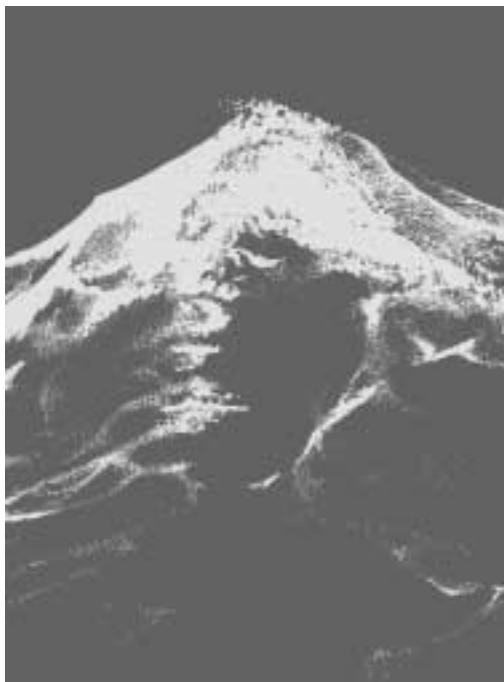


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## Magnesium, calcium and strontium in waters of the southern Tasman Sea at the confluence of the Indian, Pacific and Southern Oceans

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**Abstract.** Data are presented for magnesium (Mg), calcium (Ca) and strontium (Sr) analyses for surface samples and conductivity–temperature–depth profiles of waters along three main transects across the Subtropical Front (STF) and the Subantarctic Front (SAF) in a region between Tasmania and New Zealand down to 57°S. This area is at the confluence of the Indian, Pacific and Southern Oceans where the Subantarctic Mode Water (SAMW) is formed and which is characterized by well-mixed and thick (down to 1000 m) thermostads with uniform salinity and temperature. Such thermostads form at the end of winter, and two of such mode water-forming areas were sampled in October–November 1998. Magnesium and Ca are proving to be quasi-conservative elements down the water column, but there is systematic depletion for Mg compared with profiles measured in the North and South Atlantic Oceans. This offset is interpreted to be the result of hydrothermal activity in the region at the south-east Indian Ridge, which scavenges some Mg. The Circumpolar Deep Water (CDW) intersects this Ridge and upwells south of the SAF and eventually is transformed in the upper 1000 m of the water column into the SAMW. This explains the uniform Mg depletion throughout the entire depth profiles. Strontium, on the other hand, displays significant shifts near the ocean surface at many locations, and this is interpreted as the result of biogenic productivity, which engenders the precipitation of celestite microcrystals.

*Extra keywords:* Acantharia, Circumpolar Deep Water, Subantarctic Mode Water.

### Introduction

During recent years, there has been increasing interest in using the trace-elemental composition of planktic and benthic foraminifers for reconstructing past environmental conditions at sea. However, for this work, it has been assumed that the magnesium (Mg)/calcium (Ca) and strontium (Sr)/Ca ratio of seawater has remained constant for the Quaternary because these three elements, Mg, Ca and Sr, each have long residence time ( $1.3 \times 10^7$ ,  $1.1 \times 10^6$  and  $5.1 \times 10^6$  years respectively; Broecker and Peng 1982). Already, de Villiers (1999) has demonstrated a change of Sr concentration in a north–south transect in the Pacific Ocean along 179°E, and she suggested that this Sr-depletion in the upper ocean water is the result of selective biological uptake of Sr, possibly in the skeleton of unicellular organisms such as acantharians.

The work presented here documents a study of the trace-elemental composition of waters collected during the TASQWA cruise (TASQWA: Quaternary variability of water masses in the Southern Tasman Sea and the Southern Ocean) (SW Pacific Sector; Thiede and Nees 1999), which took

place during the austral spring (between 16 October and 12 November 1998). The aims of the cruise were to obtain a variety of modern-day parameters such as trace-elemental (presented here) and stable-isotopic chemistry (De Deckker and Müller, unpublished data) for use in the interpretation of sediment cores taken during the same cruise. We believe that our data are the first to be published for a still poorly known oceanographic region compared with the other oceanic areas. Our cruise covered the southern Tasman Sea at the confluence of the Indian and Pacific Oceans together with the Southern Ocean.

### Oceanography

The South Pacific and Southern Oceans are regions of intense oceanographic processes because of their surface-water current regimes and the formation of bottom water for the southern hemisphere. This area is characterized by different water masses that extend both vertically as well as horizontally, several of which are described below and characterized in Table 1 and Fig. 1.

**Table 1. Characteristics of the water masses recognized in the study area (42–57°S 147–177°E)**

|        | Water mass                   | Location   | Salinity  | Temperature (°C) |
|--------|------------------------------|--|-----------|------------------|
| STSW   | Subtropical Surface Water    | Challenger Plateau, northern part of South Tasman Rise   | 34.4–35.2 | >8               |
| SASW   | Subantarctic Surface Water   | South of the Subantarctic Front  | 34.2–34.4 | 8–15             |
| SAMW-1 | Subantarctic Mode Water (1)  | Type-1: north of the Subantarctic Front and south of Campbell Plateau  | 34.4      | ~7               |
| SAMW-2 | Subantarctic Mode Water (2)  | Type-2: north of the Subantarctic Front and east of Campbell Plateau   | 34.3      | ~7               |
| AAIW   | Antarctic Intermediate Water | East of Campbell Plateau, the South Tasman Rise and Challenger Plateau below SAMW-2  | 34.4–34.6 | 2–4              |
| CPDW   | Circumpolar Deep Water       | Near surface south of Subantarctic Front and in vicinity of SAMW, and below upper waters of South Tasman Rise and Campbell Plateau | ~34.7     | <2               |
| CPSW   | Circumpolar Surface Water    | South of the Polar Front   | ~33.9     | 1–4              |

### Surface waters and front systems

Three surface water masses occur in this region and are bound by three major oceanic fronts (Fig. 1a). In the northern part of the study area, referred to here as the southern Tasman Sea, the high-salinity (35.7–35.8), nutrient-poor Subtropical Surface Water (STSW) lies to the north of the Subtropical Front (STF). The nutrient-rich and low salinity (~34.5) Subantarctic Surface Water occurs south of the STF. The Subantarctic Mode Water (SAMW) is delimited to the south by the Subantarctic Front (SAF) from the fresher, cooler Circumpolar Surface Water (CPSW) found south of the SAF. The CPSW is, in turn, bound to the south by the Antarctic Convergence/Polar Front (PF). The position and the intensity of the STF and SAF are strongly influenced by sea-floor topography. To the west of New Zealand and across the Tasman Sea, the STF hovers below Tasmania at 45°S (Orsi *et al.* 1995) and, on reaching the South Island of New Zealand, the STF follows the continental slope (Southland Front). On reaching the Chatham Rise, this front continues east as the STF at approximately 43°S, before becoming diffuse and eventually looping south (Heath 1985; Carter *et al.* 1998). The STF displays some seasonal variation between 44°S in the austral winter to 42°S in late austral summer (Chiswell 1994). For more details, refer to Gordon (1972), Heath (1985), Orsi *et al.* (1995) and Carter *et al.* (1998).

### Other water masses

The Antarctic Intermediate Water (AAIW), with a depth range of ~600–1450 m, underlies the surface waters of this region. The AAIW forms by water sinking at the PF and then deepens away from the frontal zone; see Table 1 and Fig. 1b for more details. The AAIW moves unimpeded east of Chatham Rise and can be traced as far north as 15°S (Tomczak and Godfrey 1994). Of importance to the study here is the SAMW, which forms in late winter and is characterized by a thick layer that extends down to 600 m or even more and which eventually becomes part of the central

water of the southern hemisphere (Tomczak and Godfrey 1994). Beneath the AAIW lies a large, northward-flowing deep-water mass, the Circumpolar Deep Water (CPDW), which Gordon (1975) subdivided into three distinct units: the upper CPDW, the lower CPDWi and the lower CPDWii. The latter two comprise the main body of the Deep Water Bottom Current flow. We will not distinguish these different units here but treat the entire CPDW as a single water mass.

### Subantarctic mode water

In an area north of the circumpolar SAF, deep (>600 m), well-mixed waters with uniform salinity and temperature occur (Deacon 1937; McCartney 1977). This water is well developed by late winter and characteristically ranges between 6 and 7°C and 34.3 and 34.4 salinity, depending on its location around Antarctica. In the area studied here, two distinct occurrences of SAMW were found in spring 1998: SAMW-1, with salinity ~34.4 and temperature ~7.5°C, is best seen at sites in Transect 2 south of Campbell Plateau; and SAMW-2, with salinity ~34.3 and temperature ~7°C, is best seen in Transect 2 east of Campbell Plateau (Figs 1, 2). The SAMW eventually contributes to the central water, which then flows equatorward in all three oceans away from the Southern Ocean.

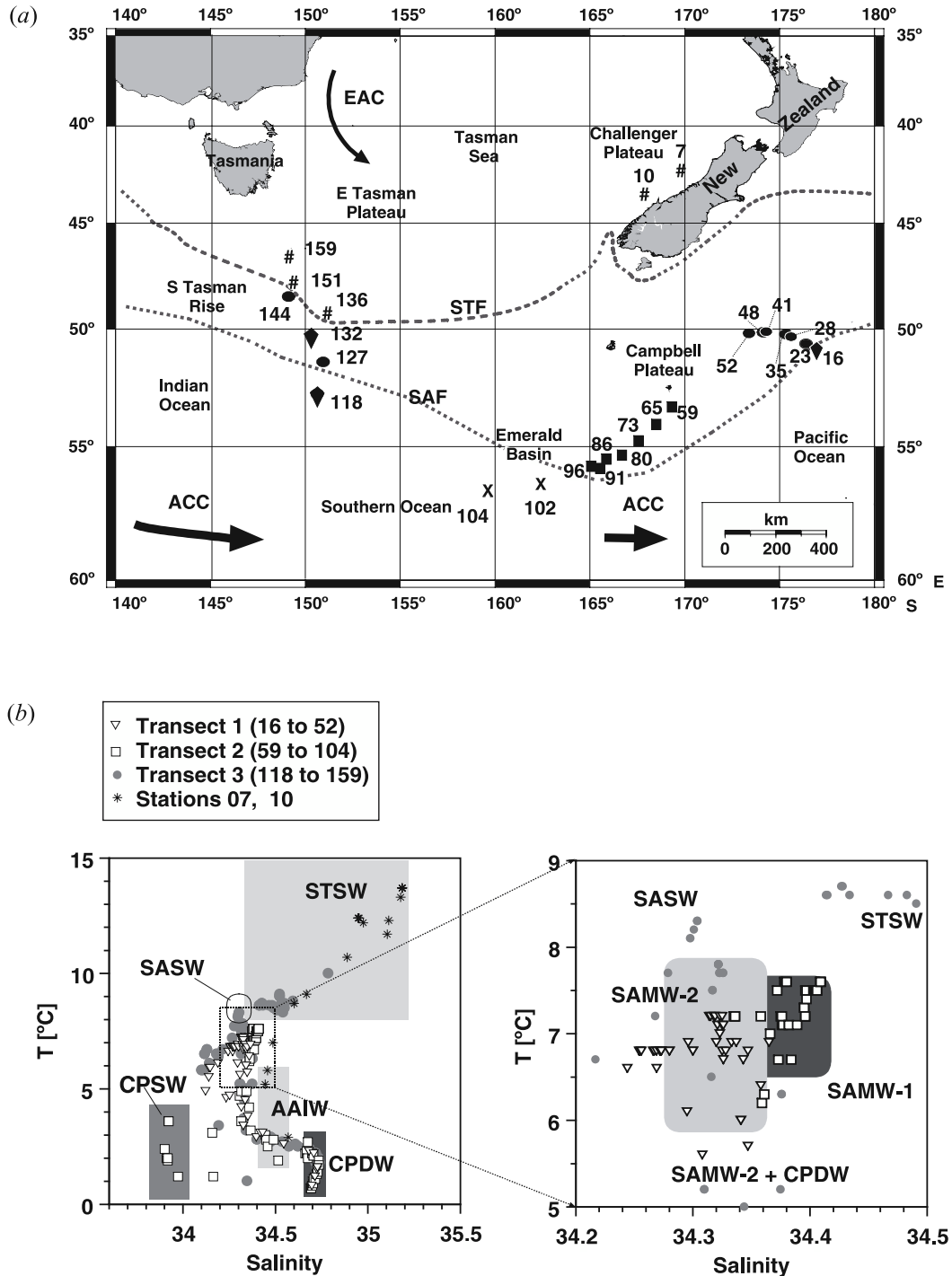
### Magnesium, calcium and strontium concentrations in seawater

#### Magnesium

Magnesium, one of the major elements in seawater, is usually conservative, but is readily scavenged near hydrothermal activity (Edmond *et al.* 1979). This is the case in our study area where the south-east Indian Ocean Ridge is a very obvious topographic feature and a place of fresh magmatic formation and alteration (Buck *et al.* 1998).

#### Calcium

Calcium concentration in seawater is usually proportional to salinity throughout the water column of all oceans.



**Fig. 1.** (a) Map showing the location of the sampling sites of cruise SO136. Three main transects are referred to in the text: Transect 1 for stations SO136-16 to SO136-52; Transect 2 for stations SO136-59 to SO136-104; and Transect 3 for stations SO136-118 to SO136-159. Two additional stations, SO136-07 and SO136-10, were taken above the Challenger Plateau. The position of the various front systems and surface water masses in the vicinity of all the sites where the CTD profiles were taken are indicated. These are the Subtropical Front or Subtropical Convergence (STF) and the Subantarctic Front (SAF). EAC, East Australian Current; ACC, Antarctic Circumpolar Current. Surface water: #, Subtropical Surface Water (STSW); ●, Subantarctic Mode Water-1 (SAMW-1) as surface waters; ◆, Subantarctic Surface Water (SASW); ×, Circumpolar Surface Water (CPSW) as surface waters. (b) TS-diagram characterizing the different water masses for the various transects.

Nevertheless, some depletion can occur in the photic zone as a result of Ca uptake by organisms, such as foraminifers and coccolithophores that form calcareous tests. Below that zone, especially below the calcite compensation depth (CCD), and within the lysocline that lies just above the CCD (James and Choquette 1983), the skeleton of some of those organisms dissolves and Ca is returned into solution.

### Strontium

Although it is commonly accepted that Sr is a conservative element in seawater, Brass and Turekian (1972) and de Villiers (1999), who analysed Pacific Ocean waters, identified a significant depletion in the upper part of the water column, which they attributed to the uptake of this element by unicellular organisms such as acantharians, which secrete a celestite-skeleton. Since seawater is undersaturated with respect to  $\text{SrSO}_4$ , after death, the skeletons of the acantharians slowly sink and Sr is returned into solution on dissolution of the celestite crystals; the Sr 'anomaly' consequently disappears.

### Methods

#### Sampling and analytical methods

During the TASQWA cruise on board the *RV Sonne* (cruise 136, referred to here as SO136- followed by the station number), water samples were taken (Fig. 1; Table 2) for analysis of Mg, Ca and Sr with standard conductivity–temperature–depth (CTD)/rosette equipment

**Table 2.** List of stations visited during the TASQWA cruise on board the *RV Sonne*

| Station   | Latitude   | Longitude   | Water depth (m) |
|-----------|------------|-------------|-----------------|
| SO136-007 | 42°17.71'S | 169°50.65'E | 950             |
| SO136-010 | 43°26.56'S | 167°51.27'E | 1500            |
| SO136-016 | 50°50.89'S | 176°53.33'E | 4500            |
| SO136-023 | 50°39.08'S | 176°22.62'E | 3451            |
| SO136-028 | 50°19.81'S | 175°34.83'E | 1571            |
| SO136-035 | 50°13.42'S | 175°18.98'E | 1359            |
| SO136-041 | 50°07.93'S | 174°07.60'E | 950             |
| SO136-048 | 50°06.30'S | 174°16.31'E | 756             |
| SO136-052 | 50°09.91'S | 173°21.97'E | 564             |
| SO136-059 | 53°20.13'S | 169°14.97'E | 603             |
| SO136-065 | 54°05.00'S | 168°30.09'E | 1000            |
| SO136-073 | 54°45.01'S | 167°29.88'E | 1110            |
| SO136-080 | 55°20.01'S | 166°39.98'E | 1678            |
| SO136-086 | 55°30.06'S | 165°52.19'E | 2070            |
| SO136-091 | 55°50.24'S | 165°30.21'E | 3058            |
| SO136-096 | 55°46.71'S | 165°09.28'E | 4136            |
| SO136-102 | 56°28.88'S | 162°15.47'E | 4228            |
| SO136-104 | 56°45.13'S | 159°34.51'E | 4000            |
| SO136-118 | 52°48.80'S | 150°36.74'E | 3886            |
| SO136-127 | 51°27.08'S | 150°55.79'E | 4030            |
| SO136-132 | 50°20.02'S | 150°20.10'E | 3391            |
| SO136-136 | 49°13.26'S | 151°05.99'E | 3026            |
| SO136-144 | 48°29.99'S | 149°06.83'E | 2178            |
| SO136-151 | 47°45.25'S | 149°23.01'E | 1840            |
| SO136-159 | 46°33.18'S | 149°04.98'E | 3688            |

(Thiede and Nees 1999). Before water samples were stored in polyethylene bottles, all 30-mL polyethylene bottles were cleaned in a 2% Mucosal solution for at least 1 week, after which they were rinsed three times with water to remove tensids. After that procedure, the bottles were washed twice and filled with Milli Q water to which 0.3 mL of purified concentrated qHCl (Kuehner *et al.* 1972) was added. The bottles were closed and stored at 60°C for 1 week, after which time they were washed twice and filled with Milli Q water to which 1 mL of purified concentrated qHNO<sub>3</sub> (Kuehner *et al.* 1972) was added. The bottles were again kept filled for 1 week at 60°C, and after that were again washed twice and filled with Milli Q water, to which 0.3 mL of purified concentrated qHCl (Kuehner *et al.* 1972) was added. All bottles were closed, sealed with Parafilm surrounding the cap and wrapped in plastic film prior the cruise. To each water sample, 0.03 mL purified concentrated qHCl (Kuehner *et al.* 1972) was added. The cap was then sealed with Parafilm and wrapped in plastic film.

In the laboratory at Geomar in Kiel, the water samples were diluted with Milli Q water by 1 to 10 to reduce salinity and the elemental concentrations. Magnesium, Ca and Sr were analysed by inductively coupled plasma atomic emission spectroscopy (ISA Jobin Yvon Pty Ltd, <http://www.jyhoriba.co.uk>) using a 10 ppm Y internal standard. In order to exclude matrix effects, sodium (1077 mg kg<sup>-1</sup>; NaCl pure) and potassium (38 mg kg<sup>-1</sup>; KCl suprapure), typical for seawater, were added to the calibration standards. Because of the purity of NaCl and KCl, contamination of seawater standards by Mg, Ca and Sr was below the detection limit. Magnesium, Ca and Sr were measured by using a polychromator selecting undisturbed and most intensive element lines (Mg 279.55 nm; Ca 317.93 nm; Sr 407.77 nm; Y 371.03 nm). The element detection was made by photomultipliers, the high tension of which was adapted to each element concentration range. After each tenth to twelfth analysis, a standard was measured in order to determine for the machine's drift. The mean value of the standard for seawater (1 : 10 diluted), standard deviation, relative standard deviation and the root mean square deviation by replicates of  $n = 21$  for Mg, Ca and Sr is shown in Table 3.

#### Necessity of filtering the water samples

Three CTD profiles (SO136-23, SO136-127, SO136-132) were taken in order to compare results between unfiltered and filtered water samples. Two water samples from each CTD bottle were taken; one was filtered with Minisart NML filter (pore size 0.2 µm); the other sample remained unfiltered. Acid was added to both types of samples while at sea.

For comparison, water samples from the North and South Atlantic were also analysed. The North Atlantic samples were taken during cruise M39/1 between 18 April and 12 May 1997 with *RV Meteor* (36–44°N, 6–11°W; Schott *et al.* 1999; Müller 2000). During cruise ANT XI/2 with *RV Polarstern*, water samples were taken (40–50°S, 11–22°W; Gersonde 1995; Nürnberg 1995) in the South Atlantic. The Atlantic Ocean water samples were treated and analysed in the same way at Geomar by the senior author using the same equipment.

### Results

#### Water masses

Three main transects are utilized to characterize surface waters and water masses below for all samples obtained during the TASQWA. Data are graphically presented in Fig. 2a–c. Information for the other two stations west of New Zealand (SO136-07, SO136-10) is presented in Fig. 2d.

Transect 1 (Fig. 2a) is characterized by SAMW-2 with a salinity of ~34.3 (34.3 ± 0.03), although we do not know its full extent at depth in the westernmost stations as our CTD

**Table 3. Comparison of trace-elemental analyses of replicate water samples collected during the TASQWA cruise**

| Element                     | Number of analyses | Arithmetic mean | s.d.  | Root mean square deviation | Relative standard deviation (%) |
|-----------------------------|--------------------|-----------------|-------|----------------------------|---------------------------------|
| Mg (mmol kg <sup>-1</sup> ) | 21                 | 5.08            | 0.067 | 0.0150                     | 1.35                            |
| Ca (mmol kg <sup>-1</sup> ) | 21                 | 0.76            | 0.006 | 0.0014                     | 0.82                            |
| Sr (μmol kg <sup>-1</sup> ) | 21                 | 7.94            | 0.038 | 0.0084                     | 0.48                            |

profiles proved too shallow (~500 m). It appears that some mixing in the lower portion of this mode water was occurring with the AAIW below, and that a thermocline was being re-established eastwards. The CPDW could be sampled at two stations only (SO136-16 and SO136-23), one on each side of the SAF. At station SO136-16, south of the front, no SAMW could be found. At that location too, the AAIW was close to the surface. Once the CPDW is reached at depth, its salinity is 'locked' around 34.7.

Transect 2 is more complex to interpret (Fig. 2b), although the mode water, called here SAMW-1 is clearly defined with a lower salinity (34.4) and a slightly more elevated temperature (>7°C) compared with SAMW-2. We interpret the waters below SAMW-1 to possibly belong to the same SAMW-2 as they are characterized by lower salinities, although they could be interpreted as being part of the AAIW. This remains unclear owing to the few stations we have sampled in this area. Nevertheless, below 500 m or so, in the middle of the transect, we note a lower salinity water clearly visible around 1000 m water depth. If it is not the SAMW-2, it appears to be some mode water that sank below the SAMW-1, which may have formed in the late winter/early spring of 1998.

The CPDW is obvious in the deepest CTD profiles (~2000 m) north of the SAF, whereas it is close to 700 m south of the SAF. Finally, extremely low salinities are encountered near the surface south of the SAF, with lowest values (<34) characterizing the CPSW, down to ~150 m. Below this horizon, we witness a transition between the CPSW and CPDW.

Transect 3 (Fig. 2c) is also complex to interpret. It is located north of the PF and transects the SAF and the STF twice because of the meandering nature of this boundary caused by large eddies with commonly dissipate in this region (Tomczak and Godfrey 1994). The latter eddies are frequently visible on satellite images, and commonly contain cores of STSW as seen at station SO136-136. At station SO136-144, we believe that SAMW-2, or a similar mode water, was sampled in the upper 1000 m and that the water was encountered below ~500 m north and south of this station (see Fig. 2c). Perhaps we ought to refer to this water as 'central water in the making', but it is characterized by a salinity of 34.3, again most prominent around 1000 m water depth. Below this is a mixture of waters that we interpret as

being AAIW and that we also label in Fig. 2c as CPDW mixing with SAMW-2. Once a water depth of 2000 m is reached, the CPDW is encountered.

#### *Filtered versus unfiltered samples*

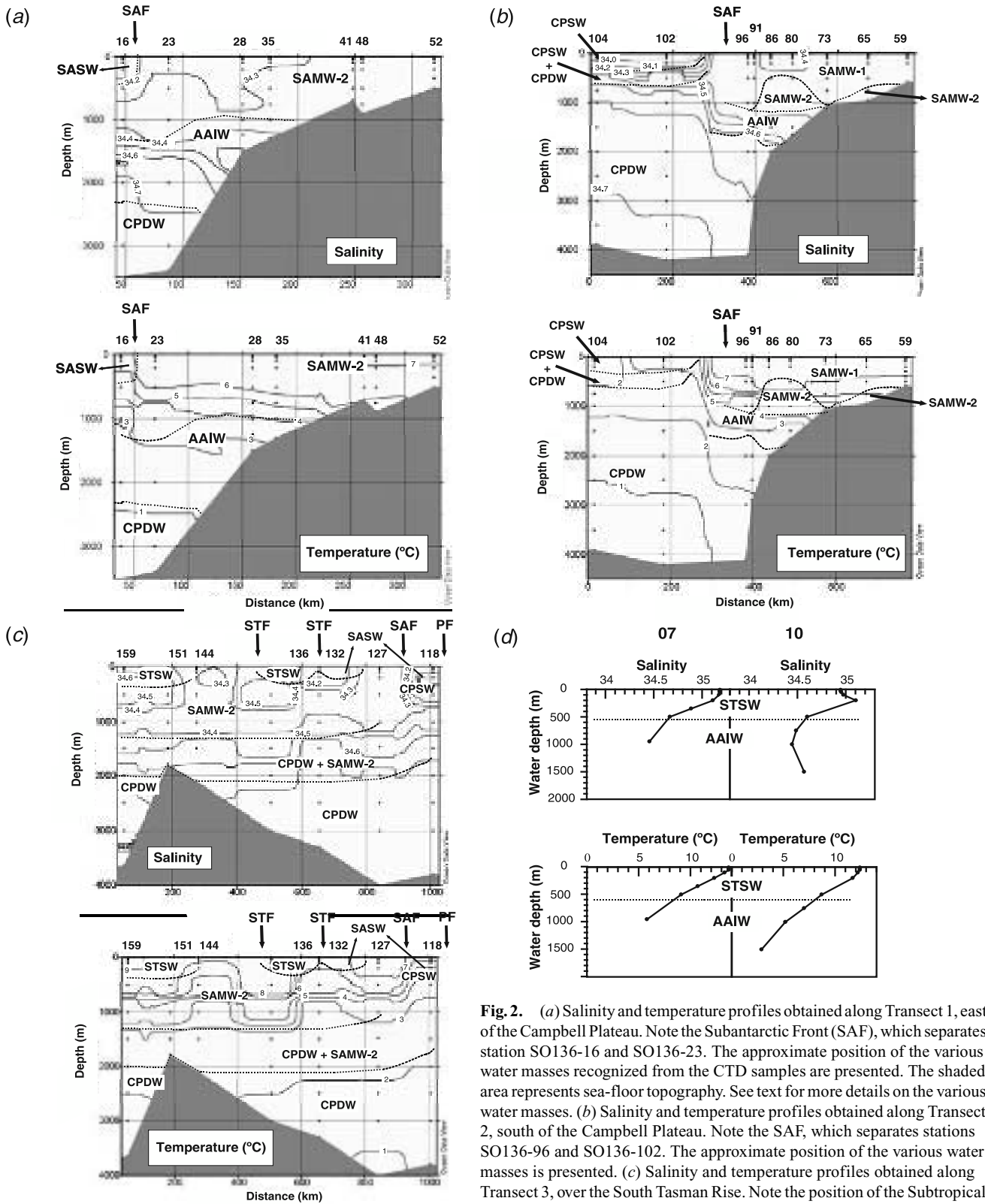
For Mg and Ca, little difference between filtered and unfiltered water samples can be observed (Mg ± 0.8 mmol kg<sup>-1</sup>; Ca ± 0.08 mmol kg<sup>-1</sup>). Negligible difference exists between filtered and unfiltered water samples with respect to Sr (± 0.9 μmol kg<sup>-1</sup>).

#### *Magnesium*

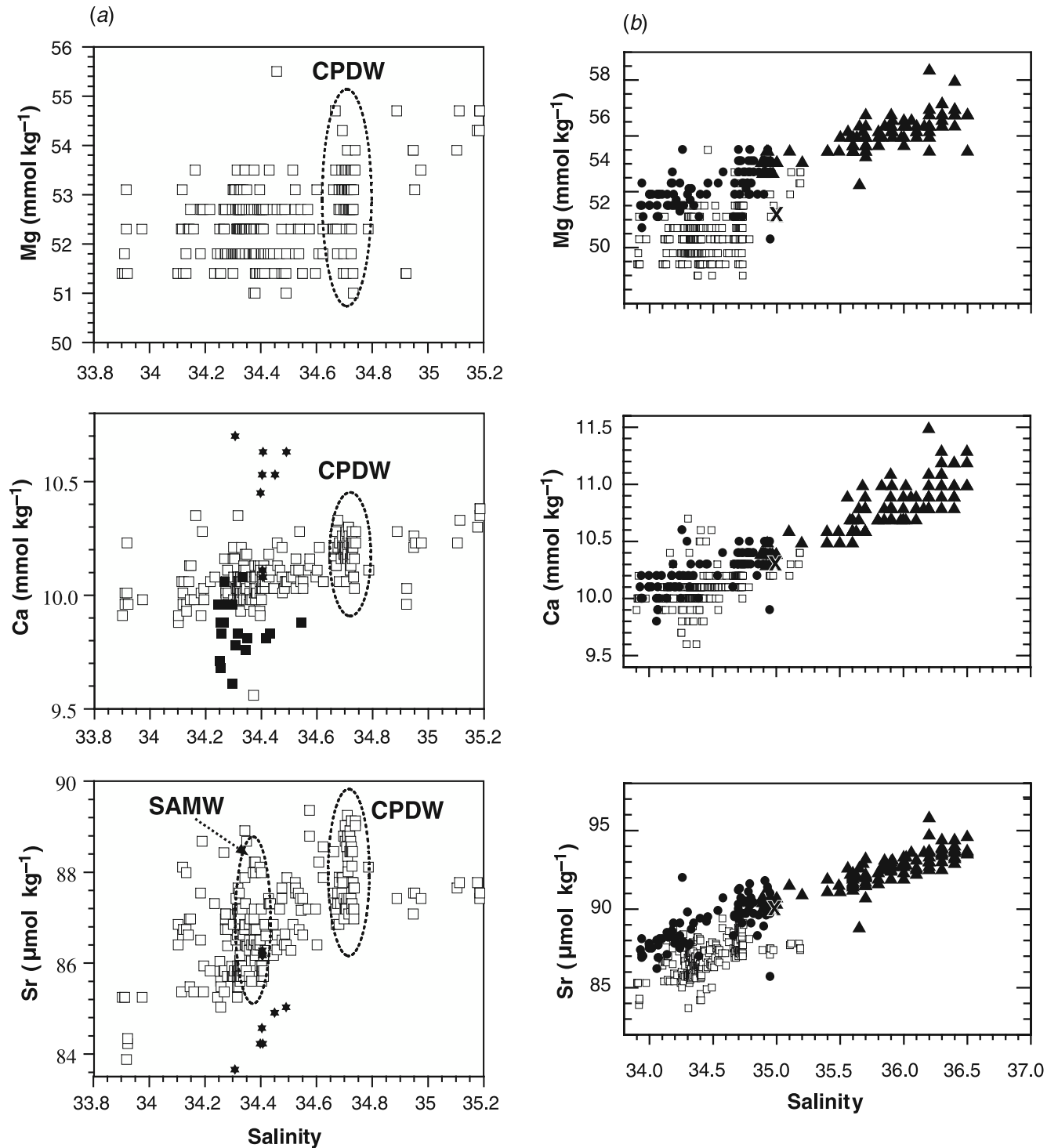
Compared with Ca, Mg values encountered in the CTD samples show much more of a scatter, but the broadest range is found within the CPDW where, for the same salinity ~34.7, Mg values range between 51.0 and 54.5 mmol kg<sup>-1</sup> (Fig. 3a). We already alluded to the fact that this broad range is caused by exchanges between the geological formations at depth in the vicinity of mid-oceanic ridges (such as the south-east Indian Mid-Ocean Ridge). A decrease of Mg in seawater was observed in nearby mid-oceanic ridges (Edmond *et al.* 1979; Berner and Berner 1987). In anticipation of direct observational proof that seawater convection occurs in oceanic crust, experiments were made to simulate the likely conditions (Andrews *et al.* 1996). Seawater was cycled through powdered basalt at elevated temperatures and appropriate pressures for varying lengths of time, using a range of water/rock ratios. Dramatic changes were observed and, over a short time (weeks to months), all seawater Mg and sulfate was transferred into the powdered basalt. Although it is difficult to quantify the amount of Mg removed from seawater by this process, it is probably the most important Mg sink in the modern ocean (Andrews *et al.* 1996). This phenomenon seems to play a major role in this area.

#### *Calcium*

Calcium values, as expected, show some minor fluctuations, but consistently increase linearly with salinity. However, there are three stations where waters depart from the trend. Station SO136-80 has unusually high values concentrating around 10.6 mmol kg<sup>-1</sup> for a salinity of 34.4. It is likely that these values, all encountered at depth, relate to the dissolution of biogenic calcium carbonate (see below). Nevertheless, it is also known that Ca values can increase at



**Fig. 2.** (a) Salinity and temperature profiles obtained along Transect 1, east of the Campbell Plateau. Note the Subantarctic Front (SAF), which separates station SO136-16 and SO136-23. The approximate position of the various water masses recognized from the CTD samples are presented. The shaded area represents sea-floor topography. See text for more details on the various water masses. (b) Salinity and temperature profiles obtained along Transect 2, south of the Campbell Plateau. Note the SAF, which separates stations SO136-96 and SO136-102. The approximate position of the various water masses is presented. (c) Salinity and temperature profiles obtained along Transect 3, over the South Tasman Rise. Note the position of the Subantarctic Front (STF), which meanders between several stations (SO136-132, SO136-136, SO136-144 and SO136-151). The SAF is located between station SO136-118 and SO136-127. Same comments as Fig. 2b. (d) Salinity and temperature profiles obtained for the two stations over Challenger Plateau. Note these stations are located north of the STF. Same comments as Fig. 2b.



**Fig. 3.** (a) Magnesium (Mg), calcium (Ca) and strontium (Sr) concentrations versus salinity for the TASQWA samples (□). The encircled values around 34.7 salinity characterize the elemental concentrations of the Circumpolar Deep Water (CPDW) and Subantarctic Mode Water (SAMW); ■ represents Ca concentration for sites SO136-28 and SO136-35, which are lower compared with the other sites. The waters at site SO136-80 (★) are characterized by high Ca values. These two anomalous Ca values explain the scatter shown in Fig. 6. (b) Comparison of the Mg, Ca and Sr concentrations versus salinity for the TASQWA samples (□) against others from the North Atlantic (▲, cruise M39/1) and South Atlantic (●, cruise ANT XI/2) (see text and Accessory Publication, available from the *Marine and Freshwater Research* web page: <http://www.publish.csiro.au/journals/mfr>). The average concentration taken from Bruland (1983) for each of the three elements (Mg, Ca and Sr in seawater) is represented by an X.



hydrothermal vents by basalt–seawater reactions near mid-oceanic ridges (Edmond *et al.* 1979). Some of the lowest Ca values ( $9.5\text{--}9.7\text{ mmol kg}^{-1}$ ) concentrate around salinity 34.3 at stations SO136-28 and SO136-35. These anomalies occur in the deepest portions of the CTD profiles and indicate that the water that is considered here to be of a transitory nature between the AAIW (below) and the SAMW-2 (above), has registered a substantial loss of Ca, very likely being biologically induced (see Fig. 3a discussion). It appears almost impossible to separate both processes and calculate the respective fluxes.

#### Strontium

Strontium values display a rather broad scatter, even for the deep samples, and particularly for the CPDW (range  $86.2\text{--}88.9\text{ }\mu\text{mol kg}^{-1}$ , around 34.7 salinity) and another wider range in the vicinity of the two mode waters (range  $88.3\text{--}88.9\text{ }\mu\text{mol kg}^{-1}$ , with one value down to  $83.5\text{ }\mu\text{mol kg}^{-1}$ ). The spread of the values (Fig. 3a), as discussed earlier, is likely to be engendered by biological processes and is discussed below.

#### Discussion

The majority of our samples were taken in the mode waters, and we believe that, for the first time, we are able to document some of the physicochemical processes that operate in combination with mode-water formation. The zone of SAMW formation occurs under the pathway of the major trade winds in the Southern Ocean, which are at their peak strength in winter (Taljaard 1967). It is during that time that the thermocline, which could have been established during the previous summer–autumn season, is dismantled and that salinities and temperatures are then homogenized. We believe that large eddies must be engendered at the time of strong trade winds leading to homogenization of the upper 600 m (at least) of the water column. These eddies would be formed during the process of cyclogenesis, and consequently force the broad mixing at a large scale of vast bodies of waters. Such large features could possibly engender the stirring of bottom sediments at the edge of the Campbell Plateau, where bottom currents are rather strong (Carter and McCave 1997), and therefore resuspend biogenic calcite, which may redissolve rapidly. In addition basalt–seawater interactions at mid-oceanic ridges can also increase seawater Ca concentration (Edmond *et al.* 1979). Both processes seem to play a role here, but we cannot separate the processes. Both phenomena would explain the high calcium anomalies found at site SO136-80 (Figs 3a, 6). Such eddies could also bring substantial concentrations of nutrients from below, and therefore provide an explanation for the depletion in Ca at sites SO136-28 and SO136-35. More than likely, calcareous nanoplankton blooms would be responsible for this ‘draw down’ of Ca when the calcitic skeletons of the nanoplankton are secreted. The study of deep-sea cores in the vicinity of those sites ought to

confirm this hypothesis. In addition, phosphate concentrations in seawater show a decrease in concentration and thus reflect a high productivity in this area (C. Willamowski in Thiede and Nees 1999) compared with Station SO136-80, where phosphate concentration increases as water depth decreases, reaching up to  $4\text{ }\mu\text{mol L}^{-1}$  at the sea surface (C. Willamowski in Thiede and Nees 1999).

It is obvious that much biological productivity is associated near any oceanic front and that some is also associated with the mode waters. This is further confirmed through examination of the CTD profiles along the three transects where Sr values are depleted. Strontium uptake in the celestite skeleton of acantharians would account for such Sr anomalies. It is also obvious that there are other sites, principally among the mode waters, where productivity is reduced (refer to Fig. 4a–c). In contrast, the two sites above the Challenger Plateau (sites SO136-07 and SO136-10) are characteristically low in Sr (Fig. 4d); this phenomenon is paralleled with high phosphate concentrations (C. Willamowski in Thiede and Nees 1999).

#### Element/calcium ratios

We list the Mg/Ca and the Sr/Ca of waters from the TASQWA cruise and compare these with those analysed by the senior author from the North and South Atlantic Ocean (Table 4; Figs 5–7). It is clear that there are some regional differences that require further explanation, but already these data call for much caution when attempting to use trace-elemental ratios such as Mg/Ca and Sr/Ca in fossils (e.g. foraminifers, ostracods, corals) for reconstructing palaeotemperature knowing that there is compelling evidence that the uptake of Mg and possibly Sr in foraminifers is controlled by temperature (e.g. Rathburn and De Deckker 1997; Lea *et al.* 1999; Martin *et al.* 1999). For example, Lear *et al.* (2000) calculated the Mg–temperature relationships through time from benthic foraminifers ignoring any possible change in Mg/Ca seawater (but see Hardie 1996). Already, a number of authors have calculated the Mg–temperature relationship in biogenic carbonates for planktic and benthic foraminifers (e.g. Rosenthal and Boyle 1993; Mitsuguchi *et al.* 1996, 2001; Nürnberg *et al.* 1996, 2000; Hastings *et al.* 1998; Lea *et al.* 1999; Martin *et al.* 1999; Lear *et al.* 2000; Müller 2000; Watanabe *et al.* 2001), and ostracods (Corrège 1993; Dwyer *et al.* 1995, 2000; Corrège and De Deckker 1997). Of significance is that the Mg/Ca ratio in seawater today is 100 to 1000 times (or more) higher than the Mg/Ca ratio in biogenic calcium carbonate. Therefore, this phenomenon should not have any impact on the Mg/Ca ratio in biogenic carbonates, because the excess in Mg in seawater is so large. However, culture experiments by Delaney *et al.* (1985) and Brown (1996) have shown that a slight change in Mg/Ca of the solution can have an impact on the Mg/Ca ratio in planktonic foraminifers; an

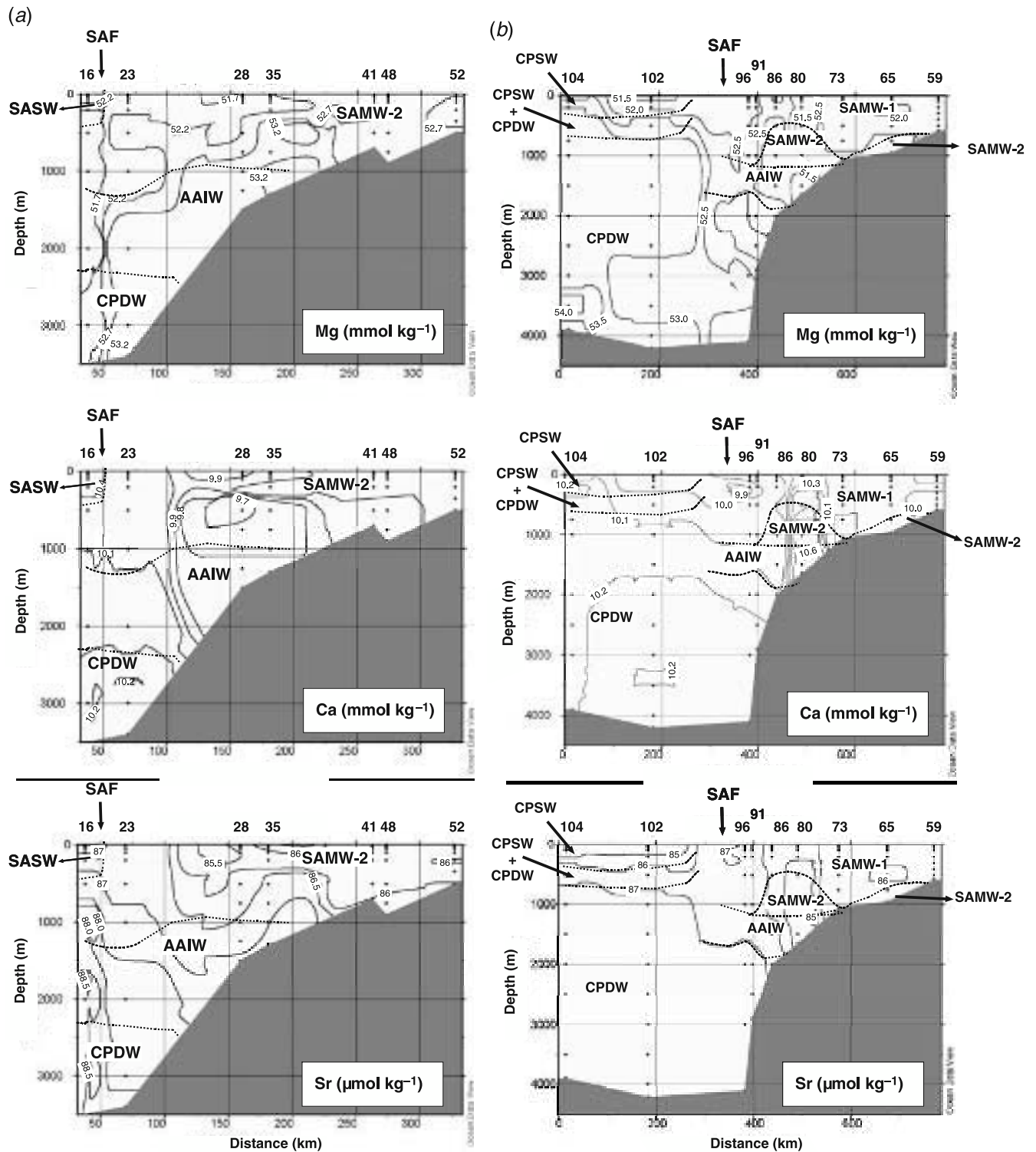


Fig. 4. Depth profiles of magnesium (Mg), calcium (Ca) and strontium (Sr) concentrations that have been normalized to a salinity of 35.0: (a) Transect 1; (b) Transect 2; (c) Transect 3; (d) stations SO136-07 and SO136-10; the grey boxes display in more detail the upper 500 m of each profile. See text for more details on the various water masses.

increase of the Mg/Ca seawater induces a Mg/Ca ratio increase in planktonic foraminifers. Additional work, especially using *in vitro* experiments, is required to

determine the veracity of the Mg-temperature dependence in biogenic carbonates grown in seawater of slightly different Mg/Ca ratios.

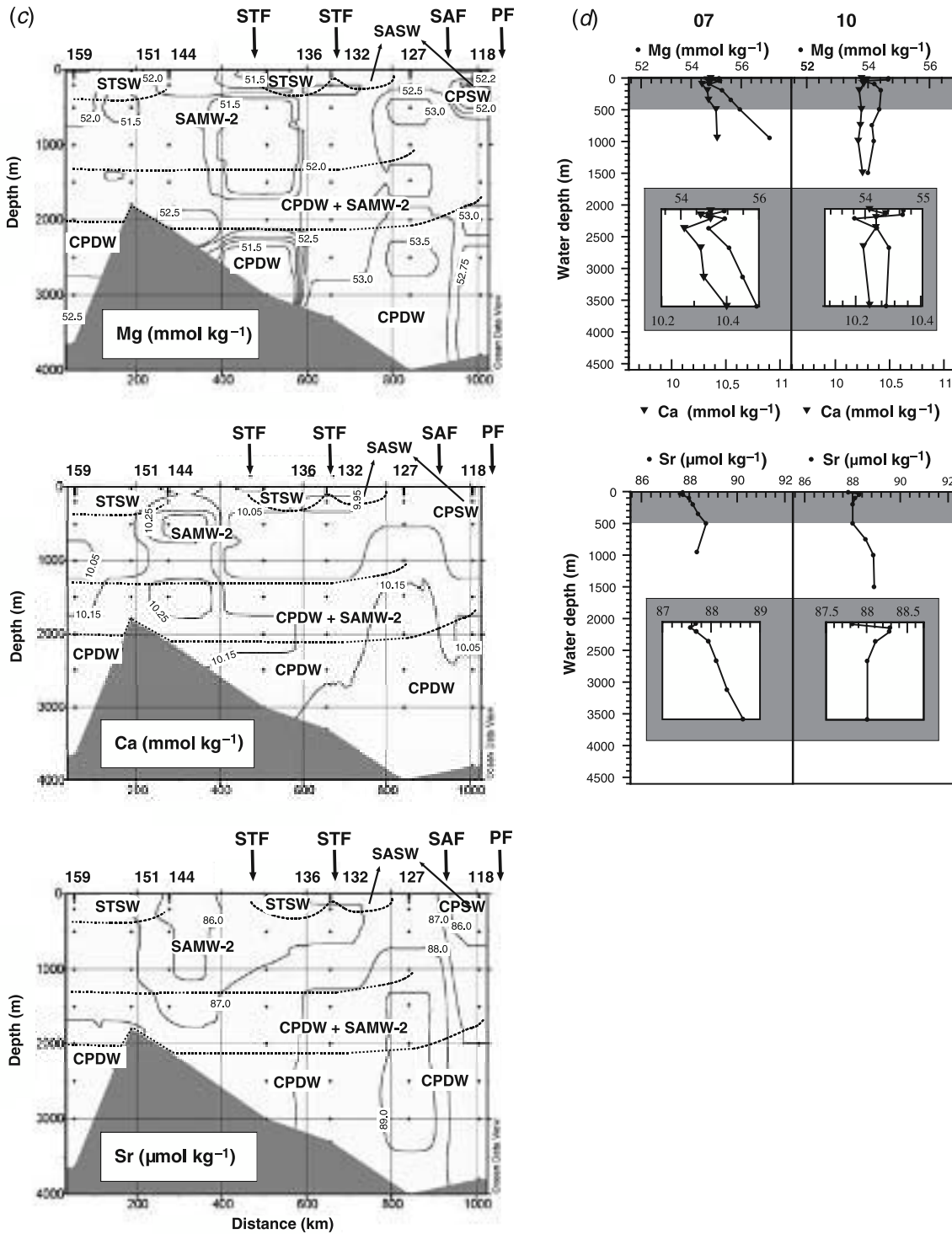
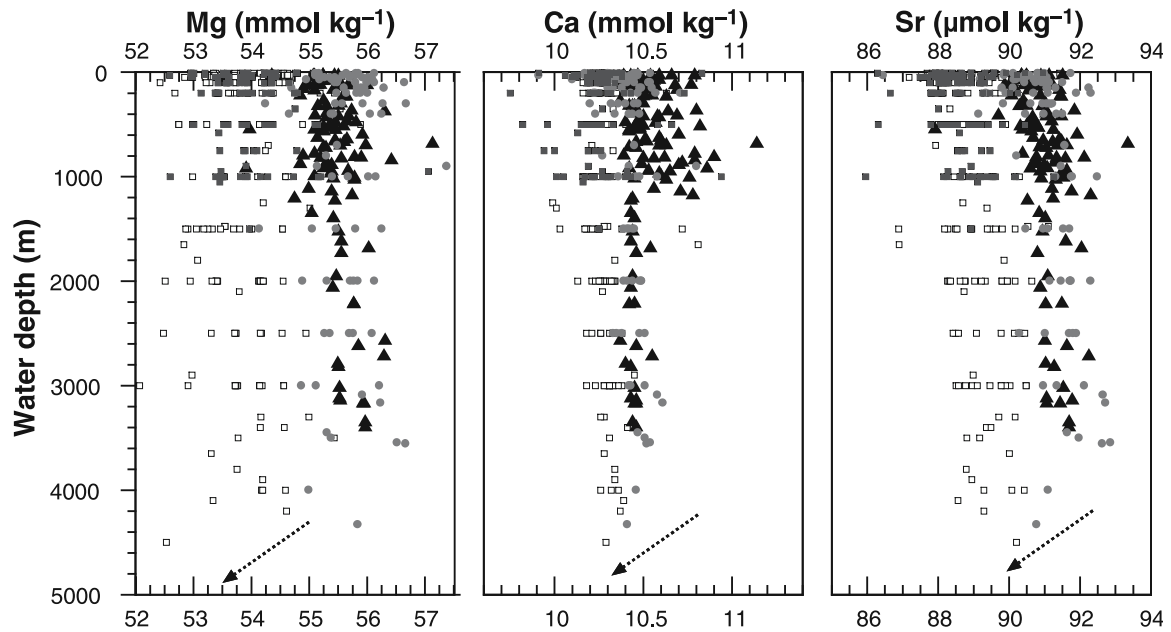


Fig. 4. (continued)

With respect to the Sr/Ca ratio of seawater, we have a totally different situation. The oceanic Sr/Ca ratio is in the same order of magnitude as the Sr/Ca of biogenic carbonate. As oceanic Sr/Ca is very similar to Sr/Ca in corals (e.g. Smith *et al.* 1979; Beck *et al.* 1992; 1997; Guilderson *et al.*

1994; Alibert and McCulloch 1997), any change in seawater Sr/Ca will have a large impact on any sea-surface temperature (SST) reconstruction based on the Sr/Ca in corals (Eisenhauer *et al.* 2001; Müller *et al.*, unpublished data). The variations in seawater Sr/Ca of ~1 mmol/mol, as



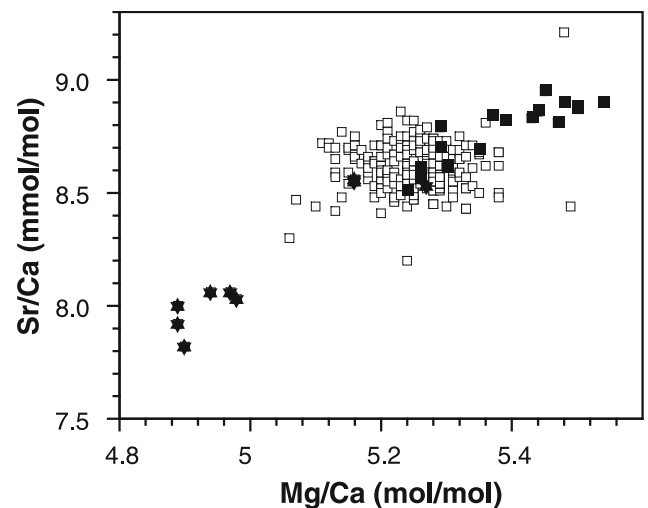
**Fig. 5.** Depth profiles for magnesium (Mg), calcium (Ca) and strontium (Sr) concentrations normalized to 35.0 salinity for TASQWA water samples ( $\square$ ) and TASQWA Subantarctic Mode Water samples ( $\blacksquare$ ) compared with data from cruise M39/1 in the North Atlantic ( $\blacktriangle$ ) and cruise ANT (XI/2) in the South Atlantic ( $\bullet$ ).

seen in our study here (Fig. 6), would be reflected by a  $>10^{\circ}\text{C}$  shift expressed in the Sr-SST based on coral Sr/Ca ratios. Several authors (Martin *et al.* 1999; Elderfield *et al.* 2000; Müller 2000; Eisenhauer *et al.* 2001; Müller *et al.*, unpublished data) have now shown that the Sr/Ca ratio in planktonic foraminifers is affected by seawater Sr/Ca as well as SST, depending on the foraminiferal species (for *Globigerina bulloides* and *Orbulina universa*, see Lea *et al.* 1999; for globorotaliids species, see Elderfield *et al.* 2000). Using the distribution coefficient (Mucci and Morse 1990) of 0.16 for foraminifers (Elderfield *et al.* 2000; Müller 2000) and a seawater Sr/Ca range from 8.0 to 9.0 mmol/mol, the Sr/Ca of the foraminiferal calcite will range from 1.28 to 1.44 mmol/mol. This range, expressed as a Sr-SST using the Sr/Ca-SST correlation of Elderfield *et al.* (2000), will fluctuate between 8 and  $12.6^{\circ}\text{C}$  for the foraminifers *Globorotalia hirsuta*, and  $4.7$  to  $14.1^{\circ}\text{C}$  for *Globorotalia inflata*. When using the Sr/Ca-SST correlation of Lea *et al.*

(1999) for *G. bulloides*, SST would fluctuate between  $21.8$  and  $36.4^{\circ}\text{C}$ , and for *O. universa*, it would be between  $13.4$  and  $22.3^{\circ}\text{C}$ . This very broad range in Sr/Ca shows how necessary and important it is to accurately know the element/Ca ratios of seawater before attempting any reconstruction of past SST from foraminiferal trace-elemental chemistry.

**Table 4.** Mean trace-elemental ratios of the waters collected during the TASQWA cruise and the North Atlantic (M39/1) and South Atlantic Ocean (ANT XI/2) cruises

| Cruise   | Mg/Ca (mol/mol) |       | Sr/Ca (mmol/mol) |      | Sample number |
|----------|-----------------|-------|------------------|------|---------------|
|          | Mean            | s.d.  | Mean             | s.d. |               |
| TASQWA   | 5.20            | 0.098 | 8.57             | 0.17 | 276           |
| M39/1    | 5.27            | 0.07  | 8.59             | 0.11 | 108           |
| ANT XI/2 | 5.35            | 0.05  | 8.70             | 0.05 | 90            |



**Fig. 6.** Strontium (Sr)/calcium (Ca) ratios versus magnesium (Mg)/Ca of all TASQWA waters. The waters at site SO136-80 ( $\star$ ) are characterized by high Ca values and therefore engender low Mg/Ca and Sr/Ca ratio, whereas waters at sites SO136-35 ( $\square$ ) and SO136-28 ( $\blacksquare$ ) are low in Ca and cause the reverse phenomenon (see Fig. 3a for more details).

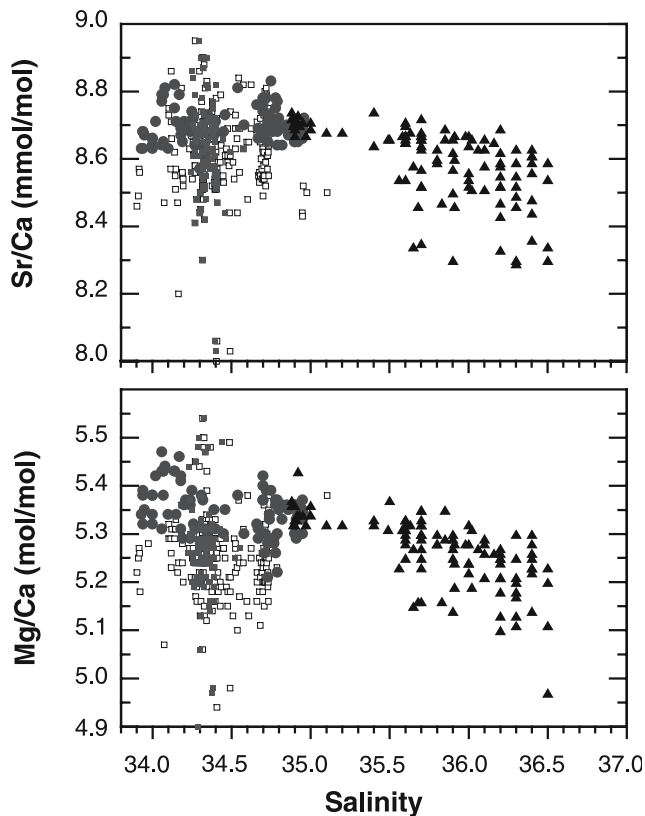


Fig. 7. Comparison of strontium (Sr)/calcium (Ca) and magnesium (Mg)/Ca ratios against salinity for TASQWA waters ( $\square$ ) and TASQWA Subantarctic Mode Water ( $\blacksquare$ ) waters against those obtained from North Atlantic ( $\blacktriangle$ ) cruise M39/1 and cruise ANT (XI/2) in the South Atlantic ( $\bullet$ ).

The oceanographic setup in the region we sampled is predominantly affected by SAMW formation. This occurred at the time of the ship's voyage, in the austral spring of 1998, when the seasonal thermocline that would have formed in summer is eroded by the strong westerlies in a broad zone between 50 and 55°S. The resulting deep thermostads display uniform salinity and temperature. One thermostad (SAMW-2), east of the Campbell Plateau, had a salinity around 34.3 and the temperature at the surface was  $\sim 7^{\circ}\text{C}$ , although a thermocline was being re-established at the time of the cruise. The second thermostad (SAMW-1) was found south of the Campbell Plateau and had a slightly higher salinity (34.4) and a uniform temperature signal of  $>7^{\circ}\text{C}$  down to 500 m at least.

The SAMW originates from the CPDW. Once this water reaches the surface, several zones of biological productivity cause Sr to precipitate in the skeleton of acantharians, and thus engender a Sr depletion in the upper 100 m of the water column. This phenomenon was already recognized by Brass and Turekian (1972) in the western Pacific Ocean.

The two stations taken above the Challenger Plateau, west of New Zealand (SO136-07 and SO136-10) are very different

from the other stations. Waters there have higher salinities and lower Sr values near the surface. These belong to the STSW and originate from the central part of the Tasman Sea where evaporation is at its maximum near 30°S. Below this STSW, the AAIW is found and originates from the south. It is a water mass that would have been initiated south of the PF.

Although the area of sampling covered only a narrow salinity range compared with what is found in the Atlantic Ocean, the Mg/Ca of TASQWA waters display a broad range of values, like found in the more saline waters of the Atlantic Ocean. In our region, we explain this difference from South Atlantic Ocean waters as resulting from hydrothermal activity scavenging Mg from oceanic water near the south-east Indian Ocean Ridge. Most of the waters we examined in the three transects either yield CPDW or SAMW, which would have originated from the CPDW through upwelling north of the SAF. We believe that this Mg/Ca 'anomaly' has to be taken into account when using the Mg/Ca in planktic and benthic foraminifers for palaeothermometry. Our study offers caution to palaeoceanographers.

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#### References

- Alibert, C., and McCulloch, M. T. (1997). Strontium/calcium ratios in modern *Porites* corals from the Great Barrier Reef as a proxy for sea surface temperature: calibration of the thermometer and monitoring of ENSO. *Paleoceanography* **12**, 345–63.
- Andrews, J. E., Brimblecombe, P., Jickells, T. D., and Liss, P. S. (1996). 'An Introduction to Environmental Chemistry.' (Blackwell Science Ltd: Oxford, UK.)
- Beck, J. W., Edwards, L., Ito, E., Taylor, F. W., Recy, J., Rougerie, F., Joannot, P., and Henin, C. (1992). Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**, 644–7.
- Beck, J. W., Recy, J., Taylor, F., Edwards, R. L., and Cabioch, G. (1997). Abrupt changes in early Holocene tropical sea surface temperature derived from coral records. *Nature* **385**, 705–7.
- Berner, K. B., and Berner, R. A. (1987). 'The Global Water Cycle.' (Prentice Hall: Englewood Cliffs, NJ, USA.)
- Brass, G. W., and Turekian, K. K. (1972). Strontium distributions in sea water profiles from the GEOSECS I (Pacific) and GEOSECS II (Atlantic) test stations. *Earth and Planetary Science Letters* **16**, 117–21.

- Broecker, W. S., and Peng, T.-H. (1982). 'Tracers in the Sea.' (Lamont-Doherty Geological Observatory: Columbia University, NY, USA.)
- Brown, S. J. (1996). 'Controls on the Trace Metal Chemistry of Foraminiferal Calcite and Aragonite.' PhD Thesis. (University of Cambridge: UK.)
- Bruland, K. W. (1983). Trace elements in sea-water. In 'Chemical Oceanography'. (Eds J. P. Riley and R. Chester.) pp. 158–220. (Academic Press: London, UK.)
- Buck, W. R., Delaney, P. T., Karson, J. A., and Lagabrilie, Y. (1998). 'Faulting and Magmatism at Mid-Ocean Ridges.' (American Geophysical Union: Washington DC, USA.)
- Carter, L., and McCave, I. M. (1997). The sedimentary regime beneath the Deep Western Boundary Current inflow to the South-west Pacific Ocean. *Journal of Sedimentary Research* **67**, 1005–17.
- Carter, L., Garlick, R. D., Sutton, P., Chiswell, S., Oien, N. A., and Stanton, B. R. (1998). 'Oceanic Circulation New Zealand.' NIWA Chart Miscellaneous Series 76. (National Institute of Water & Atmospheric Research: Wellington, New Zealand.)
- Chiswell, S. M. (1994). Variability in sea surface temperature around New Zealand. *New Zealand Journal of Marine and Freshwater Research* **28**, 179–92.
- Corrège, T. (1993). Preliminary results of paleotemperature reconstruction using the magnesium to calcium ratio of deep-sea ostracode shells from the Late Quaternary of Site 822, Leg 133 (western Coral Sea). *Proceedings of the Ocean Drilling Program Scientific Results* **133**, 175–80.
- Corrège, T., and De Deckker, P. (1997). Faunal and geochemical evidence for changes in intermediate water temperature and salinity in the western Coral Sea (northeast Australia) during the Late Quaternary. *Palaeogeography, Palaeoclimatology Palaeoecology* **131**, 183–205.
- de Villiers, S. (1999). Seawater strontium and Sr/Ca variability in the Atlantic and Pacific Oceans. *Earth and Planetary Science Letters* **171**, 623–34.
- Deacon, G. E. R. (1937). The hydrology of the Southern Ocean. *Discovery Report* **15**, 1–124.
- Delaney, M. L., Bé, A. W. H., and Boyle, E. A. (1985). Li, Sr, Mg and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. *Geochimica et Cosmochimica Acta* **49**, 1327–41.
- Dwyer, G. S., Cronin, T. M., Baker, P. A., Raymo, M. E., Buzas, J. S., and Corregge, T. (1995). North Atlantic deepwater temperature change during Late Pliocene and Late Quaternary climatic cycles. *Science* **270**, 1347–51.
- Dwyer, G. S., Cronin, T. M., Baker, P. A., and Rodriguez-Lazaro, J. (2000). Changes in North Atlantic deep-sea temperature during climatic fluctuations of the last 25,000 years based on ostracode Mg/Ca ratios. *Geochemistry, Geophysics, Geosystems* **2000GC000046**.
- Edmond, J. M., Measures, C., McDuff, R. E., Chan, L. H., Collier, R., Grant, B., Gordon, L. I., and Corliss, J. B. (1979). Ridge crest hydrothermal activity and the balance of the major and minor elements in the ocean; the Galapagos data. *Earth and Planetary Science Letters* **46**, 1–18.
- Eisenhauer, A., Müller, A., Reijmer, J. J. G., and Nürnberg, D. (2001). Secular Sr/Ca variations in seawater and its effect on the coral Sr/Ca-based SST records. *EOS Transactions, American Geophysical Union* **82** (47 Suppl.), 738.
- Elderfield, H., Cooper, M., and Ganssen, G. (2000). Sr/Ca in multiple species of planktonic foraminifera: implications for reconstructions of seawater Sr/Ca. *Geochemistry, Geophysics, Geosystems* **2000GC000031**.
- Gersonde, R. (1995). Die Expedition ANTARKTIS-XI/2 mit FS "Polarstern" 1993/1994. *Berichte zur Polar- und Meeresforschung* **163**, 133 pp.
- Gordon, A. L. (1972). On the interaction of the Antarctic Circumpolar Current and the Macquarie Ridge. The Australian-New Zealand Sector. *AGU Antarctic Research Series* **19**, 71–8.
- Gordon, A. L. (1975). An Antarctic oceanographic section along 170°E. *Deep-Sea Research* **22**, 357–77.
- Guilderson, T. P., Faibanks, R., and Rubenstone, J. L. (1994). Tropical temperature variations since 20 000 years ago: modulating interhemispheric climate change. *Science* **263**, 663–5.
- Hardie, L. A. (1996). Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m. y. *Geology* **24**, 279–83.
- Hastings, D. W., Russell, A. D., and Emerson, S. R. (1998). Foraminiferal magnesium in *G. sacculifer* as a paleotemperature proxy. *Paleoceanography* **13**, 161–9.
- Heath, R. A. (1985). A review of the physical oceanography of the seas around New Zealand – 1982. *New Zealand Journal of Marine and Freshwater Research* **19**, 79–124.
- James, N. P., and Choquette, P. W. (1983). Diagenesis 6. Limestones – the sea floor diagenetic environment. *Geoscience Canada* **10**, 162–79.
- Kuehner, E. C., Alvarez, R., Paulson, P. J., and Murphy, T. J. (1972). Production and analysis of special high purity acids purified by sub-boiling distillation. *Analytical Chemistry* **44**, 2050–6.
- Lea, D. W., Mashiotta, T. A., and Spero, H. J. (1999). Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochimica et Cosmochimica Acta* **63**, 2369–79.
- Lear, C. H., Elderfield, H., and Wilson, P. A. (2000). Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* **287**, 269–87.
- Martin, P. A., Lea, D. W., Mashiotta, T. A., Papenfuss, T., and Sarnthein, M. (1999). Variation of foraminiferal Sr/Ca over Quaternary glacial-interglacial cycles: evidence for changes in mean ocean Sr/Ca? *Geochemistry, Geophysics, Geosystems* **1999GC000006**.
- McCartney, M. S. (1977). Subantarctic Mode Water. In 'A Voyage of Discovery'. (Ed. M. Angel.) pp. 103–19. George Deacon 70th Anniversary Volume. (Pergamon: New York, USA.)
- Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., and Isdale, P. (1996). Mg/Ca thermometry in coral skeletons. *Science* **274**, 961–3.
- Mitsuguchi, T., Uchida, T., Matsumoto, E., Isdale, P. J., and Kawana, T. (2001). Variations in Mg/Ca, Na/Ca, and Sr/Ca ratios of coral skeletons with chemical treatments: implications for carbonate geochemistry. *Geochimica et Cosmochimica Acta* **65**, 2865–74.
- Mucci, A., and Morse, J. W. (1990). Chemistry of the low-temperature abiogenic calcites: experimental studies on coprecipitation, stability and fractionation. *Review of Aquatic Science* **3**, 217–54.
- Müller, A. (2000). Mg/Ca and Sr/Ca-verhältnisse in biogenem carbonat planktischer foraminiferen und benthischer ostracoden. *Berichte aus dem Institut für Meereskunde, Kiel* **313**, 187 pp.
- Nürnberg, C. C. (1995). Bariumfluss und sedimentation im südlichen südatlantik- hinweise auf produktivitätsänderungen im quartär. *Geomar Report* **38**, 105 pp.
- Nürnberg, D., Bijma, J., and Hemleben, C. (1996). Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochimica et Cosmochimica Acta* **60**, 803–14.
- Nürnberg, D., Müller, A., and Schneider, R. R. (2000). Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktic foraminifera: A comparison to sea surface temperature estimates from  $U^{K}_{37}$ , oxygen isotopes, and foraminiferal transfer function. *Paleoceanography* **15**, 124–34.
- Orsi, A. H., Whitworth, T. III, and Nowlin, W. D. (1995). On the meridional extent and fronts of the Antarctic Circumpolar Current. *Deep-Sea Research* **1**, **42**, 641–73.

- Rathburn, A. E., and De Deckker, P. (1997). Magnesium and strontium compositions of recent benthic foraminifera from the Coral Sea, Australia and Prydz Bay, Antarctica. *Marine Micropaleontology* **32**, 231–48.
- Rosenthal, Y., and Boyle, E. A. (1993). Factor controlling the fluoride content of planktonic foraminifera: an evaluation of its paleoceanographic applicability. *Geochimica et Cosmochimica Acta* **57**, 335–46.
- Schott, F., Koltermann, K. - P., Stramma, L., Sy, A., Zahn, R., and Zenk, W. (1999). North Atlantic 1997- cruise No. 39 18 April–14 September 1997. *Meteor-Berichte* **99–1**, 197 pp.
- Smith, S. V., Buddemeier, R. W., Redalje, R., and C., Houck, J. E. (1979). Strontium-calcium thermometry in coral skeletons. *Science* **204**, 404–7.
- Taljaard, T. T. (1967). Development, distribution and movement of cyclones and anticyclones in the Southern Hemisphere during the IGY. *Meteor-Berichte* **6**, 973–87.
- Thiede, J., and Nees, S. (1999). 'FS SONNE. Fahrtbericht/Cruise Report SO136. Tasqwa (Quaternary Variability of Water Masses in the Southern Tasman Sea and the Southern Ocean, SW Pacific Sector). Wellington–Hobart. October 16–November 12, 1998.' Geomar Report 89.
- Tomczak, M., and Godfrey, J. S. (1994). 'Regional Oceanography: An Introduction.' (Pergamon Press: New York, USA.)
- Watanabe, T., Winter, A., and Oba, T. (2001). Seasonal changes in sea surface temperature and salinity during the Little Ice Age in the Caribbean Sea deduced from Mg/Ca and  $^{18}\text{O}/^{16}\text{O}$  ratios in corals. *Marine Geology* **173**, 21–35.

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