Bostock, H.C., Cartapanis, O., Curry, W.B., Filipsson, H.L., Galbraith, E.D., Gottschalk, J., Herguera, J.C., Hoogakker, B. and Jaccard, S.L. (2017) Calibration of the carbon isotope composition (δ13C) of benthic foraminifera. Paleoceanography 32, 512-530.

Sieber, M., Conway, T.M., de Souza, G., Hassler, C.S., Ellwood, M.J. and Vance, D. (2020) Cycling of zinc and its isotopes across multiple zones of the Southern Ocean: Insights from the Antarctic Circumnavigation Expedition. Geochimica et Cosmochimica Acta 268, 310-324.

Sinoir, M., Ellwood, M.J., Butler, E.C., Bowie, A.R., Mongin, M. and Hassler, C.S. (2016) Zinc cycling in the Tasman Sea: distribution, speciation and relation to phytoplankton community. Marine Chemistry 182, 25-37.

Sweere, T.C., Dickson, A.J., Jenkyns, H.C., Porcelli, D., Elrick, M., van den Boorn, S.H. and Henderson, G.M. (2018) Isotopic evidence for changes in the zinc cycle during Oceanic Anoxic Event 2 (Late Cretaceous). Geology 46, 463-466.

Tendal, O. and Lewis, K. (1978) New Zealand xenophyophores: upper bathyal distribution, photographs of growth position, and a new species. New Zealand journal of marine and freshwater research 12, 197-203.

Tessier, A., Campbell, P.G. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry 51, 844-851.

Tsikos, H., Jenkyns, H., Walsworth-Bell, B., Petrizzo, M., Forster, A., Kolonic, S., Erba, E., Silva, I.P., Baas, M. and Wagner, T. (2004) Carbon-isotope stratigraphy recorded by the Cenomanian–Turonian Oceanic Anoxic Event: correlation and implications based on three key localities. Journal of the Geological Society 161, 711-719.

Urey, H.C. (1947) The thermodynamic properties of isotopic substances. Journal of the Chemical Society (Resumed), 562-581.

van Dijk, I., de Nooijer, L.J., Wolthers, M. and Reichart, G.-J. (2017) Impacts of pH and [CO32−] on the incorporation of Zn in foraminiferal calcite. Geochimica et Cosmochimica Acta 197, 263-277.

Vance, D., Little, S.H., Archer, C., Cameron, V., Andersen, M.B., Rijkenberg, M.J. and Lyons, T.W. (2016) The oceanic budgets of nickel and zinc isotopes: the importance of sulfidic environments as illustrated by the Black Sea. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 374, 20150294.

Veeramani, H., Eagling, J., Jamieson-Hanes, J.H., Kong, L., Ptacek, C.J. and Blowes, D.W. (2015) Zinc isotope fractionation as an indicator of geochemical attenuation processes. Environmental Science & Technology Letters 2, 314-319.

Wyatt, N., Milne, A., Woodward, E., Rees, A., Browning, T., Bouman, H., Worsfold, P. and Lohan, M. (2014) Biogeochemical cycling of dissolved zinc along the GEOTRACES South Atlantic transect GA10 at 40 S. Global Biogeochemical Cycles 28, 44-56.

Wyrzykowski, D. and Chmurzyński, L. (2010) Thermodynamics of citrate complexation with Mn2+, Co2+, Ni2+ and Zn2+ ions. Journal of thermal analysis and calorimetry 102, 61-64.

Xiao, H., Deng, W., Wei, G., Chen, J., Zheng, X., Shi, T., Chen, X., Wang, C., Liu, X. and Zeng, T. (2020) A Pilot Study on Zinc Isotopic Compositions in Shallow-Water Coral Skeletons. Geochemistry, Geophysics, Geosystems 21, e2020GC009430.

Xie, X., Yan, L., Li, J., Guan, L. and Chi, Z. (2021) Cadmium isotope fractionation during Cd-calcite coprecipitation: insight from batch experiment. Science of The Total Environment 760, 143330.

Xu, Y., Feng, L., Jeffrey, P.D., Shi, Y. and Morel, F.M. (2008) Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. Nature 452, 56-61.

Yu, J., Elderfield, H., Greaves, M. and Day, J. (2007) Preferential dissolution of benthic foraminiferal calcite during laboratory reductive cleaning. Geochemistry, Geophysics, Geosystems 8.

Zhao, M., Tarhan, L.G., Zhang, Y., Hood, A., Asael, D., Reid, R.P. and Planavsky, N.J. (2021) Evaluation of shallow-water carbonates as a seawater zinc isotope archive. Earth and Planetary Science Letters 553, 116599.

Zhao, Y., Vance, D., Abouchami, W. and De Baar, H.J. (2014) Biogeochemical cycling of zinc and its isotopes in the Southern Ocean. Geochimica et Cosmochimica Acta 125, 653-672.

Zorrig, W., Rouached, A., Shahzad, Z., Abdelly, C., Davidian, J.-C. and Berthomieu, P. (2010) Identification of three relationships linking cadmium accumulation to cadmium tolerance and zinc and citrate accumulation in lettuce. Journal of Plant Physiology 167, 1239-1247.

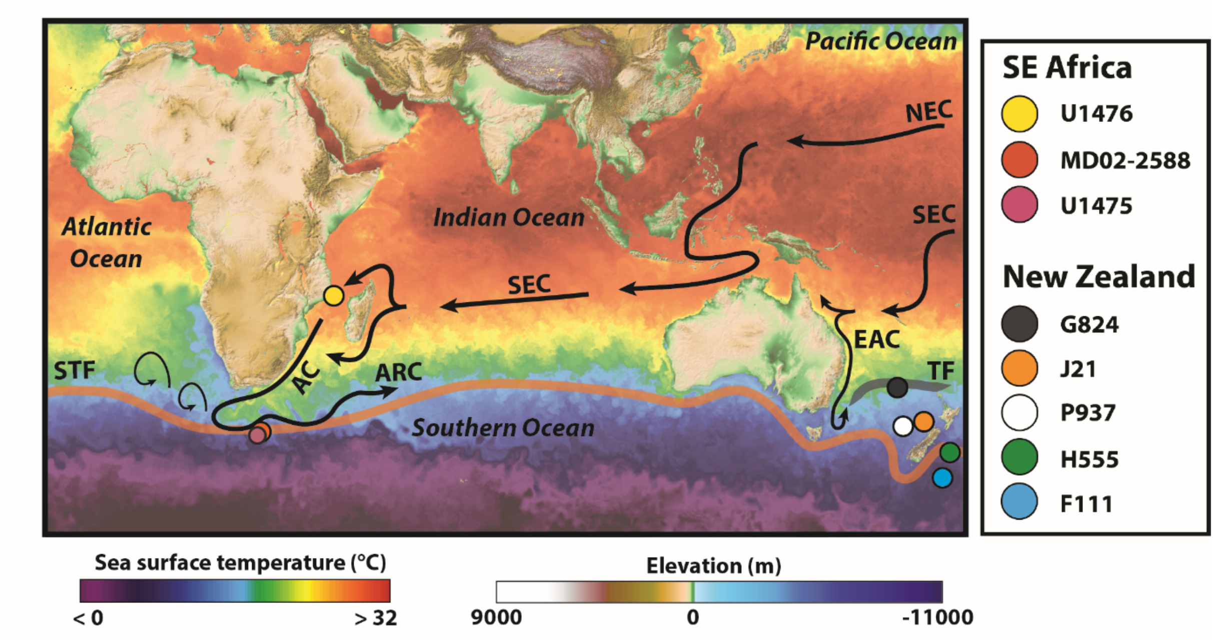

Figure 1: Location of carbonate-rich Holocene sediment from the New Zealand and southeast African continental margins overlain on a SST map. From north-south, sites include U1476, G824, J21, P937, MD02-2588 and U1475, H555 and F111. Major surface currents (black arrows) and the position of the Subtropical Front (STF; in orange) are shown. Acronyms: North Equatorial Current (NEC), South Equatorial Current (SEC), East Australian Current (EAC), Agulhas Current (AC), Agulhas Return Current (ARC), Tasman Front (TF).

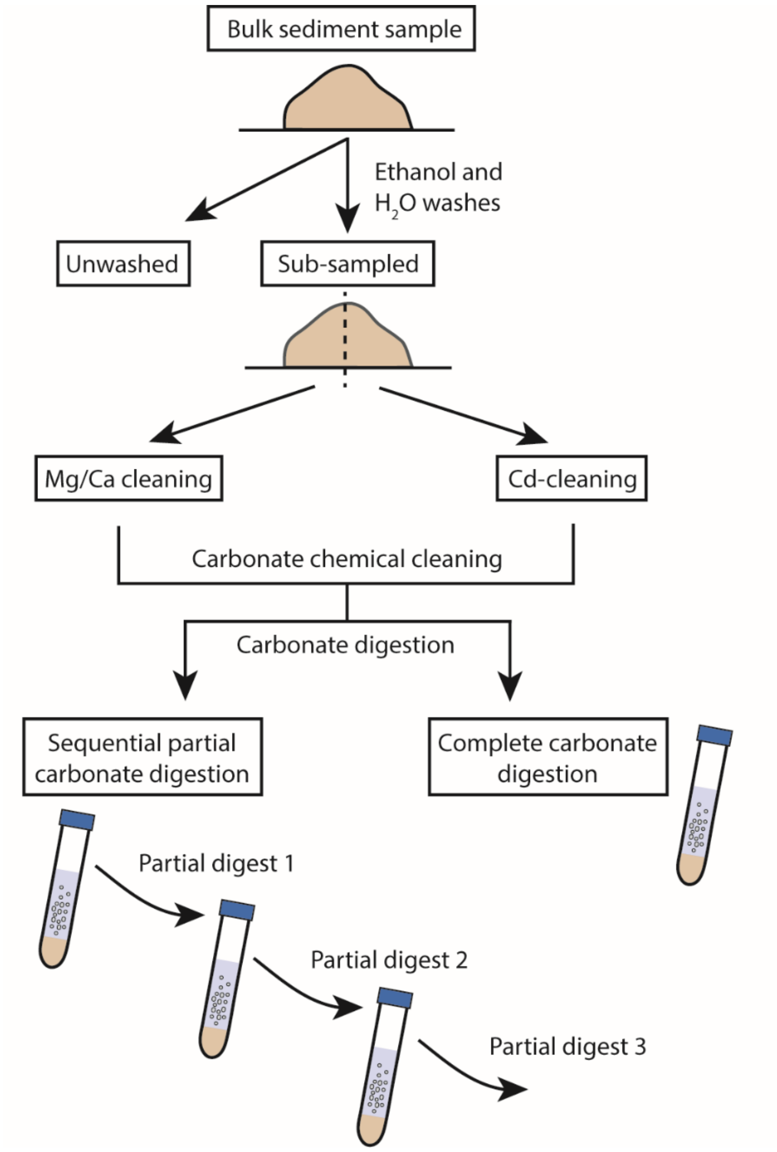

Figure 2: Protocol for bulk sediment preparation that includes; (i) obtaining an unwashed aliquot, (ii) pre-cleaning using ethanol and H_2O rinses, (iii) sub-sampling, (iv) processing using either the Mg/Ca cleaning method that uses an oxidative step only to remove organic matter and sulphides, or the Cd-cleaning method that uses reductive and oxidative cleaning to additionally remove Fe-Mn (oxyhydr)oxide coatings. Finally (v), the carbonate phase of the chemically cleaned sediment is selectively digested to completion, or sequentially partially digested a total of three times. Each digest is collected for analysis.

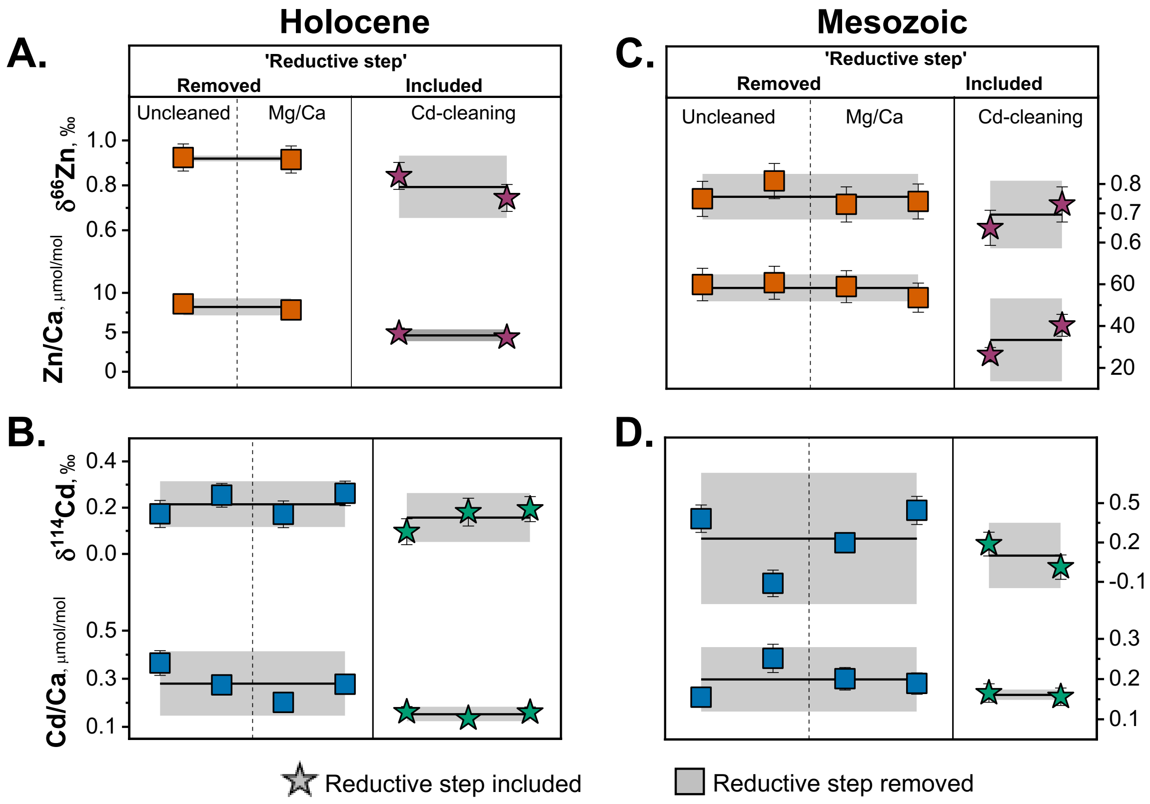

Figure 3: Carbonate δ^{66}Zn and Zn/Ca (A), and δ^{114}Cd and Cd/Ca (B) of the Holocene bulk sediment from site G824 digested to completion, (C) and (D) show results for the Mesozoic bulk sediment PM680. Samples processed without any carbonate chemical cleaning steps applied (uncleaned), or using the Mg/Ca cleaning method (Mg/Ca) that includes an oxidative step only are shown (orange and blue symbols for the Zn and Cd systems, respectively). Inclusion of the reductive step (purple and green stars for the Zn and Cd systems, respectively) in addition to an oxidative step during chemical cleaning follows the Cd-cleaning method (Cd-cleaning). The 2SD limits are shown in grey shading for repeat analyses of bulk sediment sub-samples processed using the Mg/Ca and Cd-cleaning methods.

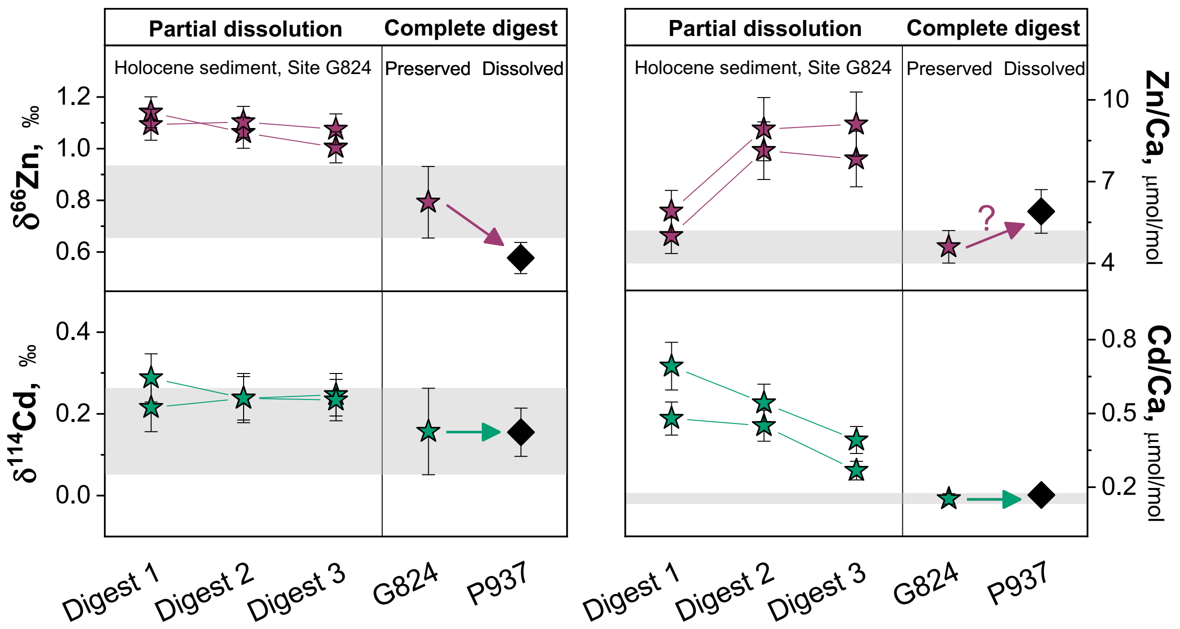

Figure 4: The δ^{66}Zn, δ^{114}Cd, Zn/Ca and Cd/Ca systematics in the carbonate digest during the sequential partial carbonate dissolution experiment (*partial dissolution*) from step 1 through to step 3 for the Holocene bulk sediment from site G824. Samples were chemically cleaned using the Cd-cleaning method that includes the reductive step (purple and green stars for the Zn and Cd systems, respectively). Mean δ^{66}Zn, δ^{114}Cd, Zn/Ca and Cd/Ca for the Holocene sediments leached to completion are shown for reference (*complete*, grey shading) alongside their respective 2SD. The δ^{66}Zn, δ^{114}Cd, Zn/Ca and Cd/Ca (black diamonds) of the carbonate phase digested to completion for the Holocene bulk sediment from site P937 following Cd-cleaning that was retrieved from the carbonate saturation horizon and is therefore naturally dissolved. Arrows indicate the potential direction of fractionation observed between well-preserved and partially digested sediments obtained from a similar water mass.

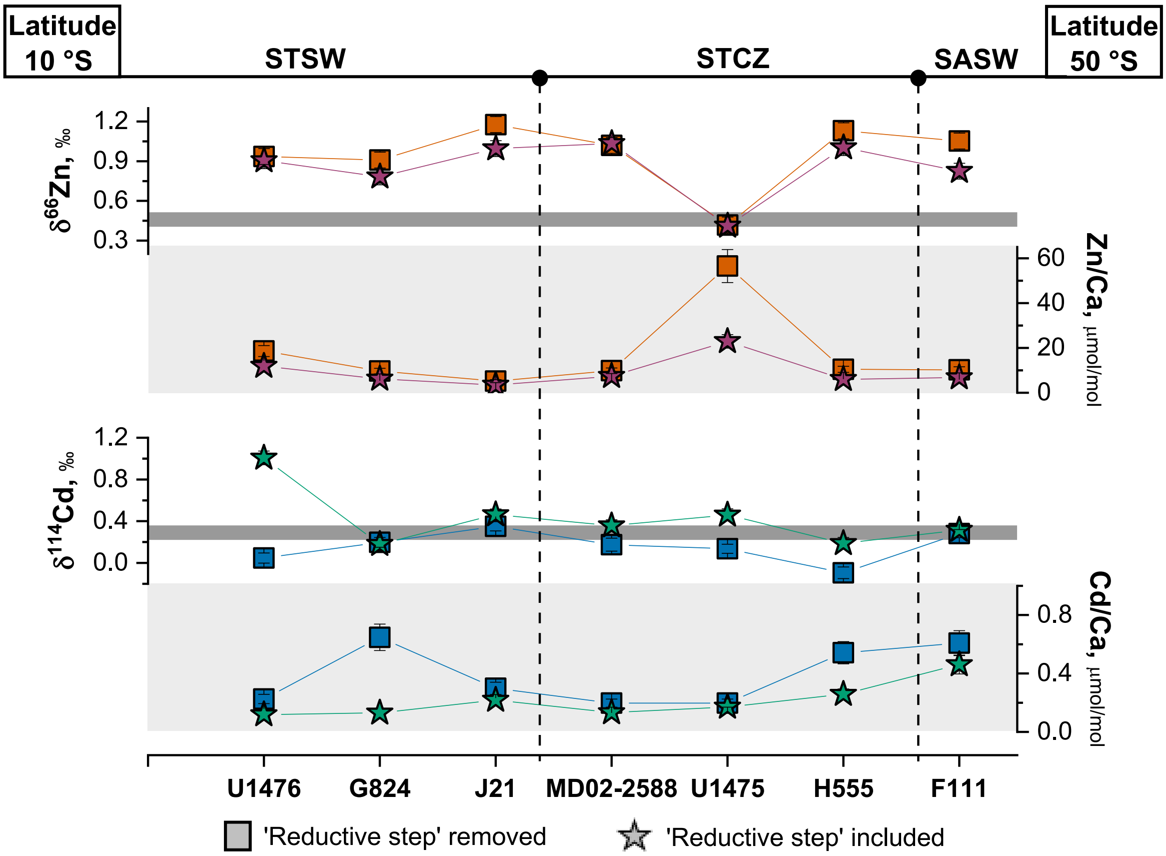

Figure 5: Measured $\delta^{66}Zn$ and Zn/Ca (upper two plots) in the carbonate phase digested to completion for the transect of Holocene (<11 ka) bulk sediments from the New Zealand and southeast African continental margins. Samples were chemically cleaned with the reductive step removed (orange squares) and with this step is included (purple stars). The $\delta^{114}Cd$ and Cd/Ca (lower two plots) are shown for sub-samples processed with the reductive step removed (blue squares) and included (green stars). The average seawater $\delta^{66}Zn$ of 0.46 ± 0.11 ‰ (2SD) and $\delta^{114}Cd$ of 0.28 ± 0.15 ‰ (2SD) from 0-50 °S and below 1000 m depth, respectively, are also shown (shaded horizontal bar). From north-south, samples were retrieved from sites U1476, G824, J21, MD02-2588, U1475, H555, and F111 (see map in figure 2). Major surface water masses include subtropical surface water (STSW) and subantarctic surface water (SASW), and the position of the Subtropical Convergence Zone (STCZ) is shown that comprises both STSW and SASW (figure 2).

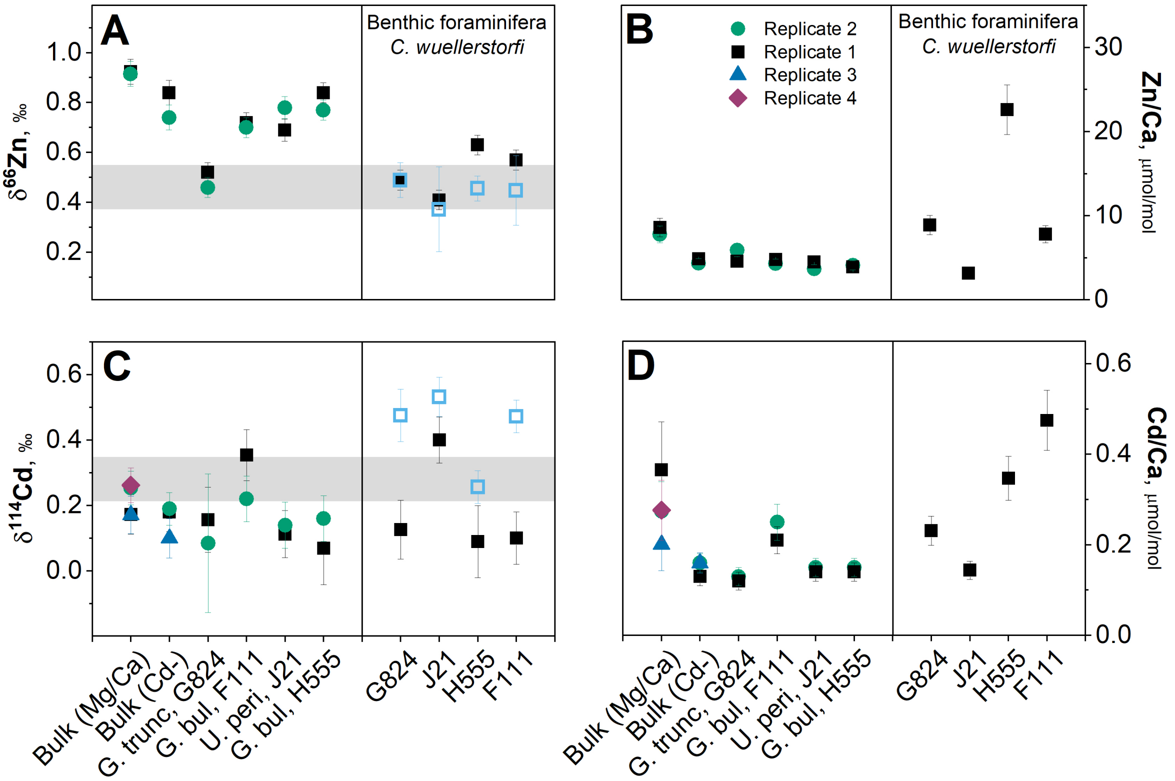

Figure 6: Replicate analysis of (A) δ^{66}Zn, (B) Zn/Ca, (C) δ^{114}Cd and (D) Cd/Ca for independently processed sub-samples of Holocene bulk sediment G824 and individual species of hand-picked foraminifera, including *G. truncatulinoides* (*G. trunc*), *G. bulloides* (*G. bul*) and *U. peregrina* (*U. per*) from sites G824, F111, J21 and H555 showing very good agreement. Samples are processed with the reductive step included using the Cd-cleaning method (Cd-) unless otherwise stated (Mg/Ca; Mg/Ca cleaning method). Accuracy is determined through analyses of the foraminifera species *C. wuellerstorfi* that lives at the sediment-water interface in the oceanic bottom waters. The mean seawater δ^{66}Zn and δ^{114}Cd (grey bands) of 0.46 ± 0.11 ‰ (2SD) and 0.28 ± 0.15 ‰ (2SD) from 0-50°S and below1000 m depth, respectively, and at a similar seawater depth to sediment the retrieval depth at each sample site is also given (open blue squares, 1SD).

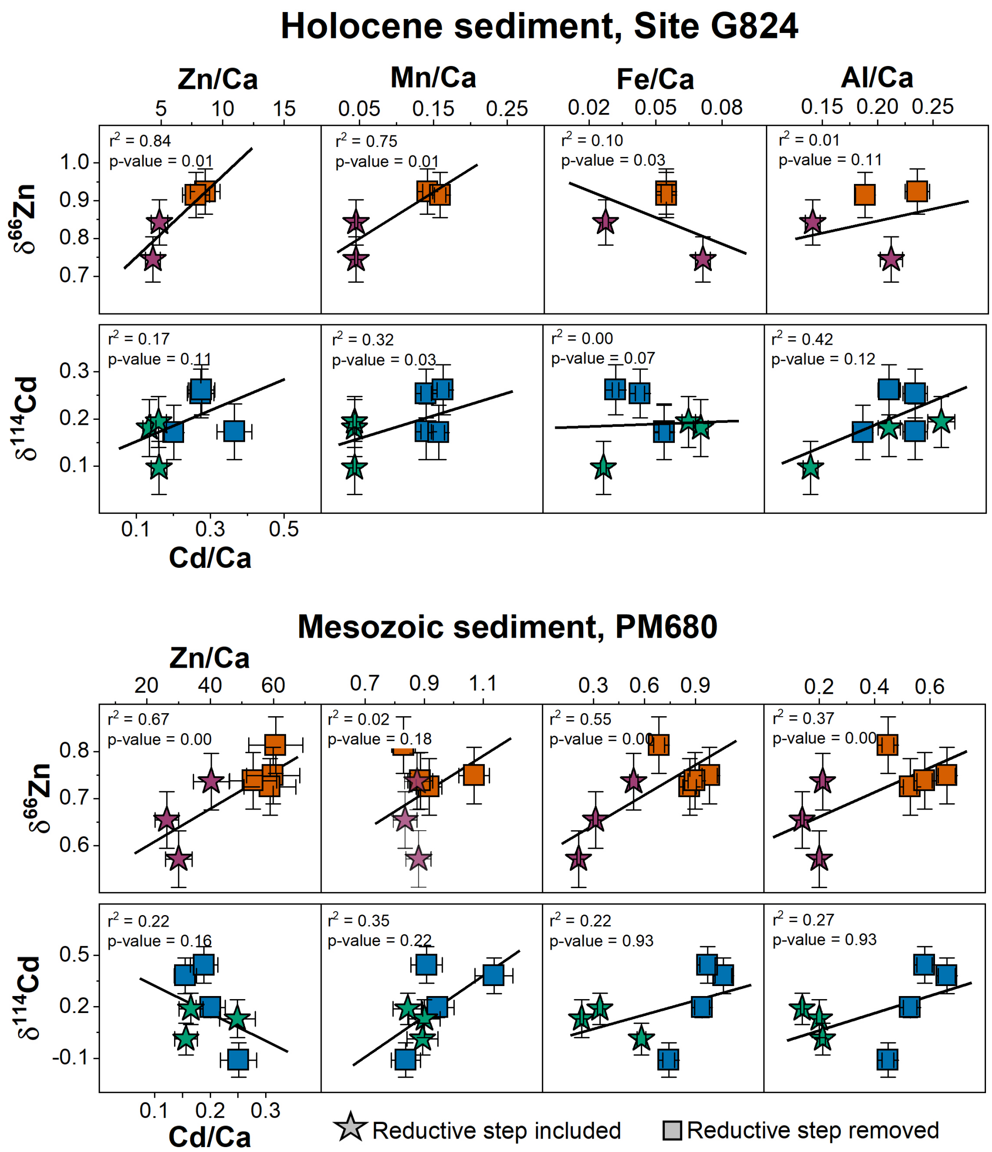

Figure 7: The $\delta^{66}Zn$ and $\delta^{114}Cd$ in the carbonate digest for aliquots of the Holocene bulk carbonate from site G824 digested to completion is shown (upper panel) and the Mesozoic sediment PM680 (lower panel), compared with Zn/Ca, Cd/Ca, Mn/Ca, Fe/Ca and Al/Ca. Samples processed without the reductive step applied (orange and blue squares for the Zn and Cd systems, respectively) and with its inclusion (purple and green stars for the Zn and Cd systems, respectively). The r^2 value and p-value for each of the correlations is given alongside the line of best fit.