Interpreting XRF-derived $CaCO_3$ records from the Agulhas Plateau during the past 150 ka: Surface ocean calcareous productivity versus $CaCO_3$ dissolution

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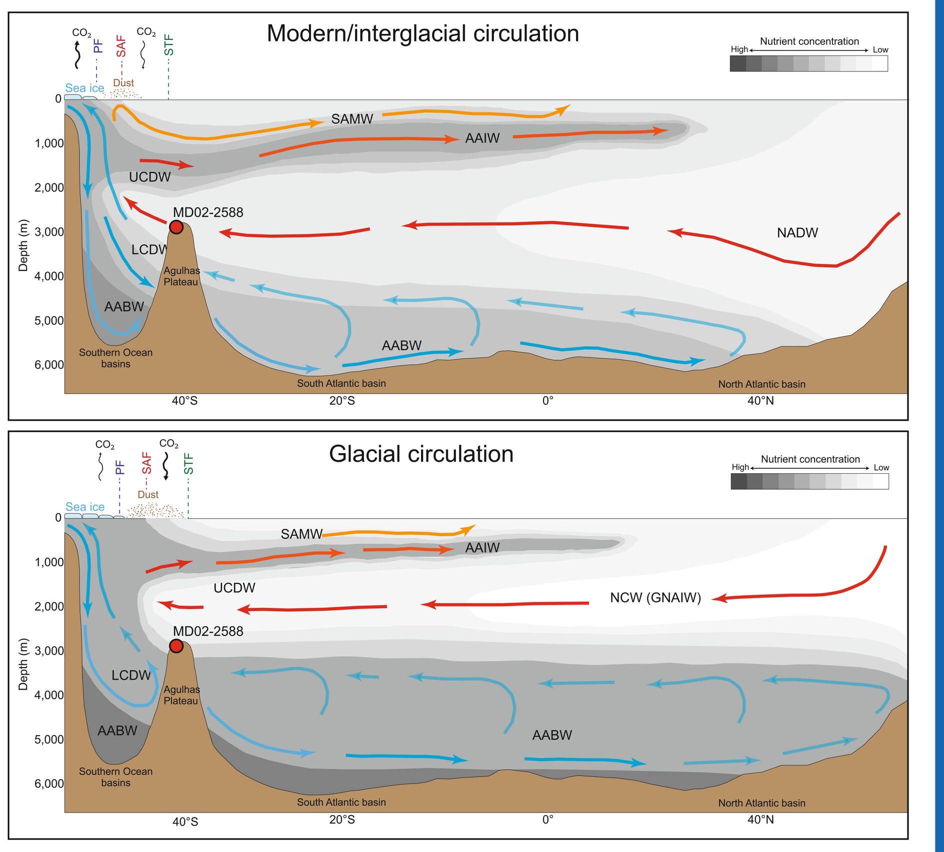
1. Introduction

The Atlantic meridional overturning circulation (AMOC) is a critical component of the global ocean circulation system and strongly influences climate through the transport of heat and freshwater (Talley, 2013; Buckley and Marshall, 2016). Past variations of the AMOC are believed to have affected Pleistocene climate change by altering the patterns of oceanic heat transport (e.g., Lynch-Stieglitz *et al.*, 2007; Adkins, 2013) and by changing the quantity of respired carbon stored in the deep ocean (e.g., Freeman *et al.*, 2016). During glacial intervals, northern-sourced Atlantic deep waters are thought to have shoaled, while southern-sourced deep waters expanded to fill a larger proportion the abyssal and deep ocean (e.g., Curry and Oppo, 2005; Marchitto and Broecker, 2006). Differences in the carbonate ion concentration of northern- and southern-sourced deep waters result in changes in the carbonate saturation state of the ocean and variable preservation of $CaCO_3$ on the seafloor on glacial-interglacial timescales. Stratigraphic records of $CaCO_3$ can therefore act as a proxy for past changes of deep ocean circulation (Hodell *et al.,* 2001, 2003).

Calcium records derived from XRF core scanning are an established proxy of marine sediment bulk $CaCO_3$ content (e.g., Rothwell and Croudace, 2015 and references therein). However, bulk sediment $CaCO_3$ content is controlled by a complex interaction between various environmental drivers, including surface ocean calcareous productivity, $CaCO_3$ dissolution on the seafloor, and dilution by other sediment components.



NADW: North Atlantic Deep Water
AABW: Antarctic Bottom Water
UCDW/LCDW: Upper/Lower Circumpolar Deep Water
AAIW: Antarctic Intermediate Water
SAMW: Subantarctic Mode Water
NCW: Northern Component Water
GNAIW: Glacial North Atlantic Intermediate Water
PF: Polar Front
SAF: Subantarctic Front
STF: Subtropical Front

In this study, we attempt to determine the relationship between $CaCO_3$ content, bottom water carbonate saturation state and surface ocean productivity at the MD02-2588 core site during the last 150 ka. This will potentially allow XRF core scanning records of Ca from neighbouring sites to be used to develop a regional reconstruction of the temporal and spatial variability of the deep water-mass geometry of the South West Indian Ocean during the Late Pleistocene.

2. Materials and methods

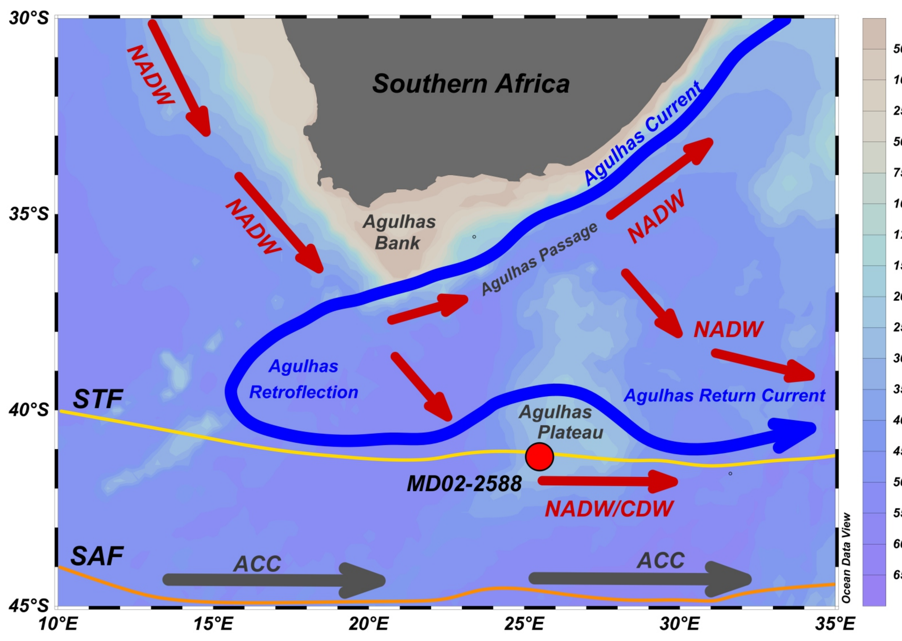
The CASQ sediment core MD02-2588 was recovered from a calcareous contourite drift located on the southwestern flank of the Agulhas Plateau (41°19.90'S, 25°49.40'E, 2907 m water depth) during RV Marion Dufresne cruise MD128 (Giraudeau, 2002). At this water depth, the core site is presently located in the transition zone between North Atlantic Deep Water (NADW) and Circumpolar Deep Water (CDW).

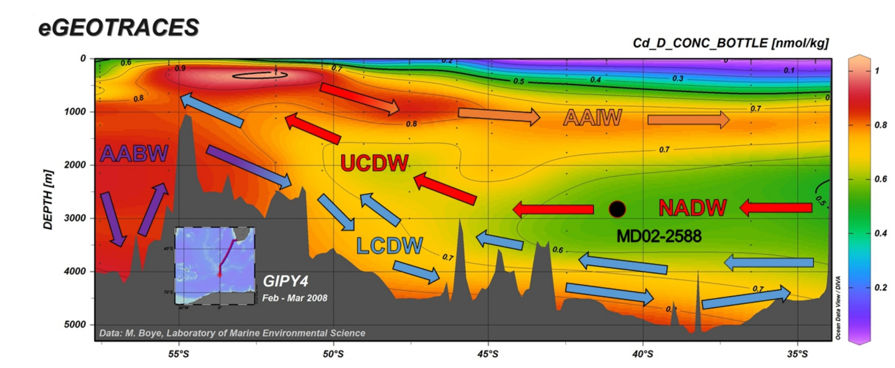
The surface ocean circulation over the Agulhas Plateau is dominated by the Agulhas Current, the Agulhas Retroflection and the Agulhas Return Current and Subtropical Front (STF).

Stable oxygen and carbon isotopes were measured on the benthic foraminifera *Cibicidoides wuellerstorfi* ($\delta^{18}O_{C.wuell.}$ and $\delta^{13}C_{C.wuell.}$, respectively), combining previously published data (Ziegler *et al.*, 2013) with new measurements made for this study. We also present a stratigraphic series of bottom water carbonate ion saturation state ($\Delta[CO_3^{2-}]$) derived from B/Ca measured in samples of *C. wuellerstorfi* (e.g., Yu and Elderfield, 2007).

XRF scanning on sediment core MD02-2588 was performed using the ITRAX XRF Core Scanner at the British Ocean Sediment Core Research Facility, Southampton, UK. Measurements were made at 2 mm intervals with the exposure time per measurement set to 15 seconds. XRF voltage and current were set at 30 kV and 50 mA, respectively, using a Mo-tube as an X-ray source. The three target elements Ca, Ba and Br were normalised to Ti and presented as log-ratios (Weltje and Tjallingii, 2008; Weltje *et al.*, 2015).

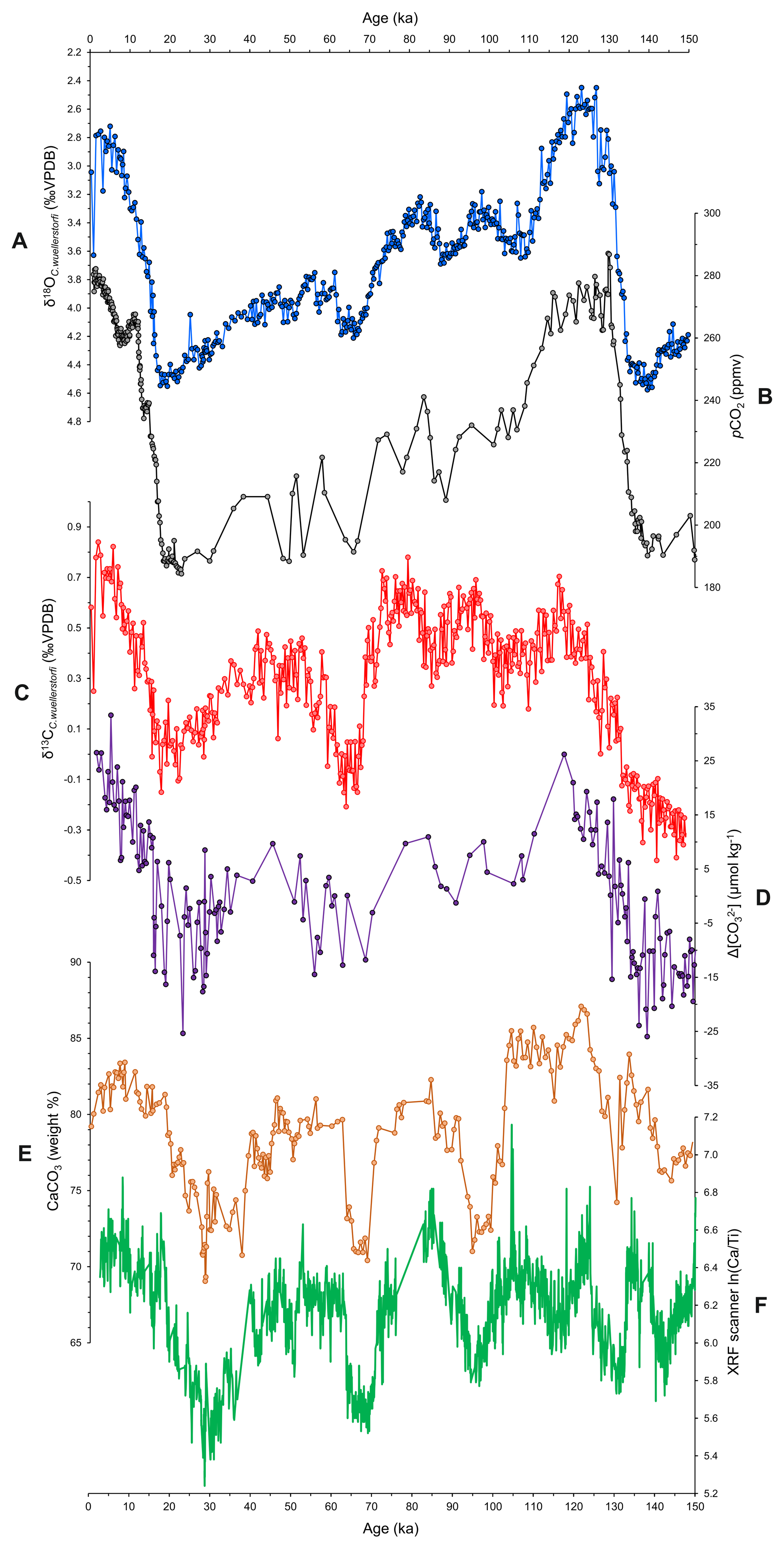
The age model for the core was developed by Ziegler *et al.*, (2013). Fifteen calibrated accelerator mass spectrometry (AMS) ^{14}C dates were used for the 0-40 ka interval. For the remainder of the core, the age model is constructed by graphical correlation of the $\delta^{18}O_{C.wuell.}$ record to the European Project for Ice Coring in Antarctica (EPICA) Dome C δD record (Jouzel *et al.*, 2007).





NADW: North Atlantic Deep Water
UCDW/LCDW: Upper/Lower Circumpolar Deep Water
AABW: Antarctic Bottom Water
STF: Subtropical Front
SAF: Subantarctic Front
ACC: Antarctic Circumpolar Current

3. Results and Discussion I



The stratigraphic record of $\delta^{18}O_{C.wuell.}$ displays a prominent orbital modulation with the largest fluctuations observed during glacial terminations (Graph A). In addition to global ice volume change, $\delta^{18}O_{C.wuell.}$ at this site also includes a component driven by changes in deep-water temperature and/or local seawater isotopic composition.

The record of $\delta^{18}O_{C.wuell.}$ from MD02-2588 displays similarities with the Antarctic ice core record of pCO_2 (Monnin *et al.*, 2001; Petit *et al.*, 1999; Pepin *et al.*, 2001) (Graph B) suggesting a link between the local bottom water conditions and global orbital-timescale climate change.

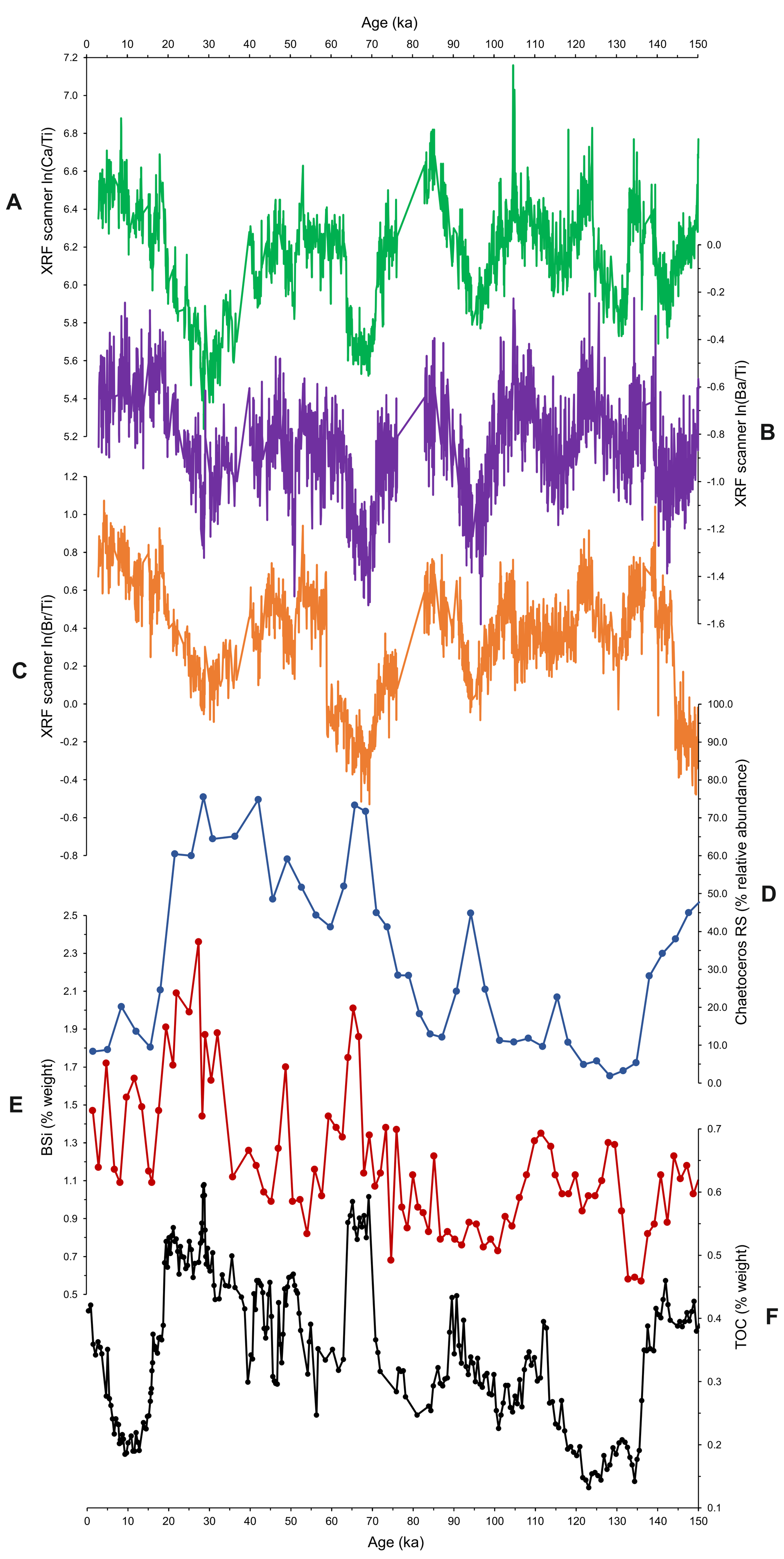
The $\delta^{13}C_{C.wuell.}$ data from MD02-2588 display fluctuations similar to those observed in the benthic foraminiferal $\delta^{13}C$ stacks from the mid-depth and deep Atlantic Ocean (Lisiecki *et al.*, 2008) (Graph C). These fluctuations indicate changes in the geometry of deep water masses in the Atlantic ocean associated with glacial-interglacial changes of the AMOC.

The downcore pattern of $\Delta[CO_3^{2-}]$ variability at the MD02-2588 core site is characterised by undersaturated conditions (< 0 µmol kg-1) during glacial stages and oversaturated conditions (> 0 µmol kg-1) during interglacial stages (Graph D). The lowest glacial values occur during MIS 6 and the most oversaturated conditions are observed during the latest part of the Holocene and during MIS 5.5. $\Delta[CO_3^{2-}]$ values during the rest of MIS 5 are intermediate between glacial maximum values and peak interglacial values but on the whole remain oversaturated. The overall trends observed in the $\Delta[CO_3^{2-}]$ record are similar to those observed for $\delta^{13}C_{C.wuell.}$. This potentially indicates a common response to changes in deep water circulation on orbital timescales.

$CaCO_3$ is the dominant component of the sediments at the MD02-2588 core site (60-87%) (Romero *et al.,* 2015). Generally, $CaCO_3$ content is highest during interglacials and lowest during glacial stages (Graph E). However, the decrease in $CaCO_3$ content recorded between 90-100 ka is not consistent with this pattern.

The XRF core scanner *ln*(Ca/Ti) record shows a good correlation to $CaCO_3$ content (Graph F) and demonstrates how XRF core scanner records of Ca could be used to develop a regional $CaCO_3$ stratigraphic model for the wider South West Indian Ocean.

4. Results and Discussion II



The available evidence indicates that the $CaCO_3$ stratigraphy of the southern Agulhas Plateau is largely driven by glacial-interglacial dissolution cycles associated with changes in regional deep water circulation and the biogeochemical properties of bottom waters (i.e., $\delta^{13}C_{C.wuell.}$ and $\Delta[CO_3^{2-}]$).

However, differences between the patterns of variability of $CaCO_3$ content of core MD02-2588 and the corresponding records of $\delta^{13}C_{C.wuell.}$ and $\Delta[CO_3^{2-}]$ suggest that dissolution cycles may not be the only driver of $CaCO_3$ content variations at this site.

The stratigraphic record of *ln*(Ba/Ti) from MD02-2588 displays a very similar pattern of variability to *ln*(Ca/Ti) (r^2=0.57) (Graphs A and B). This may suggest that a dominant proportion of Ba in the sediments of the southern Agulhas Plateau is bound or adsorbed to the carbonate fraction, as opposed to the organic fraction (e.g. Dymond *et* al., 1992). From this evidence alone, it is not possible to determine if *ln*(Ba/Ti) is an indicator of Ba deposition to the seafloor (biogenic flux) or of Ba preservation (dissolution).

The downcore variability of *ln*(Br/Ti) (Graph C) also appears to be closely associated with *ln*(Ba/Ti) although the correlation between these two ratios (r^2=0.44) is not as strong as that observed between *ln*(Ba/Ti) and *ln*(Ca/Ti). This supports the premise that the proportion of Ba deposited at the core site in settling organic particles in the form of barite may be smaller than the proportion of Ba deposited with the carbonate fraction.

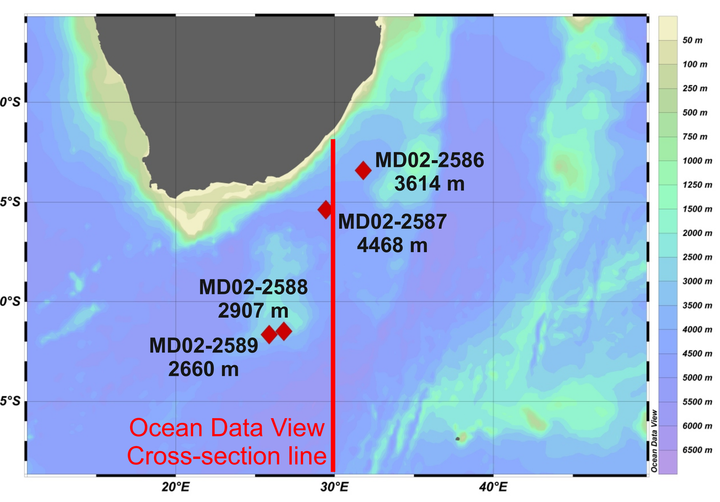
The high $CaCO_3$ content of these sediments leads us to suspect that a relatively high proportion of settling Ba particles is associated with the calcareous biogenic flux. This may explain the observed inverse relationship observed between *ln*(Ba/Ti) and *ln*(Br/Ti), and the available paleoproductivity proxies from this core, such as the relative abundance of Chaetoceros resting spores (Graph D), biogenic silica content (Graph E) and total organic carbon content (Graph F) (Romero *et al.,* 2015).

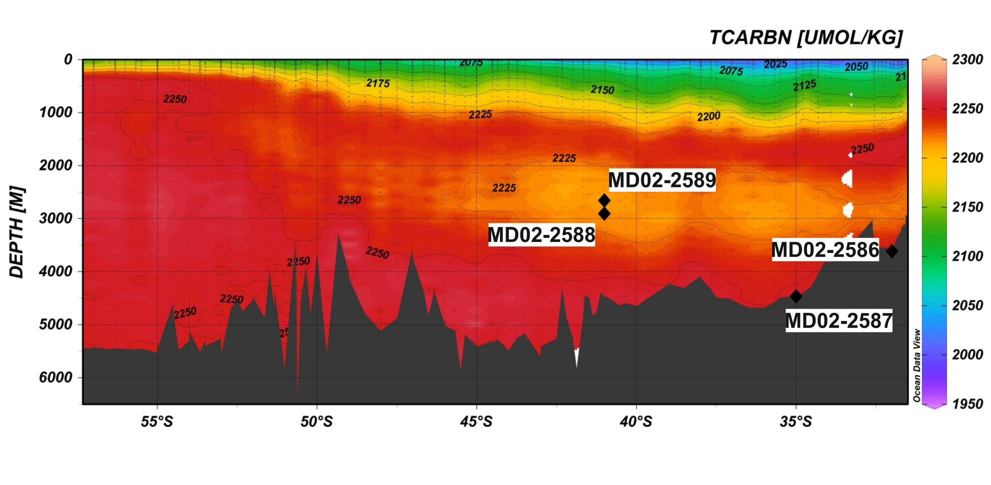
Overall, the data suggest that *ln*(Ba/Ti) and *ln*(Br/Ti) cannot be applied as paleoproductivity proxies in the calcareous-rich sediments of the southern Agulhas Plateau.

5. Conclusions

- The XRF core scanner *ln*(Ca/Ti) record shows a good correlation to $CaCO_3$ content and demonstrates the potential of using XRF core scanner records of Ca to develop a regional $CaCO_3$ stratigraphic model for the wider South West Indian Ocean.
- The $CaCO_3$ stratigraphy of the southern Agulhas Plateau appears to be driven by glacial-interglacial dissolution cycles associated with changes in regional deep water circulation. However, differences between the patterns of variability of $CaCO_3$ content observed in core MD02-2588 and the corresponding records of $\delta^{13}C_{C.wuell.}$ and $\Delta[CO_3^{2-}]$ suggest that dissolution cycles may not be the only driver of $CaCO_3$ content variations at this site.
- The very high $CaCO_3$ content of sediment core MD02-2588, and the relatively low TOC content, limits the applicability of *ln*(Ba/Ti) and *ln*(Br/Ti) derived from XRF core scanning as paleoproductivity proxies. The Ba content of these sediments appears to be associated with the carbonate-bound and carbonate-adsorbed fractions of the sediment and not with Ba deposited on the seafloor in settling organic particles in the form of barite.

6. Future work





XRF core scanning records of Ca will be produced for a number of cores located at various depths within the South West Indian Ocean (see location map and section showing Total Carbon). These records will be used to develop a regional-scale reconstruction of the spacio-temporal variability of $CaCO_3$ preservation on the seafloor.

If $CaCO_3$ can be shown to be predominantly controlled by glacial-interglacial dissolution cycles throughout the region, it may be possible to use sediment cores to map variations of water mass geometry in this part of the ocean during the Late Pleistocene.

XRF core scanning records of Ba and Br will also be acquired to examine if the relationship between these elements and Ca is consistent with that found at MD02-2588.

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