Chapter 6
Synthese and perspectives
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6. Synthesis and perspectives

Ocean circulation is generally considered as one of the main players in the climate system. How certain ocean current systems have varied over time has a profound impact on climate and also the future climate is expected to be strongly affected by changes in ocean circulation. Specific parts of the global ocean circulation have been suggested to play a key role for global climate and the Agulhas current is one of those. The Agulhas current is fuelled, amongst others, by eddies originating from the Mozambique Channel. Within this thesis, several attempts are made to develop and calibrate potential proxies for the occurrence and intensity of eddies passing through Mozambique Channel. These eddy proxies are based on differences in the geochemical composition of foraminiferal shells from sediment traps, for which the link to eddy occurrence is known in real-time. As shown in chapter 2, other processes, such as seasonality, also impact the fluxes of different foraminiferal species during the year and hence the environmental conditions recorded in the chemistry of their shells. The reliability of the proxies suggested here, critically depends on the relative impact of the different processes on the annually integrated proxy signal and hence on the relative distribution of the different species throughout the year.

6.1. Robustness of the proxy signal

6.1.1. Potential Mg/Ca differences based on flux weighted averages

In order to test the potential application of the Mg/Ca eddy proxy (Chapter 3), annual shell flux data (Chapter 2) was combined with the mooring sea water temperatures and SST during MOZ4 of sediment trap samples that were centered on eddy and non-eddy intervals. In this way the average flux-weighted temperatures could be calculated for different species, taking into account their supposed depth migration (Fig. 6.1). By comparing the offset between the annual flux-weighted average to the flux-weighted averages for eddy and non-eddy periods, the robustness of the proxy signal can be assessed. This shows appreciable differences between the surface dwelling species *G. ruber* and the thermocline dwelling species *N. dutertrei* of 8.5°C during non-eddy conditions, compared to a reduced temperature offset of only 5.8° under eddy conditions. The temperature difference (ΔΔT) between eddy and non-eddy conditions thus is estimated to be about 3.6°C (Fig. 6.1a). Furthermore, the potential ΔT during eddy conditions between *N. dutertrei* and the sub-surface dweller *G. scitula*, based on temperatures at 400 m, is 7.6°C under non-eddy condition and becomes greater under eddy condition (10.3°C). This results into an effective ΔΔT of 2.7°C (Fig. 6.1). Both these offsets are well within...
the analytical resolution of Mg/Ca and δ¹⁸O-based temperature reconstructions. The slightly larger offset between *G. ruber* and *N. dutertrei* and the smaller offset between *N. dutertrei* and *G. scitula* is likely to be caused by the temperatures at the assumed depth habitats.

**Fig. 6.1:** a) Potential calcification temperatures of surface dwelling species *G. ruber*, thermocline dwelling *N. dutertrei* and deep dwelling species *G. scitula* are calculated. Mg/Ca based temperature are calculated applying species specific calibrations. For *G. ruber* and *N. dutertrei*, satellite SST and temperatures at 110 m were used for calculations. For *P. obliquiloculata* and *G. scitula*, temperatures at two depth were applied, for *P. obliquiloculata* 110 m (red) and at 200 m (light red), for *G. scitula* temperatures at 200 m (red) and 400 m (light red) were utilized. *G. ruber*, temperatures were calculated using the calibration developed by Fallet et al. (2011). Calcification temperatures for *N. dutertrei*, we applied the calibration developed by Anand et al. (2003). For *G. scitula* we calculated calcification temperatures using the calibration developed by Anand et al. (2003) for *G. hirsuta*. For calculations of potential δ¹⁸O, the general equation of Epstein et al. (1953) was applied. Potential annual flux-weighted b) Mg/Ca and c) δ¹⁸O are calculated for eddy (red) and non-eddy (blue) conditions. Grey vertical bars indicate annual averaged Mg/Ca and δ¹⁸O.
calculated depth habitat of 110 m, based on cross calibrating Mg/Ca data and the temperature profile from the mooring deployments, is probably deeper than the true habitat depth of *N. dutertrei*, which is likely to be around 80 m (Fallet et al., 2011 and chapter 4 of this thesis).

Calculated temperature differences are subsequently translated into flux-weighted potential Mg/Ca and δ¹⁸O signals for the different species (Fig. 6.1b). This shows that the offsets should be easily detectable. Hence, combined changes in shell flux and water column eddy characteristics (e.g. the extent of the deepening of the isotherms) should theoretically be preserved in the sediment and analytically possible to differentiate, as long as the eddy occurrence and/or intensity has an offset of at least 10% from its current value.

### 6.1.2. Impact of ontogeny

Low Mg/Ca ratios in crust and cortex covering some species of planktonic foraminifera (e.g. Kunioka et al., 2006; Van Raden et al., 2011; Jonkers et al., 2012; Chapter 5) will reduce Mg/Ca of the whole shell. In chapter 5, I used potential annual flux weighted-Mg/Ca from eddy and non-eddy conditions during the sediment trap deployment (Chapter 2) and measured crust Mg/Ca composition (Chapter 5) and its contribution to overall shell wall thickness (Chapter 5) to calculate potential lamellar calcite Mg/Ca ratios using a simple mass-balance-equation:

\[ A \times X + B \times Y = C / (A + B) \]

where \( A \) is crust contribution to total shell thickness, \( X \) is the Mg/Ca ratio of the crust, \( B \) is the contribution of the lamellar calcite, \( Y \) is the Mg/Ca ratio of the lamellar calcite and \( C \) is the total Mg/Ca ratio of the shell.

Using the measured average crust composition of 1.8 mmol/mol (Chapter 5), *N. dutertrei* should have a lamellar calcite Mg/Ca ratio of 3.8 mmol/mol during eddy and 1.9 mmol/mol during non-eddy conditions. This would translate in Mg/Ca-based calcification temperatures (Anand et al., 2003) of 26.6°C and 19.3°C for eddy and non-eddy conditions, respectively. This is a different temperature range compared to using flux-weighted, whole specimen values (23.3°C and 19°C for eddy and non-eddy conditions, respectively). Still, it remains questionable whether these values can be translated to different depth ranges as until now calibrations are based on whole shell analyses. The more pronounced offset using lamellar calcite Mg/Ca ratios
rather than whole shell Mg/Ca ratios, is promising and invites future research to develop new calibrations using parts of the shell wall only. Similarly, using the measured average Mg/Ca crust composition of 0.93 mmol/mol, for *G. scitula* (Chapter 5), potential lamellar calcite Mg/Ca should be 1.6 mmol/mol for eddy conditions and 1.3 mmol/mol for non-eddy conditions. Following the example of Fallet et al. (2010) we applied the Mg/Ca-temperature calibration of Anand et al. (2003) for *G. hirsuta*, to translate Mg/Ca ratios for *G. scitula* into calcification temperatures of 17°C and 11.8°C for eddy and non-eddy conditions, respectively. Also here the offset differs from the whole shell values, but the difference is smaller, as expected given the lower temperature gradient at the depth this species would calcify.

When combined the theoretical temperature difference between lamellar calcite in *N. dutertei* and *G. scitula* is 2°C between eddy and non-eddy conditions (Fig. 6.2a). The smaller theoretical offset based on lamellar Mg/Ca ratios between *N. dutertrei* and *G. scitula* compared to whole shell Mg/Ca ratios, is due to the assumed restricted depth intervals of lamellar calcification of

![Fig. 6.2](image_url)
the last chambers. However, in chapter 5 crust calcite Mg/Ca values reported for *N. dutertrei*
are significantly different between the final chamber (F-0) and penultimate chamber (F-1), as
well as between F-1 and pre-penultimate chamber (F-2). Furthermore, the same species shows
significantly different lamellar calcite Mg/Ca between the F-0 chamber and chamber F-1 and
F-2. Hence, the smaller theoretical offset between *N. dutertrei* and *G. scitula* implies that we
somehow underestimate the differences in their depth habitat. Using single chamber analysis,
it is thus possible to capture a larger offset between these two species, which is attributed to
the species specific migration pattern (Chapter 4).

Because crust calcite is formed deeper in the water column it could theoretically provide a
better estimate for the base of the thermocline and hence be useful in reconstructing eddies.
This implies that a separate calibration is needed for crust calcite. To test the potential of
this approach we can calculate the potential values for crust carbonate using a mass balance
approach, similar to the lamellar calcite above. Assuming that crust Mg/Ca is a function of
the whole shell chemistry, depending on the specimen’s calcification depth and the condition
(i.e. temperature) it encounters, crust Mg/Ca values can be calculated from whole specimen
Mg/Ca values. Because the actual thickness of the crust is known from the Mg/Ca and U/Ca
profiles, a mass-balance equation can be used to calculate changes in potential crust Mg/Ca
and potential annual flux-weighted Mg/Ca to calculate Mg/Ca ratios of the lamellar calcite.
Assuming that crust Mg/Ca is ~35% lower than the average shell Mg/Ca, the recalculated crust
Mg/Ca values for *N. dutertrei* are 1.8 mmol/mol and 1.2 mmol/mol for eddy and non-eddy
conditions respectively. Recalculated crust Mg/Ca values for *G. scitula*, assuming that crust
Mg/Ca is ~37% lower than the average shell Mg/Ca, are 0.8 and 0.7 mmol/mol for eddy and
non-eddy conditions respectively. Using the recalculated crust Mg/Ca values for *N. dutertrei*,
the potential lamellar Mg/Ca value during eddy conditions would be 3.6 mmol/mol Mg/Ca
(translating into a calcification temperature of 26.2°C) and 2.5 mmol/mol (translating into a
calcification temperature of 22°C) during non-eddy conditions. Using the recalculated crust
Mg/Ca values for *G. scitula*, the potential lamellar Mg/Ca value during eddy conditions is 1.7
mmol/mol Mg/Ca (translating into a calcification temperature of 12.2°C) and 1.5 mmol/mol
(translating into a calcification temperature of 11°C) during non-eddy conditions. Ultimately,
the potential temperature difference between *N. dutertrei* and *G. scitula* is 3.1°C (Fig. 6.2b)
and larger than assuming a constant crust value. In contrast, the potential temperature
difference of 3.7°C between *G. ruber* and *N. dutertrei* (Fig. 6.2b) between eddy and non-
eddy conditions, is only half the value produced by assuming a constant crust Mg/Ca. These
theoretical calculations underline the importance to further investigate Mg/Ca distribution
between crust and ontogenetic calcite in order to improve proxy application and show the
potential for developing proxies that are considering the geochemistry of both, crust/cortex and lamellar calcite.

6.1.3. The potential imprint of inter annual variability

Besides a strong seasonal climatic contrast, there are also inter-annual modulations of Indian Ocean climate. The down-core application of the eddy proxy, suggested in this thesis (Chapter 3), might be biased by climate phenomena such as e.g. El Niño Southern Oscillation (ENSO), Indian Ocean Dipole (IOD) and the Pacific Decadal Oscillation (PDO), events depending on the associated temperature anomaly. ENSO (McPhadden et al., 2006) and IOD (Saji et al., 1999) are two prominent features of the inter-annual variability influencing the Indian Ocean. ENSO is characterized by periodic warming (La Niña) and cooling (El Niño) of the eastern equatorial Pacific, arising from changes in the Walker circulation (McPhadden et al., 1996). During positive ENSO events (La Niña) there is a corresponding warming of the Indian Ocean, which peaks during boreal spring (March – May). The associated temperature impact is between 0.5 and 1 degree at the sea surface (Manyilizu et al., 2014), but might also impact thermal stratification. Sometimes coinciding, the IOD, develops in June and peaks in October (Saji et al., 1999). The IOD has an impact similar to ENSO, but is centered on another time of the year. The IOD impacts also the thermocline as associated strong monsoon winds occasionally result in shoaling of the eastern equatorial thermocline, opposite to the effect of the warm-core eddies. On a much lower frequency, one cycle being between 50-70 years, also the PDO might impact the western Indian Ocean, with SSTs rising during a positive PDO phase. The amplitude on SST of the PDO is not exactly known, but estimated to be exceeding the impact of ENSO (Krishnan et al., 2003). There also seems to be a link between these phenomena, whereby they might reinforce each other. The strongest inter-annual signal in the Indian Ocean is related to ENSO, modulated by inter-decadal climate variability of the PDO (Cole et al., 2000; Crueger et al., 2009) and negative IOD are often connected with a La Niña event. The associated combined temperature changes in the Mozambique Channel are hence probably up to 2°C inter-annually. Although this is lower than the temperature difference associated with eddies, it could still suppress signals integrated over multiple years, when somehow mechanistically linked.

6.1.4. Glacial/interglacial cycle

On a geological time scale, our present day climate varies between glacials and interglacials. During glacial periods, SSTs were lower (~2.5°C during the LGM in the Indian Ocean), but more importantly for reconstructing eddies, the overall temperature gradient within the
upper water column might have been reduced. When the temperature difference in the upper thermocline becomes too small, the reconstruction of past eddy intensity might be hampered. Moreover, a shift in seasonality and a possible moving of the biogeographic zonation could result in a general change in foraminiferal assemblages. The application of species specific offsets to reconstruct eddy intensity over glacial-interglacial transitions therefore will need a multi-proxy context to assess reliability. Also including other species and different size fractions could help to improve the proxies proposed in this thesis to more non-analogous conditions.

6.1.5. Diagenesis

Diagenesis could potentially interfere with the proxies proposed here in several ways. For instance the Mg/Ca of foraminifera shells is susceptible to dissolution (Hecht et al., 1975; Lorens et al., 1977). Rosenthal and Boyle (1993) demonstrated the relationship between Mg/Ca and δ18O and related decreasing Mg/Ca with increasing water depth. Furthermore, studies indicate that Mg-rich lamellar calcite is preferentially dissolved compared to Mg/Ca-low calcite related to the keel or crust (Brown and Elderfield, 1996; Johnstone et al., 2010). Also overgrowth of non-biogenic high Mg calcite could interfere with the proxies proposed here, especially the one based on crust chemistry. Analyzing test wall profiles using laser ablation ICP-MS seems therefore crucial for the robust application, even when used only as a regular check.

6.1.6. Is it important how many eddies go through the MC?

The number of eddies might be important, if the total number and duration of eddies is too few to be transferred, by foraminifera fluxes of species recording eddy signals, into the sedimentary record. This would mean that eddy frequency will be overprinted by seasonal or annual frequencies. Looking at the flux data for *G. ruber* it seems that the difference between winter-summer and eddy-non-eddy is quite comparable. Using the flux difference between the annual mean and the seasonal contrast (summer/winter) we can estimate the seasonal flux imprint to be about 235 shells m⁻² d⁻¹ using:

\[
\text{Seasonal effect} = \Delta_{\text{season-annual}} \text{flux}_{\text{min}} - \text{flux}_{\text{max}}
\]

Based on the seasonal effect, the eddy/non-eddy effect can be estimated by:

\[
\text{Eddy/non-eddy effect} = \Delta_{\text{eddy/noneddy-season}} \text{flux}_{\text{min}} - \text{flux}_{\text{max}}
\]

For *G. ruber* this results in an eddy estimate of ~190 shells m⁻² d⁻¹ and for non-eddy conditions
of ~250 shells m\(^{-2}\) d\(^{-1}\). This implies that the seasonal and eddy related impacts on \(G.\ ruber\) flux are comparable.

### 6.2. The potential use of intra shell differences in \(\delta^{13}C\) for calcification depth reconstruction

Single shell \(\delta^{13}C\) of planktonic foraminifera living at different depths, seem to record ambient \(\delta^{13}C_{\text{DIC}}\) and can be used to reconstruct seawater carbonate chemistry, carbon uptake but also vital effects during the calcification process (Rollion-Bard and Erez, 2010). Single shell differences of \(\delta^{13}C\) in \(N.\ dutertrei\) and \(G.\ scitula\) seem to record eddy induced changes in the deepening of the nutricline (Chapter 4). Still, these data are based on whole shell analyses and do not allow resolving intra-shell differences expected to result from a gradual shift in depth habitat as found in Mg/Ca.

Recently, Vetter et al. (2013) showed that \(\delta^{18}O\)\textsubscript{calcite} and elemental tracers seem to be precipitated synchronously within the test wall, with no measurable spatial offsets. We have profiled foraminiferal shell walls and distinguished crust, cortex and lamellar calcite using LA-ICP-MS (Chapter 5). Analysing intra-shell \(\delta^{18}O\)\textsubscript{calcite} using Nano-SIMS, could help to better unravel the growth history of the foraminiferal shell. Moreover, NanoSIMS would also allow studying intra-shell carbon isotopes. The proposed calcification model based on single chamber Mg/Ca and single shell \(\delta^{18}O\) (Chapter 3) might ultimately be refined by high-resolution \(\delta^{13}C\) NanoSIMS measurements on single chambers using a planktonic foraminifera species with a wide ontogenetic depth migration (e.g. \(G.\ truncatulinoides\), \(N.\ dutertrei\)), crossing a \(\delta^{13}C\) DIC gradient that can be analytically resolved.

### 6.3. What can U/Ca tell us?

U/Ca in planktonic foraminiferal shells has been suggested to show a strong temperature effect (Yu et al., 1998). Controlled growth experiments, however, showed U/Ca records carbonate chemistry without an appreciable temperature effect (Russel et al., 2003). Also more recent studies primarily linked U/Ca in foraminiferal shell carbonate to the seawater carbonate system (Raitzsch et al., 2011; Russel et al., 2004; Keul et al., 2013). Comparing the results from the Mozambique Channel sediment trap to the culture results of Keul et al. (2013), no inverse relationship between U/Ca incorporation and [CO\(_3\textsuperscript{2-}\)] (Log\(D_U=2.3-0.0027*\text{[CO}_3\textsuperscript{2-}\]) is observed, using in situ CO\(_3\textsuperscript{2-}\) values (locations between 37–43°E and 24.7°S, World Ocean
Incorporation of U in planktonic foraminifera hence appears not solely controlled by $[\text{CO}_3^{2-}]$. Single chamber LA-ICP-MS shows that U/Ca calcite concentrations are species specific and, of the species studied here, have the lowest values in *N. dutertrei* (10 nmol/mol) and the highest values in the deep dwelling species *G. scitula* (27 nmol/mol) (Fig. 6.3). Overall U/Ca results are comparable with previous studies, reporting U/Ca values of 10 nmol/mol for mixed species (Delaney and Boyle, 1983) and species-specifically between 3 and 15 nmol/mol for cultered and coretop specimens (Russel et al., 1994; Yu et al., 2008). Using an average seawater U/Ca ratio of 1305 nmol/mol, the U/Ca values I measured correspond to the empirical partition
coefficients $D_{\text{U/Ca}}$ [$D_{\text{U/Ca}} = (\text{U/Ca})_{\text{calcite}}/(\text{U/Ca})_{\text{sw}}$] of 0.012 to 0.021. These partition coefficients are generally lower than partition coefficients determined for inorganic calcite precipitated from seawater of $0.04 < D < 0.26$ (Kitano and Oomori, 1971) and $0.046 < D < 0.2$ (Meece and Benninger, 1993), suggesting a firm biological control over the incorporation of U into foraminiferal calcite.

LA-ICP-MS profiling shows that crust U/Ca is generally lower than lamellar calcite. In *N. dutertrei* U/Ca values in crust calcite are about 6 nmol/mol compared to higher U/Ca values of 21 nmol/mol in lamellar calcite (Fig. 6.3). Average cortex calcite of *P. obliquiloculata* has a U/Ca value of 6 nmol/mol compared to the 20 nmol/mol in lamellar calcite. Also *G. scitula* shows lower crust U/Ca ratios of 16 nmol/mol, compared to lamellar calcite with a U/Ca ratio of 29 mmol/mol (Fig. 6.3). Empirical partition coefficients $D_{\text{U/Ca}}$ for crust calcite show lower values, between 0.004 and 0.012, compared to partition coefficients of lamellar calcite, which are between 0.015 and 0.022. This implies, that biological discrimination against U appears to be even higher in crust calcite compared to lamellar calcite, similar to what is observed for Mg. This is in agreement with my findings in chapter 5, where I showed that Mg/Ca ratios in crust calcite are generally lower than in lamellar calcite. Such differences may be caused by differences in calcification rate between lamellar and crust calcite (Chapter 5). Irrespective, the fact that a strong difference is observed between ontogenetic and crust calcite for both Mg and U is in line with a strong biological control for both elements.
For *G. scitula* only crust U/Ca ratios between F-0 and F-1 are significantly different (t-test, p = 0.047). The U/Ca ratios in lamellar calcite of *G. scitula* seems to suggest an increasing U/Ca trend from the earlier (F-3) towards the younger chambers. Lamellar U/Ca ratios between F-2 and F-3 show no significant difference, however U/Ca in F-0 is significantly different from lamellar U/Ca ratios in F-2 and F-3 (p<0.001). Also, lamellar U/Ca ratios in F-1 are significantly different compared to U/Ca values in F-3. For the total calcite U/Ca in *G. scitula*, I find that total U/Ca between all chambers are significantly different from one another, except total calcite U/Ca ratios between chambers F-1 and F-2, as well as between chambers F-2 and F-3. Generally I find that lamellar U/Ca ratios in all three species are higher in the last and the youngest chamber of the final whorl. This is also true for the crust U/Ca values in *N. dutertrei* and *G. scitula*. Only *P. obliquiloculata* shows no differences in cortex U/Ca ratios between chambers. Comparing these differences in U/Ca with the observed differences in Mg/Ca between the different growth stages suggests that U/Ca and Mg/Ca incorporation are tightly linked. This is likely an effect of species-specific vital-effects and environmental variations within the species depth habitat (vertical migration), however we cannot exclude effects of co-precipitation.

In conclusion, it seems that also U/Ca partitioning is strongly biologically controlled in lamellar but also crust and cortex calcite. This is in agreement with observations of Mg/Ca (Chapter 5). Slower precipitation rates during the terminal stages of foraminiferal calcification can potentially explain higher U/Ca incorporation.

### 6.4. Towards understanding crust and cortex formation

Many of the here proposed proxies and life cycle changes are based primarily inversely on using inter- and intra-shell differences in chemistry. To tie these observations to reality, stratified plankton tows are needed. At the same time these tows could improve understanding crust and cortex formation, both in time and space. The precise depth where the foraminifera are captured holds valuable information. Detailed investigations could decipher the depth distribution of specimens with and without crust/cortex and constrain the here presumed formation depth. Additionally, measurements of hydrographic parameters (temperature, salinity, trace metal concentrations and seawater chemistry) could be used to understand the mechanisms triggering crust and cortex formation and allow the calibration of the individual parts of the shell, i.e. lamellar versus crust calcite.