

Seasonally resolved diatom $\delta^{18}\text{O}$ records from the west Antarctic Peninsula over the last deglaciation

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Abstract

Understanding the response of the Antarctic ice sheets during the rapid climatic change that accompanied the last deglaciation has implications for establishing the susceptibility of these regions to future 21st Century warming. A unique diatom $\delta^{18}\text{O}$ record derived from a high-resolution deglacial seasonally laminated core section off the west Antarctic Peninsula (WAP) is presented here. By extracting and analysing single species samples from individual laminae, season-specific isotope records were separately generated to show changes in glacial discharge to the coastal margin during spring and summer months. As well as documenting significant intra-annual seasonal variability during the deglaciation, with increased discharge occurring in summer relative to spring, further intra-seasonal variations are apparent between individual taxa linked to the environment that individual diatom species live in. Whilst deglacial $\delta^{18}\text{O}$ are typically lower than those for the Holocene, indicating glacial discharge to the core site peaked at this time, inter-annual and inter-seasonal alternations in excess of 3‰ suggest significant variability in the magnitude of these inputs. These deglacial variations in glacial discharge are considerably greater than those seen in the modern day water column and would have altered both the supply of oceanic warmth to the WAP as well as regional marine/atmospheric interactions. In constraining changes in glacial discharge over the last deglaciation, the records provide a future framework for investigating links between annually resolved records of glacial dynamics and ocean/climate variability along the WAP.

Keywords: Antarctic; biogenic silica; ENSO; isotope; melting; oxygen

1 Introduction

The East and West Antarctic Ice Sheets (EAIS/WAIS), accounting for 90% of the world's freshwater, play a major role in regulating the global climate system (Mayewski et al., 2009). Antarctic surface air temperature

has increased by 0.1°C/decade since the 1950s (Steig et al., 2009) and further warming is forecast for the 21st Century (Chapman and Walsh, 2007; Bracegirdle et al., 2008), hence, the stability of the EAIS and WAIS has been identified as one of the largest uncertainties surrounding predictions of future climate change (IPCC, 2007; Joughin and Alley, 2011; Rignot et al., 2011). The need to develop a detailed understanding as to how ice sheets respond to abrupt climatic change is emphasised by the potential for a collapse of the WAIS to trigger a global sea-level rise in excess of 3 m (Bamber et al., 2009; Mitrovica et al., 2009) with associated impacts on both the regional water column (Meredith et al., 2008a, 2010), aquatic ecosystem (Montes-Hugo et al., 2009; Schofield et al., 2010), carbon draw-down of the Southern Ocean (Sigman et al., 2010) and other global scale ocean-atmospheric processes (Hickey and Weaver, 2004; Stouffer et al., 2007; Trevena et al., 2008; Swingedouw et al., 2009; Holden et al. 2010; Menviel et al., 2010; Ma and Wu, 2011). One solution towards developing a greater understanding of the behaviour and stability of the Antarctic ice sheets is to analyse the environmental record over intervals in the past known to be marked by equally abrupt change. A key example of this is the last deglaciation (c. 19,000 to 11,000 BP) when temperatures across Antarctica rose by c. 10°C (Stenni et al., 2001, 2010; Vimeux et al., 2002; Kawamura et al., 2007; Jouzel et al., 2007) triggering melting and glacial retreat around the continent (Heroy and Anderson, 2007; Smith et al., 2011) that continued through the Holocene (Hall, 2009).

The west Antarctic Peninsula (WAP), the most northerly part of Antarctica (Fig. 1), is particularly vulnerable to future change having undergone a c. 3°C increase in surface air temperature since 1950, the most of anywhere in the Southern Hemisphere (Vaughan et al. 2003; Turner et al., 2005; Thomas et al., 2009). Accompanying this increase in air temperatures are increases in summer sea surface temperature (SST) (Meredith and King, 2005) and the duration of the annual melting period (Torinesi et al., 2003; Vaughan, 2006). With critical thresholds for increased ice sheet/shelf breakup including summer air temperatures $>-1.5^{\circ}\text{C}$ (Scambos et al., 2004) and mean annual temperatures $>-9^{\circ}\text{C}$ (Morris and Vaughan, 2003), changes in air temperature and SST (Shepherd et al., 2003) can be related to the trend of increasing glacier retreat and basal melting of the ice-sheet across the WAP since the 1940s (Cook et al., 2005; Pritchard et al. 2012) together with the recent collapse of the Larsen A and B ice shelves (Doake et al., 1998; Rignot et al., 2004).

Palmer Deep (Fig. 1) is a bathymetric depression on the WAP inner continental shelf, c. 30 km south of Anvers Island, where the combination of upwelling upper Circumpolar Deep Water (UCDW), seasonal sea ice and injections of glacial discharge (comprised of iceberg and brash-ice discharge together with basal melting of floating glaciers/ice shelves) created a highly productive photic zone that resulted in a high-resolution sedimentary archive of the last deglaciation (Leventer et al., 1996; 2002). In the ODP Site 1098A sediment core (Basin I of Palmer Deep) (Fig. 1) this is marked from 12,899-11,061 cal BP (45.03-40.59 m composite depth) by an exceptionally preserved, 4.4 m long, seasonally laminated section

(Domack et al., 2001; Leventer et al., 2002; Maddison et al., 2005) (Fig. 2). Low-resolution $\delta^{18}\text{O}_{\text{diatom}}$ measurements on non-lamina-specific samples comprised of bulk diatom species show variations of 5.0‰ through this interval (Pike et al., In press) (Fig. 3), hinting at a highly dynamic deglacial environment marked by variable levels of glacial discharge. Here we extend this work to present a unique season and single-taxon specific $\delta^{18}\text{O}_{\text{diatom}}$ record from individual laminations between 12,719-12,183 cal BP, an interval synchronous with the first half of the Younger Dryas/Greenland Stadial 1 (GS1) (c. 12,800-11,500 BP) and the end of the Antarctica Cold Reversal (ACR) (c. 14,500-12,800 BP). The production of a $\delta^{18}\text{O}_{\text{diatom}}$ record at a seasonal- to decadal-resolution, the highest ever obtained, provides an unparalleled opportunity to: 1) extend the lower-resolution Holocene $\delta^{18}\text{O}_{\text{diatom}}$ record into the last deglaciation; 2) investigate the environmental conditions that the deglacial laminations formed in; and 3) provide constraints on the link between environmental/atmospheric variability and glacial discharge during the last deglaciation, and potential insights on the sensitivity of WAP ice sheets to future climatic changes (Bentley, 2010).

2 Methodology

2.1 Sample description

The deglacial section in cores from ODP Site 1098A are marked by 191 pairs of orange-brown and blue-grey laminations (Maddison et al., 2005). Orange-brown laminae are dominated by near-monospecific *Hyalochaete Chaetoceros* spp. resting spores (CRS) and are interpreted as representing austral spring deposition linked to increased sea ice melt in the photic zone (Leventer, 1991; Crosta et al., 1997). This leads to more stable/stratified water column conditions that trigger high levels of biological productivity by trapping nutrients in the photic zone and enabling diatoms to remain suspended in the water column for longer periods of time (Leventer, 1991; Leventer et al., 1993, 1996; Crosta et al., 1997; Armand et al., 2005). In contrast, blue-grey laminae reflect summer deposition of (i) terrigenous material linked to the seasonal movement of the nearby grounded ice sheet and (ii) a more diverse diatom assemblage (Leventer et al., 2002; Maddison et al., 2005; Domack et al., 2006). Of note are a series of intermittent sub-laminae in the blue-grey laminae characterising the end of summer, the most common of which are dominated by *Thalassiosira antarctica* resting spores (RS) (n = 47; Maddison et al., 2005). Vegetative cells of *T. antarctica* are linked to ice-free/lower nutrient conditions that prevail in summer in non/weakly stratified waters following the melting of sea ice and depletion of nutrients by other taxa (Leventer and Dunbar, 1987; Sommer et al., 1991; Cremer et al., 2003; Maddison et al., 2005; Pike et al., 2009). As conditions become colder, reductions in temperature and light availability, together with sea ice advances and increases in salinity via brine rejection, inhibit diatom growth and lead to the production of *T. antarctica* RS which dominate the *T. antarctica* fossil record. For this study 64 individual CRS and 42 *T. antarctica* RS seasonal laminations were sampled (Maddison et al., 2005; Maddison, 2006) from 44.39-42.50 mcd (12,719-12,183 cal BP) from discrete intervals where individual laminae are sufficiently thick to prevent sampling across lamina boundaries. In the

chosen sample intervals, every CRS lamina was sampled together with as many *T. antarctica* RS laminae as possible (not all *T. antarctica* RS laminae were thick enough to sample). The sampling of successive spring CRS and summer *T. antarctica* RS across consecutive production seasons allows a detailed investigation of both inter-seasonal and inter-annual variations in $\delta^{18}\text{O}_{\text{diatom}}$ and the seasonal evolution of deglacial environmental conditions.

2.2 Chronology

A relatively robust age model has been published for ODP Site 1098 (Domack et al., 2001). However, more recent studies have developed their own composite depth scales (e.g. Shevenell et al., 2011) due to problems with the initial shipboard splice. In order to apply the published age data to the $\delta^{18}\text{O}_{\text{diatom}}$ curve, the published down core magnetic susceptibility records (Shipboard Scientific Party, 1999) and lamina-to-lamina correlations were used to re-evaluate the composite depth scale for the A and C hole, and then the published particulate organic carbon (POC) AMS radiocarbon ages for Hole 1098C (Domack et al., 2001) were used to produce an age model for our data (Pike et al., In press) that provides ages within 5% of the original age model. AMS ages were calibrated to calendar years using Calib 6.0.2 (Stuiver and Reimer, 1993), the Marine09 calibration curve and a reservoir correction of 1,230 years (Domack et al., 2001).

2.3 Diatom extraction and analysis

Diatoms were extracted and cleaned for isotope analysis using adaptations of existing techniques that were modified for use on coastal Antarctic diatoms (Swann et al., 2008; Snelling et al., in press). In summary, samples were placed in c. 1 ml of 30% H_2O_2 at room temperature for approximately four hours to disaggregate samples without using alkaline chemicals that risk dissolving and causing isotopic fractionation. Samples were subsequently centrifuged in sodium polytungstate three times with progressively lower specific gravities: 2.25 g/ml^{-1} , 2.20 g/ml^{-1} and 2.10 g/ml^{-1} at 2,500 rpm for 20 minutes. Extracted material was then re-immersed in H_2O_2 at 70°C for one week to remove all organic material adhering to the diatom frustule and then left overnight in 5% HCl to dissolve any carbonates still remaining. Between each stage samples were centrifuge washed three times at 1,500 rpm for five minutes. To extract single species samples for isotope analysis samples were sieved at varying size fractions using nylon sieve cloths (Table 1). For the spring laminae, the <10 μm fraction was dominated by CRS and used to produce a taxon-specific spring bloom isotope record. For sub-laminae present in the blue-grey laminae the >15 μm fraction was dominated by *T. antarctica* RS and used to generate a summer isotope record. The spring CRS and summer *T. antarctica* RS records form the focus of our results given their dominance and the ability to relate measurements of $\delta^{18}\text{O}_{\text{diatom}}$ to specific seasons. In order to examine intra-seasonal variations in $\delta^{18}\text{O}_{\text{diatom}}$, the spring >10 μm fraction and summer <15 μm fraction which contain a variety of other taxa were also analysed. Sample purity was assessed for all samples using a combination of light microscopy and scanning

electron microscope.

Samples were analysed for $\delta^{18}\text{O}_{\text{diatom}}$ following a step-wise fluorination procedure (Leng and Sloane, 2008) verified through an inter-laboratory calibration exercise (Chapligin et al., 2011). In brief, samples were outgassed in nickel reaction vessels and reacted with BrF_5 for 6 minutes at 250°C to remove contaminant oxygen present in Si–OH bonds. Oxygen from Si–O–Si bonds was subsequently released overnight using further reagent at 550°C before being converted and collected as CO_2 following Clayton and Mayeda (1963). Isotope measurements were then made on a Finnigan MAT 253 with values converted to the VSMOW scale using the NIGL within-run laboratory diatom standard BFC_{mod} which has been calibrated against NBS28. Replicate analyses of sample material indicate an analytical reproducibility (1σ) of 0.3‰ through the laminated interval.

3. Results

3.1 Spring vs summer laminations

All fossil diatom samples are exceptionally well-preserved (Fig. 2, Leventer et al., 2002; Maddison et al., 2005), showing no signs of dissolution or diagenesis which would tend to lower $\delta^{18}\text{O}_{\text{diatom}}$ (c.f. Moschen et al., 2006). Of the selected samples, 52 out of 64 spring laminations and 26 out of 42 summer laminations produced sufficient clean material for single-taxon CRS and *T. antarctica* RS analysis. Measurements of the spring CRS samples, ranging from +39.3‰ to +44.3‰, show significant variability through the laminated interval with values typically higher than those documented in the bulk species $\delta^{18}\text{O}_{\text{diatom}}$ measurements from 12,820-12,734 cal BP (Fig. 4a). From 12,429-12,203 cal BP and 12,659-12,500 cal BP spring CRS values range by 1.7‰ and 2.6‰, respectively. Outside of these intervals fluctuations of up to 3.8‰ occur. Results from the summer *T. antarctica* RS laminae are, in most instances, lower than those for CRS (Fig. 4a). With values ranging from +39.0‰ to +43.8‰ and with abrupt changes of >3‰ occurring throughout, values for *T. antarctica* RS are broadly similar in range to the bulk species $\delta^{18}\text{O}_{\text{diatom}}$ data. The scale of $\delta^{18}\text{O}_{\text{diatom}}$ variability through the deglaciation in both the CRS and *T. antarctica* RS samples is considerably greater than that seen at any stage in the Holocene samples from Palmer Deep (Fig. 3).

3.2 Intra-seasonal variability

The spring >10 μm fraction is comprised of diatoms including *Eucampia antarctica*, *Corethron pennatum*, *Proboscia inermis*, *T. antarctica* RS, *Thalassiosira lentiginosa* and CRS (which failed to pass through the sieve cloth) as well as other, less abundant species. The summer <15 μm fraction contains a greater diversity of taxa including CRS, with small amounts of *T. antarctica* RS also present. Comparison of spring CRS vs spring >10 μm samples (Fig. 4b) and summer *T. antarctica* RS vs summer <15 μm samples (Fig. 4c) show similar changes but with intra-seasonal offsets of up to 4.2‰ in the spring laminations (mean = 0.9‰) and

2.3‰ in the summer laminations (mean = 1.5‰).

4. Discussion

4.1 Controls on $\delta^{18}\text{O}_{\text{diatom}}$ along the WAP

To date, there have been no studies calibrating the $\delta^{18}\text{O}_{\text{diatom}}$ signal along the WAP coastal margin. However, a multitude of work over the last 20 years have developed $\delta^{18}\text{O}_{\text{diatom}}$ as a palaeoenvironmental proxy in both marine and lacustrine systems as well as through the use of laboratory cultures (Swann and Leng, 2009). This has shown that $\delta^{18}\text{O}_{\text{diatom}}$ is comparable to the $\delta^{18}\text{O}$ from planktonic foraminifera in reflecting the temperature and $\delta^{18}\text{O}$ of ambient water ($\delta^{18}\text{O}_{\text{water}}$), although diatoms will occupy the uppermost section of the water column which is most sensitive to changes in atmospheric and continental processes. Within the context of the WAP four processes are capable of directly altering $\delta^{18}\text{O}_{\text{diatom}}$: 1) SST at a coefficient of c. $-0.2\text{‰}/^{\circ}\text{C}$ (Brandriss et al., 1998; Moschen et al., 2005; Crespin et al. 2010; Dodd and Sharp, 2010); 2) ocean circulation due to the different $\delta^{18}\text{O}_{\text{water}}$ of individual water masses; 3) sea ice abundance; and 4) glacial discharge due to its lower isotopic value relative to seawater.

Using contemporary information on the controls of $\delta^{18}\text{O}_{\text{diatom}}$ and oceanographic conditions along the WAP, the sub-sections below outline the relative importance of these processes. Estimating the combined influence of temperature, water masses and sea-ice on $\delta^{18}\text{O}_{\text{water}}$, and so $\delta^{18}\text{O}_{\text{diatom}}$, is problematic as the controls on each are at least partially inter-related. Whilst we cannot fully rule out that temperature, water masses and sea-ice combine to regulate small changes in $\delta^{18}\text{O}_{\text{diatom}}$, we believe that any influence is within the $\delta^{18}\text{O}_{\text{diatom}}$ analytical error (0.3‰). Instead we conclude that deglacial changes in $\delta^{18}\text{O}_{\text{water}}$, hence $\delta^{18}\text{O}_{\text{diatom}}$, are primarily regulated by variations in glacial discharge, similar to the modern day coastal margin.

4.1.1 Sea surface temperature (SST)

Diatom assemblages along the WAP primarily reflect changes in sea-ice, nutrient supply, stratification and the proximity/behaviour of ice-mass along the WAP. Whilst these parameters are linked to SST, any relationship is indirect and so taxonomic counts cannot be used to provide information on SST along the margin (Leventer et al., 2002; Maddison et al., 2005). Holocene variations in TEX₈₆-derived SST at ODP Site 1098 (Shevenell et al., 2011) have only a negligible impact on $\delta^{18}\text{O}_{\text{diatom}}$ (either close to or within the analytical error for $\delta^{18}\text{O}_{\text{diatom}}$ of 0.3‰ (1 σ)) (Pike et al., In press). No SST measurements are available for the deglacial interval analysed in this study (Fig. 4a) and so we assume that any deglacial SST impact on $\delta^{18}\text{O}_{\text{diatom}}$ is also minimal.

4.1.2 Water masses

Water masses in the region are dominated by Circumpolar Deep Water (CDW), separated into lower

(LCDW) and upper (UCDW), with surface waters representing a mixture of UCDW and Antarctic Surface Water (AASW) formed along the Antarctic continent. Whereas austral winter AASW extends down to depths of c. 50-100 m, warming spring water and the injection of glacial discharge reduces salinities and splits AASW into a less dense surface water mass which overlies denser Winter Water (WW) (Smith et al., 1999). Given the relatively low $\delta^{18}\text{O}_{\text{water}}$ variation in modern day water masses, (c. 0.6‰ through the entire water column; 0.3‰ in the upper 100 m) (Schmidt et al., 1999; Meredith et al., 2008a, 2010), deglacial $\delta^{18}\text{O}_{\text{diatom}}$ fluctuations of 2-4‰ are highly unlikely to be directly driven by changes in ocean circulation.

4.1.3 Sea-ice

Today the area south of Anvers Island is marked by sea-ice breakup from December to February and open waters/pack ice from February to May (Stammerjohn et al., 2003). Whilst the subsequent sea-ice formation locks up large volumes of water and is characterised by significant inter-annual variability, its impact on $\delta^{18}\text{O}_{\text{water}}$ can be discounted by the low fractionation factor of 1.0026–1.0035 for ice formed in isotopic equilibrium with seawater (Majoube, 1971; Lehmann and Siegenthaler, 1991; Macdonald et al., 1995). Monitoring has also shown that melting sea-ice in spring/summer on average c. 0.5% (maximum <2%) of all water in the mixed layer along the WAP, altering $\delta^{18}\text{O}_{\text{water}}$ by less than 0.1‰ (Meredith et al., 2010). Sensitivity tests have further shown that the impact of sea-ice on $\delta^{18}\text{O}_{\text{diatom}}$ is negligible for realistic changes in Holocene/deglacial sea-ice concentrations, with the proportion of surface water derived from sea-ice melt required to increase from 0.5% to 14% at the expense of UCDW just to alter $\delta^{18}\text{O}_{\text{diatom}}$ beyond analytical error (0.3‰) (Pike et al., In press).

4.1.4 Glacial discharge

Mean annual modern day surface water along the WAP can be simplified as comprising 95.5% UCDW ($\delta^{18}\text{O} = -0.08‰$), 0.5% sea ice melt ($\delta^{18}\text{O} = +2.1‰$) and 4% meteoric water, comprised of glacial discharge (c. $\delta^{18}\text{O} = -20‰$) with additional contributions originating from precipitation (c. $\delta^{18}\text{O} = -13‰$) (Jacobs et al., 1985; Meredith et al. 2008a, 2010). By assuming that meteoric water during the last deglaciation is similar to the modern day in being primarily derived from Antarctic glacial discharge, a relatively small change in volume is capable of significantly altering $\delta^{18}\text{O}_{\text{water}}$ due to the very isotopically depleted nature of the glacial discharge. For example, changing the relative proportion of glacial discharge by only 1.5% at the expense of UCDW in a simple mass-balance calculation (Meredith et al. 2008a) alters $\delta^{18}\text{O}_{\text{water}}$ beyond the $\delta^{18}\text{O}_{\text{diatom}}$ analytical error (0.3‰). This calculation, using a modern day Ryder Bay Antarctic meltwater value of $-20‰$, demonstrates the ability for a small change in modern Antarctic glacial discharge to alter $\delta^{18}\text{O}_{\text{water}}$. It is also reasonable to assume that the isotopic impact of these inputs would have increased in the last deglaciation in response to lower glacial discharge $\delta^{18}\text{O}$ values. For example, ice-core records from across Antarctica document c. 6‰ lower values during the last glacial compared to modern day (EPICA Community Members,

2006; Jouzel et al. 2007).

The proposition that glacial discharge is the main control on $\delta^{18}\text{O}_{\text{diatom}}$ along the WAP is supported by evidence from the modern WAP environment that: 1) glacial discharge, which primarily occurs in summer, is a greater contributor of freshwater to the mixed layer than sea-ice melt, which primarily occurs in spring (Meredith et al., 2008a, 2010); and 2) meteoric water, dominated by glacial discharge, play a major role in regulating seasonal $\delta^{18}\text{O}_{\text{water}}$ variations of c. 0.4-0.7‰ along the WAP by forming c. 6% of all mixed layer water in austral summer compared to 2-4% in other months (Meredith et al., 2008a; 2010).

Whilst we conclude that the $\delta^{18}\text{O}_{\text{diatom}}$ record presented here documents changes in glacial discharge and provides an insight into the stability of glaciers along the WAP during the last deglaciation, the sensitivity of $\delta^{18}\text{O}_{\text{diatom}}$ at ODP Site 1098 to glacial discharge will alter over time in response to the proximity of the ice-sheet and its associated advance/retreat. As the Antarctic Peninsula Ice Sheet moves away from the core site, the increased dilution of the isotope signal from the ice-sheet margin across the mixed layer means that progressively larger glacial discharges are required to trigger the same magnitude change in $\delta^{18}\text{O}_{\text{diatom}}$. Such considerations are further complicated by temporal changes in the isotopic composition of glacial discharge, although the relatively short timeframe, c. 500 years, analysed in this study suggests that these issues may be negligible over the documented interval. Whilst the presence of mixed layer processes do prevent simple mass-balance calculations from being used to quantitatively reconstruct absolute changes in glacial discharge, variations in $\delta^{18}\text{O}_{\text{diatom}}$ nonetheless provide a qualitative indicator of ice-sheet melting and glacial discharge.

4.2 Intra-seasonal differences in $\delta^{18}\text{O}_{\text{diatom}}$

If diatom-water fractionation is consistent across species, allowing measurements of $\delta^{18}\text{O}_{\text{diatom}}$ to be used as an indicator of glacial discharge from the Antarctic continent, different taxa from the same seasonal lamina should have the same $\delta^{18}\text{O}$ value. Whilst $\delta^{18}\text{O}_{\text{water}}$ will vary through a single season in response to changes in glacial discharge, these differences should be averaged out across the sediment material analysed in a given lamination. A surprising finding of this study are the intra-laminae/seasonal offsets between: 1) spring CRS and spring $>10\ \mu\text{m}$ fraction (Fig. 4b); and 2) summer *T. antarctica* RS and summer $<15\ \mu\text{m}$ fraction (Fig. 4c). Issues of secondary isotope exchange (Schmidt et al., 1997, 2001; Brandriss et al., 1998; Moschen et al., 2006) can be discounted as these processes would be expected to alter different species/size fractions from the same sediment horizons to the same extent. At present there is insufficient data to understand the summer lamination offsets (Fig. 5a, b) and no relationship exists between the offsets and the relative abundances of dominant taxa in the sediment assemblages (e.g., CRS, *Fragilariopsis curta*, *Fragilariopsis cylindrus* and *T. antarctica* RS). However a strong linear regression between CRS $\delta^{18}\text{O}_{\text{diatom}}$ and the intra-laminae spring

offsets (CRS $\delta^{18}\text{O}_{\text{diatom}}$ minus $>10\ \mu\text{m}$ fraction $\delta^{18}\text{O}_{\text{diatom}}$) ($R^2 = 0.57$, $p < 0.001$) suggests that lower values of CRS are associated with a more negative offset (Fig. 6a, b). This implies that the intra-lamination offsets in the spring laminae may be linked to the magnitude of spring glacial discharge and diatom depth habitats rather than a non-equilibrium vital effect.

One explanation is that during deglacial spring seasons of increased glacial discharge (low CRS $\delta^{18}\text{O}_{\text{diatom}}$), increased water column stability inhibits the mixing/dilution of glacial discharge (low $\delta^{18}\text{O}_{\text{water}}$) with sub-surface water masses (UCDW - high $\delta^{18}\text{O}_{\text{water}}$) (Fig. 7a). CRS, inhabiting the uppermost sections of the photic zone dominated by greater relative proportions of glacial discharge, would therefore form their frustules from water with lower $\delta^{18}\text{O}_{\text{water}}$. Diatoms in the spring $>10\ \mu\text{m}$ fraction would occupy deeper parts of the photic zone where the proportion of glacial discharge relative to UCDW is reduced, resulting in frustules formed in ambient water with a higher $\delta^{18}\text{O}_{\text{water}}$ and leading to more negative offsets. In years of reduced spring glacial discharge reductions in water column stability increase mixing, reducing/eliminating the vertical $\delta^{18}\text{O}_{\text{water}}$ gradient between depths inhabited by CRS and those inhabited by other taxa (Fig. 7b). This interpretation is in agreement with the observations made here that the larger offsets, as well as the interval of greatest variability, are focused towards the early parts of the studied section prior to 12,450 cal BP when the ice sheet would have been in closer proximity to Palmer Deep, leading to a more dynamic water column environment and greater inter-annual variability in spring glacial discharge (Fig. 6a, b). Whilst this scenario explains instances where the spring isotope offset is negative and is supported by modern day observations showing that changes in the mixed layer depth are linked to amount of surface freshwater (Meredith et al., 2010), it does not explain positive offsets ($n = 6$) which remain unexplained. These positive offsets may be linked to localised variations in $\delta^{18}\text{O}_{\text{water}}$ in a less well stratified water column, although the modern day variability through the upper 100 m of the water column is only c. 0.3‰ (Meredith et al., 2010).

The presence of large spring and summer intra-seasonal offsets in $\delta^{18}\text{O}_{\text{diatom}}$ has implications for future $\delta^{18}\text{O}_{\text{diatom}}$ studies both along the WAP and in other marine/lacustrine systems. Records of planktonic foraminifera $\delta^{18}\text{O}$ have long been derived from single taxa to avoid inter-species vital effects related to non-equilibrium fractionation and depth/habitat related issues. In contrast, research using $\delta^{18}\text{O}_{\text{diatom}}$ has been dominated by bulk species analyses, with a few exceptions (e.g., Barker et al., 2007). Results presented here suggest that significant offsets can exist between different taxa blooming in the same season due to variations in depth habitat and life strategies. Together with the large inter-seasonal differences between the spring CRS and summer *T. antarctica* RS measurements, this documents the need for careful planning and utilisation of diatom isotope records in future work. Consideration of the diatom species within the sediment assemblages, their spatial and temporal distribution in the water column and the desire to extract seasonal or lower resolution information either throughout or at specific depths in the water column will determine whether

bulk, single and/or season-specific taxa should be used in future work. Where bulk species are analysed, consideration should be given in any interpretation as to the extent to which temporal or spatial signals are blurred relative to one another. For example, in the post-lamination Holocene interval at Palmer Deep where spring, summer and autumn frustules are mixed together in the sediment, measurements of $\delta^{18}\text{O}_{\text{diatom}}$ were generated on bulk species samples to increase the amount of diatom material extracted and ensure sufficient material existed for analysis (Fig. 3) (Pike et al., In press). For most samples extracting sufficient material for a single species analyses would only have been achievable by considerably increasing the temporal span of each sample. Analysing bulk samples was therefore performed at the expense of a single-taxon season-specific record to avoid blurring any isotope signal, which would have prevented the detection of the 400-500 year cyclicality during the late Holocene linked to ENSO activity (Pike et al., In press).

4.3 Inter-seasonal evolution of the deglacial $\delta^{18}\text{O}_{\text{diatom}}$ signal

Deglacial $\delta^{18}\text{O}_{\text{diatom}}$ values are typically lower than those for the Holocene and indicate peak glacial discharge delivery to Palmer Deep at this time (Fig. 3). Recurrent variations of $>3\text{‰}$ in both the spring CRS and summer *T. antarctica* RS laminae from 12,719-12,183 cal BP, as well as the bulk species samples from 12,820-12,734 cal BP (Fig. 3, 4a), further highlight significant inter-annual and inter-seasonal variability in the magnitude of glacial discharge. This variability reflects the rapid retreat of regional ice sheet along the peninsula during the last deglaciation (Domack et al., 2001, 2006; Heroy and Anderson, 2007; Johnson et al., 2011; Simms et al., 2011; Smith et al., 2011) and is in contrast to both: 1) the comparatively stable Holocene (Fig. 3); and 2) typical modern day intra-annual and inter-annual variability of c. 0.3‰ (Meredith et al., 2008a, 2010). Direct comparisons of the deglacial spring CRS and summer *T. antarctica* RS laminae indicate increased glacial discharge to the photic zone (lower $\delta^{18}\text{O}_{\text{diatom}}$) during summer months (Fig. 4a), an observation reinforced by comparisons of neighbouring spring and summer laminations (i.e. those from the same year, $p < 0.01$) with only 5 out of the 23 paired samples showing higher spring melting relative to summer (mean seasonal difference = 1.2‰) (Fig. 8). These differences are not attributable to seasonal variations in SST with modern day summer/spring differences of c. 1.5°C (Meredith et al., 2008a, 2010) equivalent to a $\delta^{18}\text{O}_{\text{diatom}}$ shift of only 0.3‰ (i.e. within our analytical error). Increased accumulation of glacial discharge in the deglacial summer photic zone is supported by similar patterns of seasonality observed in the modern day (Meredith et al., 2008a, 2010) and by the higher levels of glacier-derived material in deglacial summer laminae (Maddison et al., 2005). However, the absence of any correlation ($r = 0.21$) and relationship ($p > 0.3$) between spring and summer $\delta^{18}\text{O}_{\text{diatom}}$ implies that the magnitude of summer glacial discharge during deglaciation is not linked to that occurring in the preceding spring months, suggesting that the deglacial ice sheets are responding to seasonal, as opposed to mean annual, conditions. Whilst the isotopic difference between these paired samples provide information on spring-summer seasonality (Fig. 8b), it is not currently possible to link variations to an overriding atmospheric or oceanic

mechanism due to the absence of similar high-resolution records of those potential forcings.

4.3.1 Palaeoenvironmental forcing and the role of glacial discharge in forming deglacial laminations

Contemporary observations of freshwater inputs to the WAP have been associated with inter-annual variability in the El Niño – Southern Oscillation (ENSO) and Southern Annular Mode (SAM). As well as impacting upon the depth of the mixed layer, and so diffusion of glacial discharge through the water column via stronger northerly winds (Meredith et al., 2010), changes in the ENSO and SAM have been linked to alterations in wider atmospheric circulation patterns over Antarctica (Russell and McGregor, 2010) as well as coastal SST and sea ice cover (Thompson and Solomon, 2002; Turner, 2004; Meredith et al., 2008b; Stammerjohn et al., 2008; Mayewski et al., 2009; Ciasto and England, 2011) that in turn influence the flux of oceanic heat delivered to continents and so basal melting (Pritchard et al., 2012). These linkages have been key to explaining Holocene records of SST and glacial discharge variability at Palmer Deep (Shevenell et al., 2011; Pike et al., In press). Recent research has suggested the presence of a decoupled ENSO state during the last deglaciation characterised by enhanced La Niña-like conditions (Makou et al., 2010) together with increased westerlies (Fletcher and Moreno, 2011) indicating positive SAM-like conditions. Alongside the regional shift to warmer conditions which accompanies the transition from a glacial to interglacial state, the establishment of La Niña-like and enhanced positive SAM-like circulation would generate further atmospheric warmth along the WAP (Russell and McGregor, 2010), thereby maximising the flux of glacial discharge into the photic zone and the retreat of the dynamically unstable ice sheets. Variability in the ENSO/SAM-like states may further explain the significant (>3‰) inter-annual variability in glacial discharge documented by both spring and summer laminae $\delta^{18}\text{O}_{\text{diatom}}$. This, however, remains speculative in the absence of a comparable annually-resolved record of ENSO/SAM conditions through the last deglaciation. Indeed, with no synchronicity between deglacial changes in $\delta^{18}\text{O}_{\text{diatom}}$ and Antarctic ice-core records from coastal or continental locations (Fig. 4a), there is likely a need to consider internal glacial processes (Bamber et al., 2007) as well as the regional role of the oceans and other climatic teleconnections in driving variations in the flux of glacial discharge to the photic zone (Mackintosh et al., 2011).

Regardless of the processes controlling the rate of glacial discharge and its subsequent flow into the coastal water column, large inputs of glacial discharge during the last deglaciation would have significantly reduced sea surface salinity (SSS) along the WAP, increasing water column stability. This stability would have been enhanced by the increased importance of salinity in regulating water column structures at low temperatures (Feistel, 2003, 2008) and by the deglacial blockage of the Gerlache Strait (Sjunneskog and Taylor, 2002) limiting the northerly export of glacial discharge. The creation of a stable water column in spring months has further consequences for photic zone biological productivity, first by allowing phytoplankton to remain in the photic zone for longer and secondly by increased transportation of bioavailable nutrients entrained within

glacial discharge from the ground ice sheet as glacial-flour (e.g., Dierssen et al., 2002; Raiswell et al., 2006; 2008; Statham et al., 2008; Hood and Scott, 2008; Hodson et al., 2010; Crusius et al., 2011). These events would have been essential in establishing the low-salinity/nutrient-rich conditions that triggered the highly productive photic zone and rapid sedimentation that led to the formation of the spring laminations at Palmer Deep (Leventer et al., 1996, 2002).

T. antarctica RS measurements typically suggest greater glacial discharge in summer than spring and so similar processes may have also established the high levels of productivity documented in the grey-blue sub-laminae, only to be terminated by the winter expansion of sea ice over the region. However, the presence of taxa including *Corethron pennatum*, *Coscinodiscus bouvet*, *Odontella weissflogii* together with *T. antarctica* RS in both the blue-grey laminae and sub-laminae has been interpreted to indicate a more open/mixed water column in summer months (Maddison et al., 2005). Understanding these changes is important in the context of modern day glacial discharge and associated discussions on its role in driving water column stratification, sea ice formation, changes in the ecosystem and the associated export of this water to lower latitudes (Meredith et al., 2008a, 2010; Montes-Hugo et al., 2009; Schofield et al., 2010). If the diatom assemblages do accurately indicate more mixed conditions in summer, the greater diffusion of an isotope signal through such a water column would imply that the seasonal difference between spring (less glacial discharge – higher $\delta^{18}\text{O}_{\text{diatom}}$) and summer (more glacial discharge – lower $\delta^{18}\text{O}_{\text{diatom}}$) is greater than that implied from the $\delta^{18}\text{O}_{\text{diatom}}$ data alone.

4.3.2 Palaeoclimatic implications of deglacial glacial discharge inputs along the WAP

Previous low-resolution work from the Atlantic and Indian sectors of the Southern Ocean south of the Antarctic Polar Frontal Zone, but distal from the Antarctic continental margin, has documented $\delta^{18}\text{O}_{\text{diatom}}$ changes of up to 3‰ through the Holocene and last glacial cycle (Shemesh et al., 1992, 1994, 1995, 2002). Robust chronologies have never been established for these cores preventing a detailed understanding as to the origin, timing and/or significance of these changes. Extended intervals of low $\delta^{18}\text{O}_{\text{diatom}}$ at Palmer Deep during the last deglaciation characterised by rapid inter-annual variations of >3‰ provide, for the first time, conclusive well-dated evidence of a series of deglacial discharge pulses into the Southern Ocean along the WAP. Given the magnitude of these changes, and depending on the spatial representativeness of these conditions elsewhere along the WAP and Antarctic margin, these meltwater fluxes could have: 1) reduced the supply of oceanic warmth to the coastal region by lowering the contribution of relatively warm UCDW to AASW, influencing climatological connections between the marine and atmospheric systems and further glacial discharge; 2) altered surface water mixing/stability which has implications for understanding localised changes in ocean-atmosphere fluxes of CO_2 (Sigman et al., 2010); and 3) impacted more widely upon hemispheric/global ocean circulation (Menviel et al., 2010; Ma and Wu, 2011). Given chronological

uncertainties that exist in radiocarbon dating around Antarctica (Ohkouchi and Eglinton, 2008), it is not possible to relate specific injections of glacial discharge along the WAP to known changes in global sea-level rise or oceanic patterns. However, large seasonal inputs of glacial discharge over the studied interval (12,719-12,183 cal BP), in addition to that recorded in the bulk species $\delta^{18}\text{O}$ samples (12,820-12,734 cal BP), can be broadly associated with the end of the ACR in Antarctica and the establishment of the Younger Dryas (GS1) stadial in the North Hemisphere. This highlights the need to consider the wider climatological and oceanographic impact of these glacial discharge fluxes over the last deglaciation.

5. Conclusions

The construction of single-taxon and season-specific $\delta^{18}\text{O}_{\text{diatom}}$ records from the deglacial laminated interval at Palmer Deep (ODP Site 1098A), WAP, highlights the considerable potential that exists in using diatom isotope measurements to document atmospheric-terrestrial-marine interactions in sediments which do not contain biogenic/endogenic carbonates. However, with individual spring and summer laminae documenting inter-species variations linked to the life-habits of individual taxa, any future work both around the Antarctic margin as well as in other marine and lacustrine sediment cores is contingent upon the consideration of the origin of the $\delta^{18}\text{O}_{\text{diatom}}$ signal.

Evidence of lower $\delta^{18}\text{O}_{\text{diatom}}$ in summer months during the deglaciation is supported by modern day observations that glacial discharge fluxes from the Antarctic continent peak at this time (Meredith et al., 2008a; 2010). However, the absence of a relationship between: 1) the magnitudes of spring and summer glacial discharge; and 2) glacial discharge and ice-core records from the continental interior, suggests the need to investigate the past/future stability of ice sheet along the WAP from a seasonal and regional, rather than a mean annual perspective. In extending the lower resolution centennial scale Holocene $\delta^{18}\text{O}_{\text{diatom}}$ record for ODP Site 1098, conclusive evidence is documented showing significant, up to 3%, inter-seasonal and inter-annual variations in the magnitude of glacial discharge from the Antarctic continent during the last deglaciation (Figs. 3, 4). This is significantly greater than the c. 0.3% variability observed in the modern day (Meredith et al., 2008a, 2010). With these pulses having the potential to impact upon both regional and global ocean circulation and ocean/atmosphere interactions, further work is now required to examine the spatial representativeness of these changes both along the WAP and elsewhere across the coastal Antarctic margin.

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Supplementary data

Supplementary Table 1: Deglacial lamination $\delta^{18}\text{O}_{\text{diatom}}$ data from ODP Site 1098.

Figures

Figure 1: Location of ODP Site 1098 (64°52.72'S, 64°12.47'W) along the WAP. Core recovered during ODP Leg 178 from 1012 m water depth (Shipboard Scientific Party, 1999). Figure adapted from Hey (2009).

Figure 2: A) Backscattered secondary electron imagery (BSEI) photomosaic from the deglacial seasonally laminated core section at ODP Site 1089 showing the progression from (i) spring biogenic laminae dominated by CRS through to the (ii) summer terrigenous laminae and (iii) late-summer sub-laminae characterised by increases in *T. antarctica* RS. B & C) Secondary electron imagery (SEI) photographs of CRS and *T. antarctica* RS from the spring and late-summer respectively. SEI images taken prior to extraction/cleaning for isotope analysis and highlight the excellent preservation of diatoms in the sediment matrix. Scale bars = 3 mm (A); 20 μm (B/C). Figure adapted from Maddison (2006).

Figure 3: Holocene and lamination bulk species records of $\delta^{18}\text{O}_{\text{diatom}}$ from Palmer Deep (Pike et al., In press) together with spring and summer laminae measurements (this study). Shaded interval represents the seasonally laminated deglacial interval analysed in this study.

Figure 4: A) Comparison of spring CRS and summer *T. antarctica* $\delta^{18}\text{O}_{\text{diatom}}$ data with ice-core $\delta^{18}\text{O}$ data from Dronning Maud Land (EPICA Community Members, 2006). B) Comparison of spring CRS and spring >10 μm fraction $\delta^{18}\text{O}_{\text{diatom}}$. C) Comparison of summer *T. antarctica* RS and summer <15 μm fraction $\delta^{18}\text{O}_{\text{diatom}}$.

Figure 5: A) Comparison of summer *T. antarctica* RS and the summer isotope offset (*T. antarctica* RS minus >10 μm fraction). B) Linear regression of summer *T. antarctica* RS against summer isotope offset (solid line) ($n = 6$).

Figure 6: A) Comparison of spring CRS and the spring isotope offset (CRS minus >10 μm fraction). B) Linear regression of spring CRS against spring isotope offset (solid line) with the 95% confidence intervals (dashed line) ($n = 21$) ($R^2 = 0.57$, $p < 0.001$). If only negative offsets are considered $R^2 = 0.68$, $p < 0.01$. If the two lowest CRS $\delta^{18}\text{O}_{\text{diatom}}$ values are removed $R^2 = 0.16$, $p = 0.08$ and $R^2 = 0.32$, $p = 0.03$ when considering the whole dataset and negative offsets respectively.

Figure 7: Schematic diagram attributing the isotope offset between spring CRS and the spring >10 μm fraction to increased glacial discharge and water column stratification. A) Increased glacial discharge leads to greater water column stability. CRS bloom close to the surface in water with a higher proportion of glacial discharge, leading to frustules with low $\delta^{18}\text{O}$. Taxa in the >10 μm fraction occupy water at deeper depths that contains less glacial discharge, leading to frustules with higher $\delta^{18}\text{O}$ relative to CRS. B) Lower glacial discharge input reduces water column stability, leading to increased homogenisation of the isotopes between the water column depths occupied by CRS and >10 μm fraction taxa and bringing the magnitude of the spring offset closer to zero.

Figure 8: A) Comparison of spring CRS and summer *T. antarctica* RS $\delta^{18}\text{O}_{\text{diatom}}$ data from neighbouring laminations. (i.e. from the same year). B) Seasonal offset between CRS $\delta^{18}\text{O}_{\text{diatom}}$ (spring) and *T. antarctica* RS (summer) from neighbouring laminations. Positive (negative) values indicate higher (lower) levels of summer glacial discharge relative to spring.

Tables

Table 1: Summary of size fractions and terminology used in manuscript

Laminae	Size fraction	Taxa present	Term used in text
Spring	<10 μm	CRS	CRS
Spring	>10 μm	Various	Spring >10 μm fraction
Summer	>15 μm	<i>T. antarctica</i> RS	<i>T. antarctica</i> RS
Summer	<15 μm	Dominated by CRS	Summer <15 μm fraction

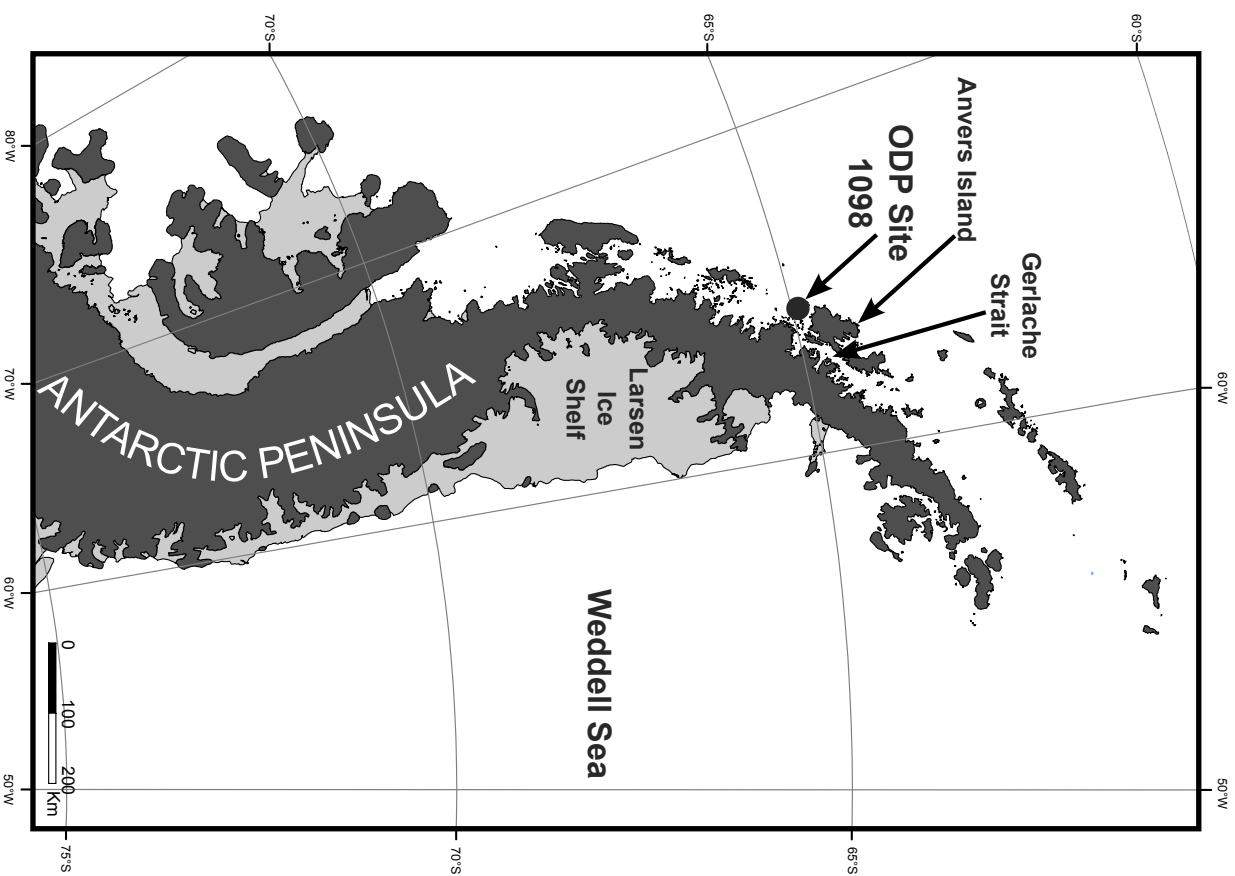


Figure 1

Figure 3

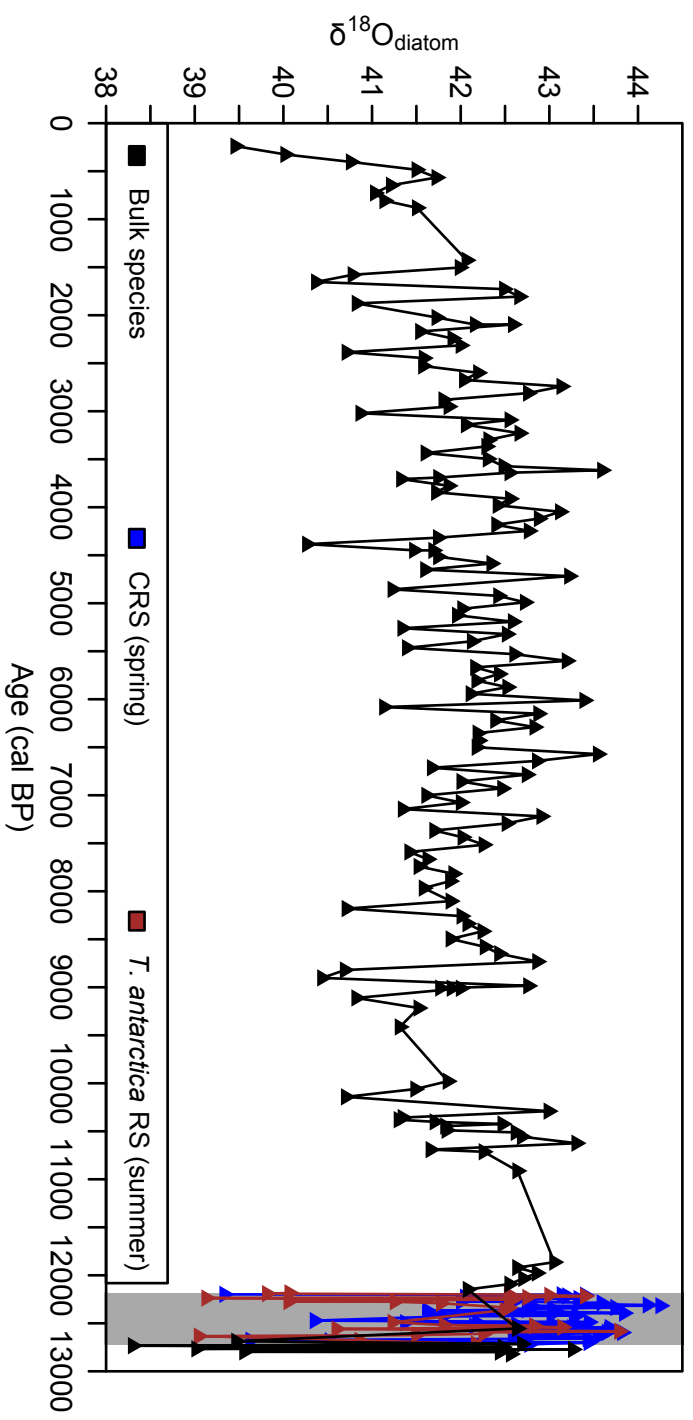


Figure 4

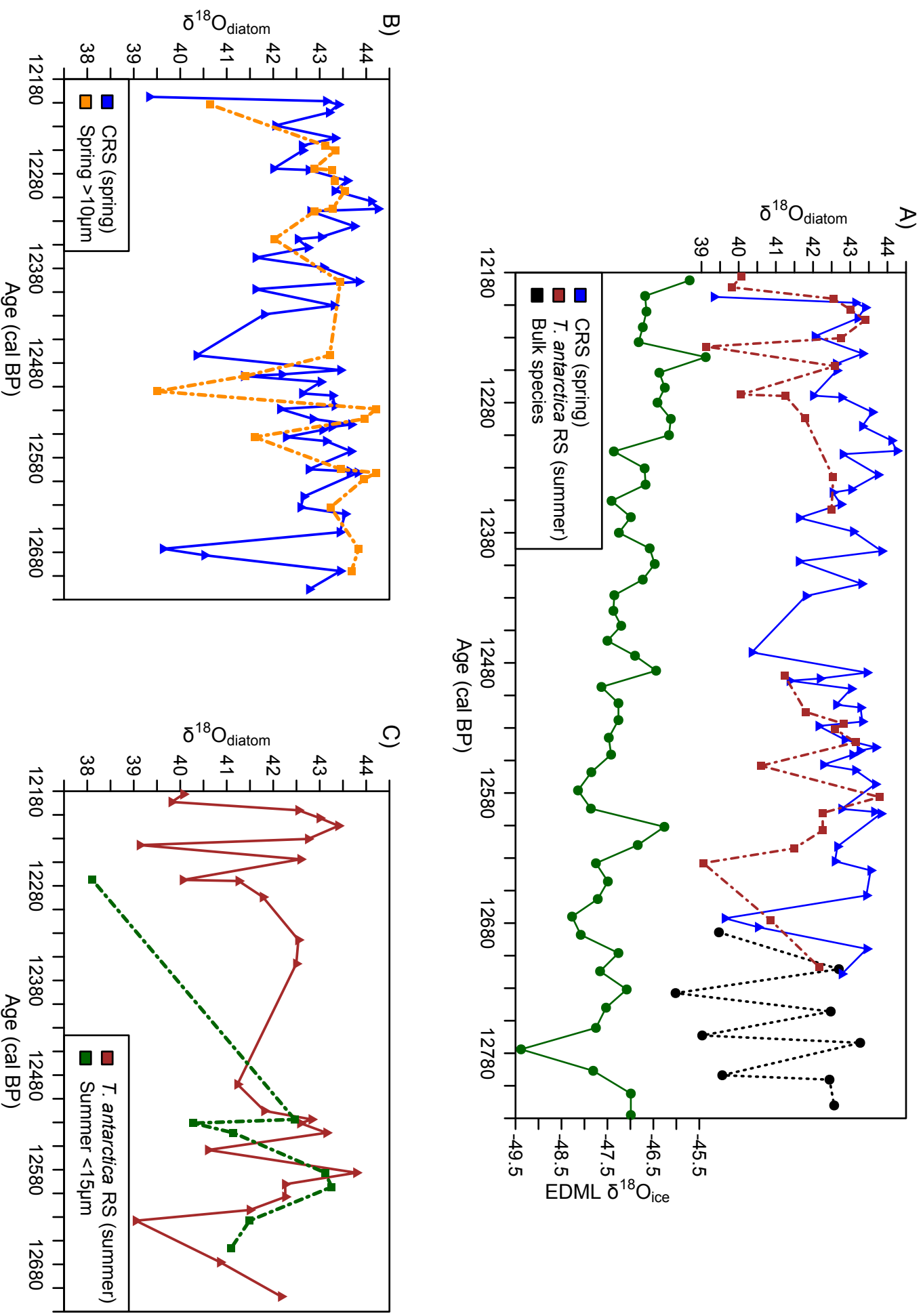


Figure 5

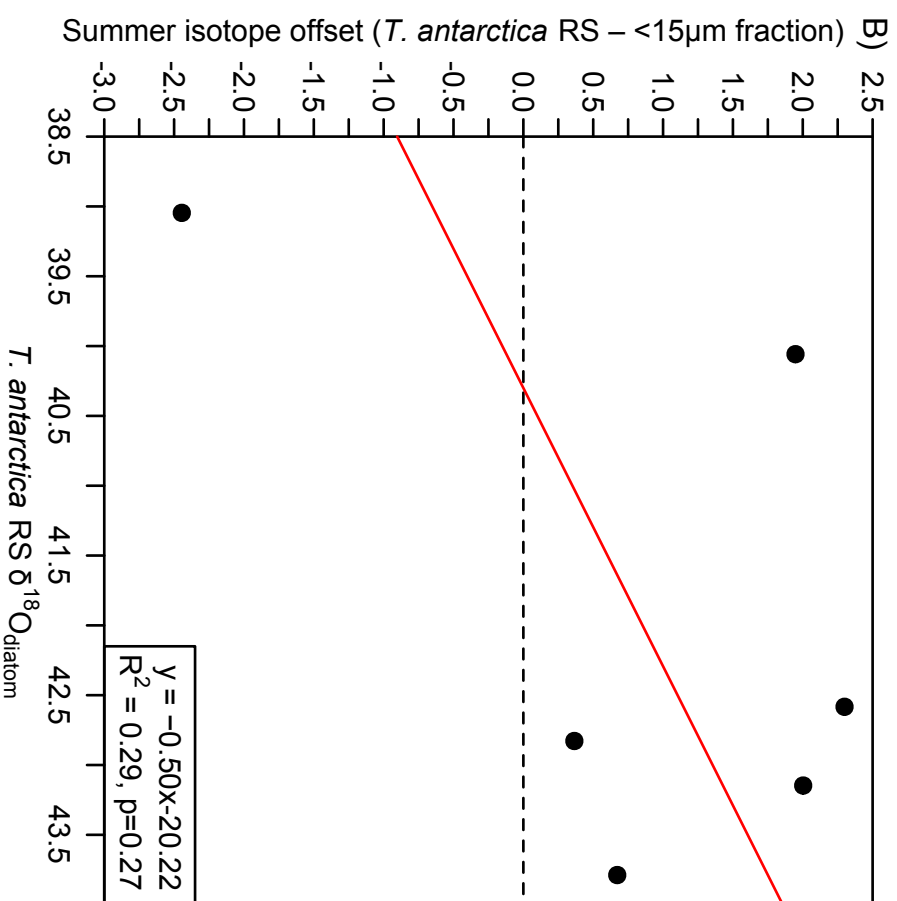
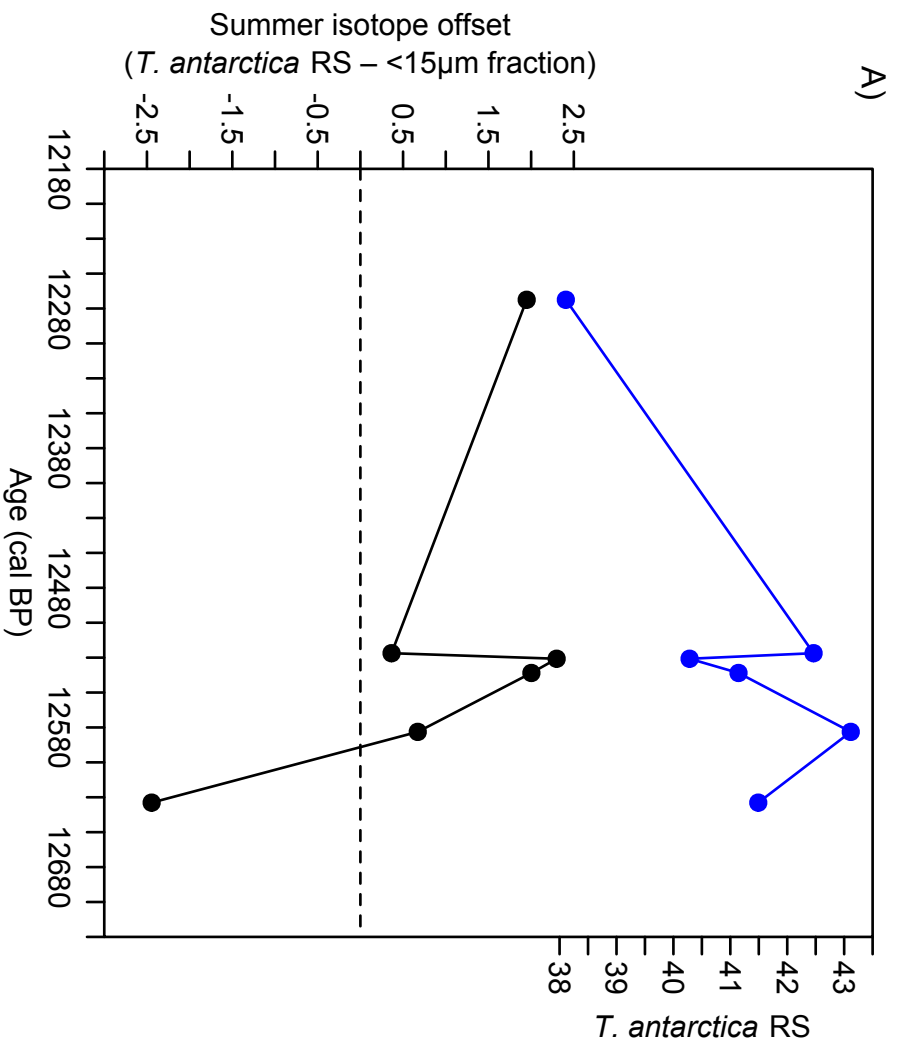


Figure 6

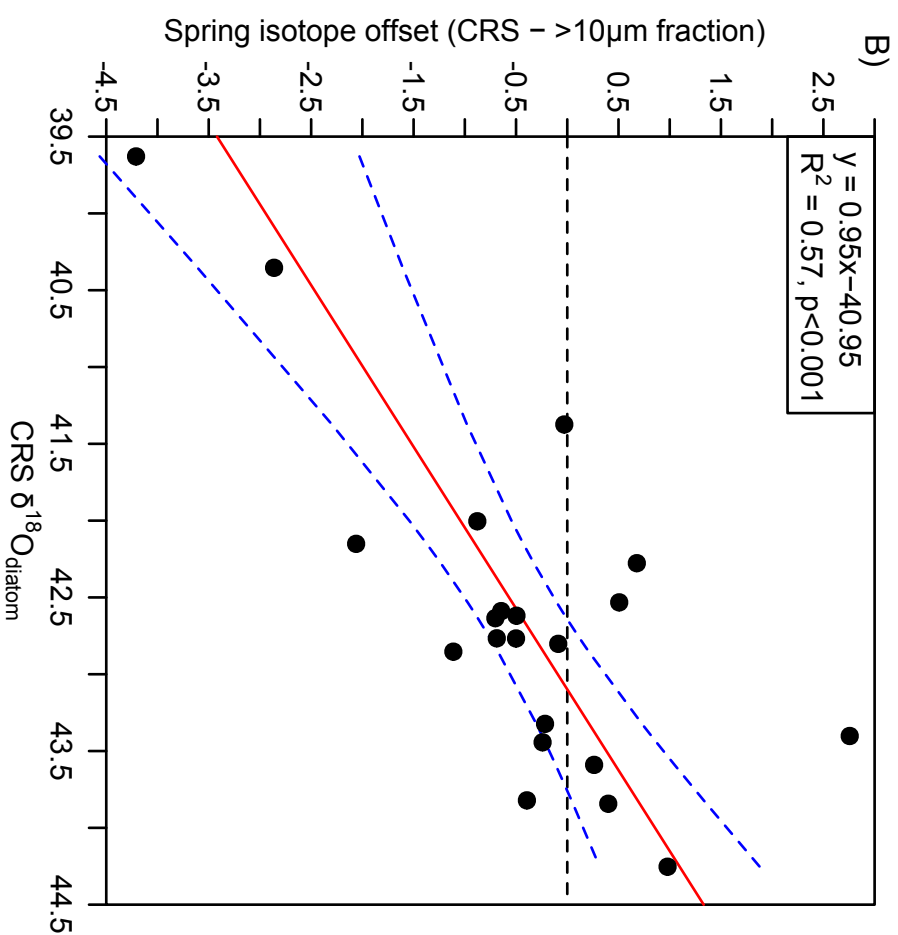
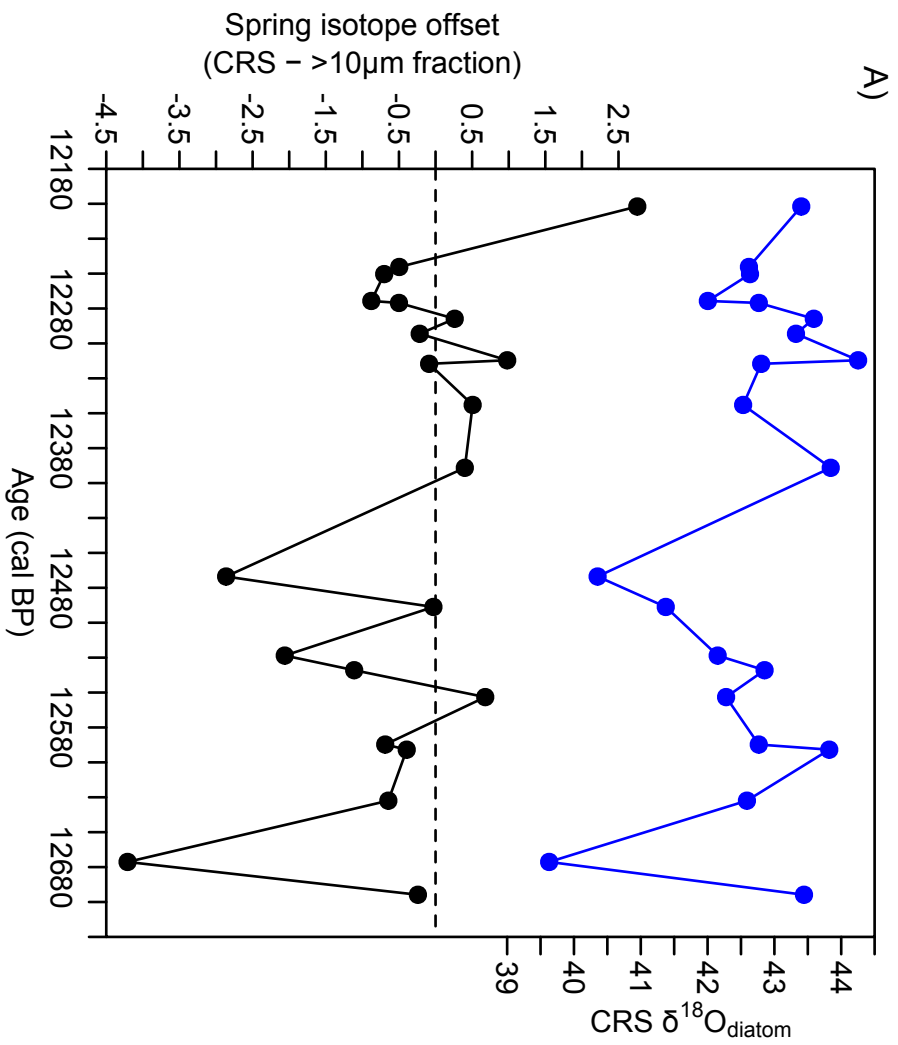


Figure 7

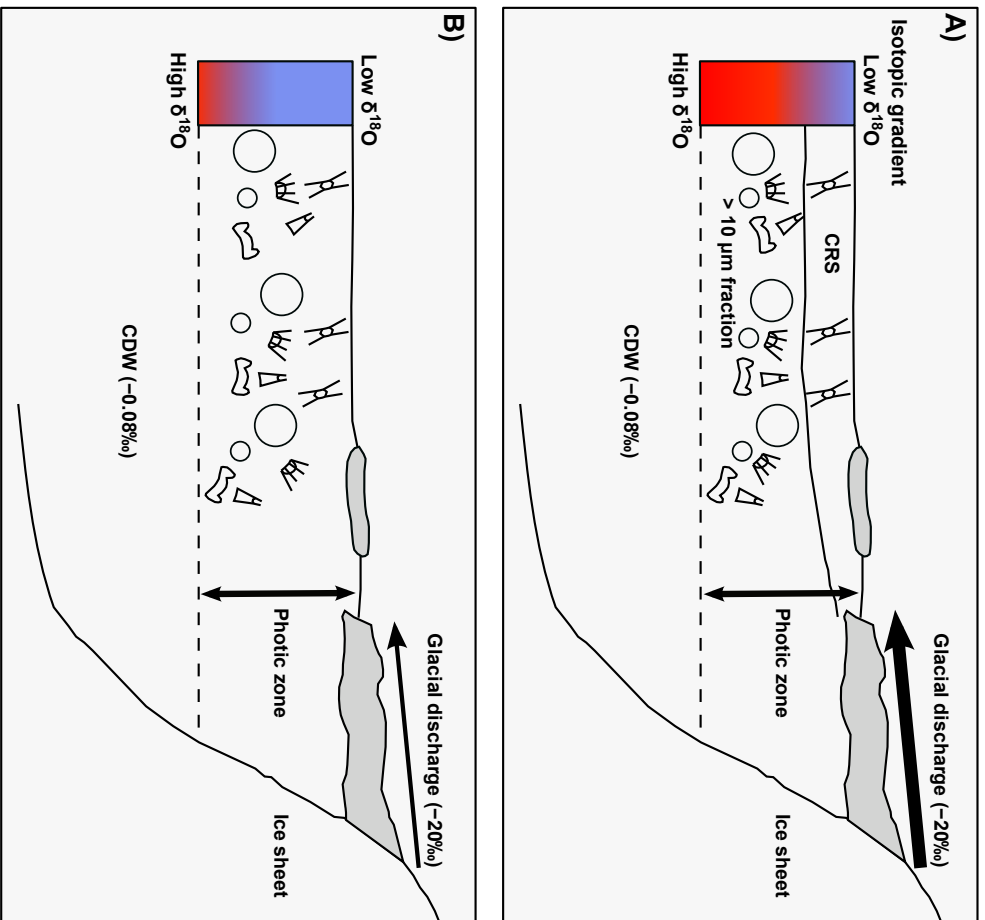


Figure 8

