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Cretaceous calcareous dinoflagellate cysts as recorder of $\delta^{44/40}Ca_{seawater}$ and paleo-temperature using Sr/Ca thermometry

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ABSTRACT

We evaluate the potential of calcareous dinoflagellates as archives for Sr/Ca-based paleo-temperature reconstructions and $\delta^{44/40}Ca_{seawater}$ fluctuations on sediments from Ocean Drilling Program Expedition 113 (Hole 690C, Weddell Sea, Southern Ocean). Between 73 and 68 Ma, Sr/Ca ratios of two Cretaceous dinoflagellate species, *Pirumella krasheninnikovii* and *Orthopithonella globosa* show a pronounced decrease, consistent with a significant drop in sea-surface temperature as reflected by the $\delta^{18}O$ of planktic foraminifers. The apparent temperature sensitivity of the dinoflagellate cysts' Sr/Ca is ~0.06 and ~0.08 mmol/mol °C^{-1}, using $\delta^{18}O$-derived paleo sea-surface temperatures, which is significant and large enough to resolve paleoenvironmental temperature changes at current analytical precision. As the chemical composition of the cyst calcite appears to have a good preservation, the Sr/Ca of calcareous dinoflagellates has a potential to serve as paleo-temperature proxy, although the chemical composition of the Cretaceous seawater and potential impacts on the cyst geochemistry is pending further inspection.

The Ca isotope composition of the two dinoflagellate species shows identical trends of increasing $\delta^{44/40}Ca$ between 73 and 67 Ma. The planktic foraminifer *Archaeoglobigerina australis* and the benthic foraminifer *Nuttallides truempyi* reveal the same increase of about 0.4‰ but are offset relative to the dinoflagellates by about +0.5‰, presumably due to species-specific Ca isotope fractionation. Bulk carbonate sediment shows significant scatter, likely caused by changes in faunal composition and does not reproduce the trend revealed by the dinoflagellate and foraminifer records. These observations demonstrate the importance of taxon-specific records and careful determination of fractionation factors of selected archives and highlight complications arising from utilizing less suitable archives, such as bulk sediments, for $\delta^{44/40}Ca_{seawater}$ reconstructions. Our records indicate strong changes in the marine Ca cycle associated with the global temperature decrease towards the end of the Cretaceous.

1. Introduction

Paleoenvironmental reconstructions based on reliable proxies are fundamental for our understanding of Earth's history and the development and/or verification of climate models. The interpretation of proxy data, however, is in some cases complicated as a proxy signal can be ambiguous or different proxies may provide discrepant results. Consequently, the development and validation of new proxies is important for future advances in paleo-environmental research. Among other calcareous microfossil groups, calcareous dinoflagellates have shown a great potential to serve as recorder of past environmental conditions and received recently increasing attention (Zonneveld et al., 2007; Minnoletti et al., 2014; Kohn and Zonneveld, 2010; Kohn et al., 2011; Ziveri et al., 2012; Van de Waal et al., 2013). Dinoflagellates can form cysts composed of organic-material, silicate or calcium carbonate and significantly contribute to the oceanic primary production. Since the morphology of their cysts is species-specific, they are often used as stratigraphic and/or paleoenvironmental indicators (Willems, 1995; Vink et al., 2001; Vink et al., 2002; Esper and Zonneveld, 2007; Radi et al., 2007; Marret et al., 2008). The dinoflagellates that form calcite cysts, the so-called calcareous dinoflagellates, provide archives for long-term changes in ocean chemistry and past environmental changes (e.g. Hildebrand-Habel and Willems, 2000). Dinoflagellate cysts form at the deep chlorophyll maximum depth in the water column (Zonneveld, 2004), and are thus particularly useful as proxy archives recording ocean surface conditions (e.g. temperature and pH). Furthermore, the applicability as long-term archive is indicated by the observation that their cysts are comparatively insensitive to dissolution (Zonneveld,

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2004).

For the modern ocean, it has been shown that the $\delta^{18}O$ of the dominant calcareous dinoflagellate species *Thoracosphaera heimii* records sea-surface temperatures (SST) in specimens from laboratory cultures, surface waters and sediment samples (e.g. Zonneveld, 2004; Zonneveld et al., 2007; Minnoletti et al., 2014; Kohn and Zonneveld, 2010; Kohn et al., 2011; Heinrich et al., 2011). However, recent studies suggest that in addition to temperature, the carbonate ion concentration of sea water also impacts $\delta^{18}O$ and $\delta^{13}C$ of *T. heimii* cysts (Ziveri et al., 2012; Van de Waal et al., 2013).

Besides promising proxy results obtained from faunal analyses of dinoflagellate species and stable oxygen and carbon isotopes analyses on the dominant calcareous species *T. heimii*, culture experiments have demonstrated a significant dependence of Sr/Ca ratios of *T. heimii* cysts on temperature (Gussone et al., 2010). The reported temperature sensitivity of 0.016 mmol/mol °C^{-1} is sufficiently large to be applied as SST proxy and was suggested to be used for unravelling the influences of salinity and temperature on the $\delta^{18}O$ of carbonate shells. Furthermore, Ca isotope fractionation in cultured *T. heimii* does not depend on the environmental parameters salinity and pH, and shows only a small, insignificant, temperature dependence of (0.005 ± 0.005‰/°C), suggesting that dinoflagellates are promising archive for the reconstruction of $\delta^{44/40}Ca_{seawater}$ through Earth history (Gussone et al., 2010).

In this study, we aim to test the applicability and preservation potential of calcareous dinoflagellate cysts as recorders of paleo-SSTs using Sr/Ca ratios and as a measure for changes in the oceanic Ca budget over geological time scales using $\delta^{44/40}Ca$. We present new Sr/Ca and $\delta^{44/40}Ca$ analyses of two Campanian/Maastrichtian calcareous dinoflagellate species from the southern South Atlantic (ODP Hole 690C, Maud Rise, Weddell Sea) and compare them to $\delta^{44/40}Ca$ of benthic and planktic foraminifers, which are, apart from the dinoflagellates the most abundant microfossils in these sediments and can be separated for monospecific subsamples. This approach using multiple-monospecific subsamples is applied, because it reduces the risk of interferences of environmental parameters, such as temperature, on Ca isotope fractionation or changes of the taxon-specific fractionation characteristics over time. This risk is more pronounced in older records, because of the different and less known ocean chemistry (e.g. pH, Ca^{2+} and carbonate ion concentration). The dinoflagellate records shed new light on the applicability of calcareous dinoflagellate cyst Sr/Ca ratios as paleo-SST proxy and Ca isotope seawater recorder. Furthermore, they allow us to estimate Sr/Ca ratios of Late Cretaceous seawater, which is poorly constrained, as previous reconstructions are highly variable ranging from about two to 14 mmol/mol (Coggon et al., 2010, Lear et al., 2003, Tripati et al., 2009, Steuber and Veizer, 2002). The new records of microfossil $\delta^{44/40}Ca$ are used to reconstruct $\delta^{44/40}Ca_{seawater}$ fluctuations through the Late Campanian to Maastrichtian, a time interval that is marked by the transition from the super-greenhouse climate of the middle Cretaceous to the cooler Cenozoic climate (Huber et al., 2002; Friedrich et al., 2012) and important perturbations of the global C cycle during e.g. the so-called Campanian/Maastrichtian boundary event (e.g., Barrera et al., 1997; Barrera and Savin, 1999; Friedrich et al., 2009) or the mid-Maastrichtian Event (e.g., MacLeod and Huber, 1996; Jung et al., 2013).

2. Material and methods

2.1. Sampling site and sample material

We investigated microfossils from sediments of ODP Hole 690C (Expedition 113) located at the southwestern flank of Maud Rise (eastern Weddell Sea, southern South Atlantic; 65°09.62′ S; 1°12.28′ E; Fig. 1), a site close to the potential source region of Late Cretaceous southern component waters (e.g. Friedrich et al., 2009; Robinson et al., 2010). Campanian/Maastrichtian sediments at Hole 690C are composed of calcareous chalks and oozes (Shipboard Scientific Party, 1988)

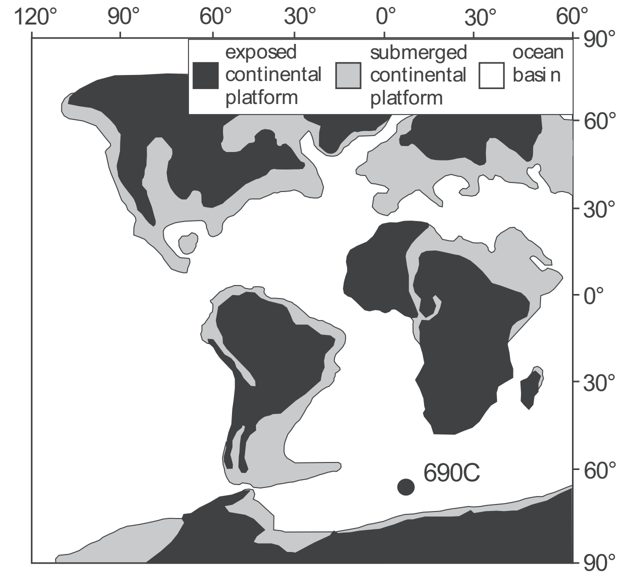

Fig. 1. Sample location. ODP Site 690 located in the Weddel Sea, close to the potential source region of Late Cretaceous southern component waters (e.g. Friedrich et al., 2009; Robinson et al., 2010). Paleogeographic reconstruction of the Maastrichtian modified after Li and Keller (1998).

deposited in an estimated paleo-water depth of ~1800 m (Thomas, 1990). From the time interval 73–68 Ma (based on the age model provided in Barrera and Savin, 1999), we separated calcareous cysts of the abundant dinoflagellate species *Pirumella krasheninnikovii* and *Orthopithonella globosa* from the size fraction 63–125 µm for the core interval 690C-17-1-29 cm to 690C-20-6-149 cm (Fig. 2, Tables 1 and 2). For these samples, $\delta^{18}O$ values of planktic foraminifers have been analyzed by Friedrich et al. (2009).

From the same samples, the benthic foraminifer *Nuttallides truempyi* and the planktic foraminifer *Archaeoglobigerina australis* were collected for Ca isotope analyses. The latter taxon has been chosen because it is supposed to reflect the upper mixed-layer (e.g., Huber et al., 1995; Barrera and Savin, 1999) and therefore the very same environment as it has been inferred for the two dinoflagellate cyst species investigated herein (Friedrich and Meier, 2003). *Nuttallides truempyi* has been chosen because it is a commonly used benthic species in Late Cretaceous geochemical studies.

In addition, bulk carbonate and the size fractions < 20 µm and 20–64 µm were analyzed for comparison (Table 2), as bulk carbonate sediment is still used as $\delta^{44/40}Ca_{seawater}$ archive, although serious concerns against this type of archive have been raised during the past decade (Sime et al., 2007; Gussone et al., 2007; Tipper et al., 2016). The bulk carbonate of the core is composed of foraminifer-bearing nannofossil ooze and chalk (Shipboard Scientific Party, 1988) and therefore mainly records a surface-water signal due to dominance of calcareous nannofossils and planktic foraminifers.

Preservation of the investigated calcareous microfossils is good to very good and most tests appear glassy when wet. They show no evidence of significant test dissolution, overgrowth or recrystallization as evidenced by light-microscope and scanning-electron microscope investigations (see studies by Barrera and Huber, 1990; Friedrich and Meier, 2003, 2006; Friedrich et al., 2009 for additional details).

2.2. Cleaning of microfossils

2.2.1. Dinoflagellate cysts

Calcareous dinoflagellate cysts (about 200 individuals per sample) were handpicked under the microscope and weighed. Samples where gently crushed and the cleaning procedure follows the method for Ca