Seasonal stable oxygen isotope cycles in an Antarctic bivalve shell (*Laternula elliptica*): a quantitative archive of ice-melt runoff

YOHEI TADA[1], HIDEKI WADA[2] and HIDEKI MIURA[3]

[1]*Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan*
[2]*Department of Biology and Geosciences, Faculty of Science, Shizuoka University, 836 Oya, Suruga-ku, Shizuoka, 422-8529, Japan*
[3]*Division of Geoscience, National Institute of Polar Research (NIPR), 1-9-10 Kaga, Itabashi-ku, Tokyo, 173-8515, Japan*
ytada@eps.s.u-tokyo.ac.jp

Abstract: Oxygen isotope ratios in the shell of a Recent Antarctic marine bivalve *Laternula elliptica* are shown and their potential for environmental reconstruction is discussed. The shell $\delta^{18}O$ profiles of this species represent the seasonal change in melted ice water inflow. Oscillations in the shell $\delta^{18}O$ values reflect seasonal change in seawater $\delta^{18}O$ values, caused by an addition of meltwater in summer. Since annual temperature variation is minimal and the inflow of the regional ice-melt is the dominant control on the shell $\delta^{18}O$ values, the oxygen isotope record of *L. elliptica* is a quantitative indicator of the palaeo-ice-melting events in the Antarctic continental margin.

Introduction

Oxygen isotope ratios in marine bivalve shells are well known to reflect both seawater temperatures and the isotopic compositions of their habitats (Epstein *et al.* 1953). These two independent factors must be combined to explain the shell $\delta^{18}O$ records of marine bivalves. In the seas around Antarctica, sea-surface temperature is fairly constant throughout the year (Ishii *et al.* 1998). Therefore, the isotopic composition of seawater should be the dominant control on shell $\delta^{18}O$ values for Antarctic nearshore bivalves.

A laternulid bivalve species, *Laternula elliptica* (King & Broderip, 1831), is widely distributed in the Antarctic nearshore waters, burrowing deep into sediments and feeding on phytoplankton (Ahn & Shim 1998). Profiles of shell carbon and oxygen isotope ratios of this species have been documented by several workers. Barrera *et al.* (1994) constructed an oxygen isotopic thermometry equation based on the analysis of 70 samples collected from right and left valves of a single specimen. Brey & Mackensen (1997) reconstructed the seasonal change of sea-surface temperatures based on the $\delta^{18}O$ values of 43 samples collected at intervals of 1 mm along the growth axis of a single shell. However, the impact of changing seawater $\delta^{18}O$ values was not taken into consideration in these studies. Melted ice and/or snow (hereafter called 'meltwater') flowing into the Antarctic continental margins during the southern hemisphere summer, is extremely depleted in ^{18}O (Craig 1961, Johnsen *et al.* 1972, Lorius *et al.* 1979, 1985, Matsubaya *et al.* 1979, Miura *et al.* 1998). Inflow of meltwater into the sea should cause the seasonal lowering of the $\delta^{18}O$ values around the Antarctic continental margin. Using the $\delta^{18}O$ values of the homogenized shells,

Berkman (1991) concluded that the low $\delta^{18}O$ values of *Adamussium colbecki* (Smith, 1902), Antarctic scallops, are caused by an inflow of the freshwater. Khim *et al.* (2001) suggested that the extremely low $\delta^{18}O$ values of Antarctic marine benthic foraminiferal tests, recovered from two gravity cores in Maxwell and Admiralty bays, were caused by a significant decrease in the $\delta^{18}O$ value of seawater as a result of a meltwater discharge event. In comparison with homogenized bivalve shells and benthic foraminiferal tests, a series of $\delta^{18}O$ values from high-resolution sequential sampling of Antarctic bivalve shells would be expected to have a much more detailed record of meltwater runoff, e.g. it would show the seasonal variation of marine salinity with a potential resolution of days to months. Fossil specimens of *L. elliptica* probably hold just such a record of the inflow of meltwater and the history of ice sheet retreat in the Antarctic coastal region.

In this study, we present a much higher resolution $\delta^{18}O$ record from a single live-caught specimen of *L. elliptica* than those reported by previous authors and try to reconstruct the present-day seasonal variation of meltwater inflow by comparing isotope records with the seasonal measurements in the region. In edition, we will try to calculate the amount of meltwater inflow in this region and compare it with the estimate by Berkman (1994) based on the shell $\delta^{18}O$ values.

Material and methods

A single Recent specimen, SUM-HM-W0007 of *L. elliptica* was examined in this study (Fig. 1). It was collected alive on Fukuro-ura Beach in Langhovde, the Sôya Coast, the eastern part of Lützow-Holm Bay, East Antarctica (Fig. 2),
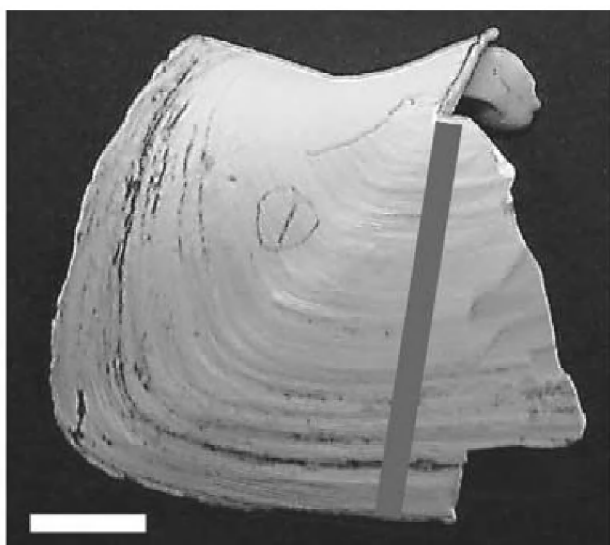
Fig. 1. The shell of *Laternula elliptica* (left valve) examined, showing the dorso-ventral line from which small amounts of carbonate samples were extracted successively for isotopic analysis. Crests on the shell surface correspond to the hatched zones in Fig. 3. Scale bar = 1 cm.

on 11 October 1985, during the 26th Japanese Antarctic Research Expedition (JARE-26, 1984–86). This specimen is one of numerous specimens which were transported onshore by a recent storm; the cold temperatures preserved their fresh soft tissues (Murayama 1987).

Both outer and inner shell layers of *L. elliptica* are composed entirely of aragonite, confirmed by X-ray diffraction analysis. For stable isotopic analysis, small amounts of powdered shell samples, *c.* 60.3 ± 26.4 μg in weight, were carefully obtained from the external shell surface under a binocular microscope using a small knife. A series of samples (*n* = 101) were taken consecutively along the dorso-ventral axis (see Fig. 1). Each sample was 0.3 mm wide.

Isotopic measurements were made following the procedure described in Wada *et al.* (1984). Shell carbonate samples were reacted with pyro-phosphoric acid at 60.00°C (Wada *et al.* 1984, modified from McCrea 1950) in an evacuated reaction system. All the isotopic compositions were determined using a Finnigan MAT 250 mass spectrometer at Shizuoka University. The isotopic analyses are reported in standard delta (δ) notation in per mil units (‰) relative to the Pee Dee Belemnite (PDB) international standard (Craig 1957). The working reference standard CO_2 was calibrated against NBS19 and 20. Iterative measurements of the working standard gas indicated that the standard error of the measurements is ± 0.04‰ for oxygen. This value was verified twice every day by measurement of the in-house machine standard CO_2.

The soft tissue and the shell of this specimen are now housed in the Yokohama National University and the Shizuoka University, respectively.
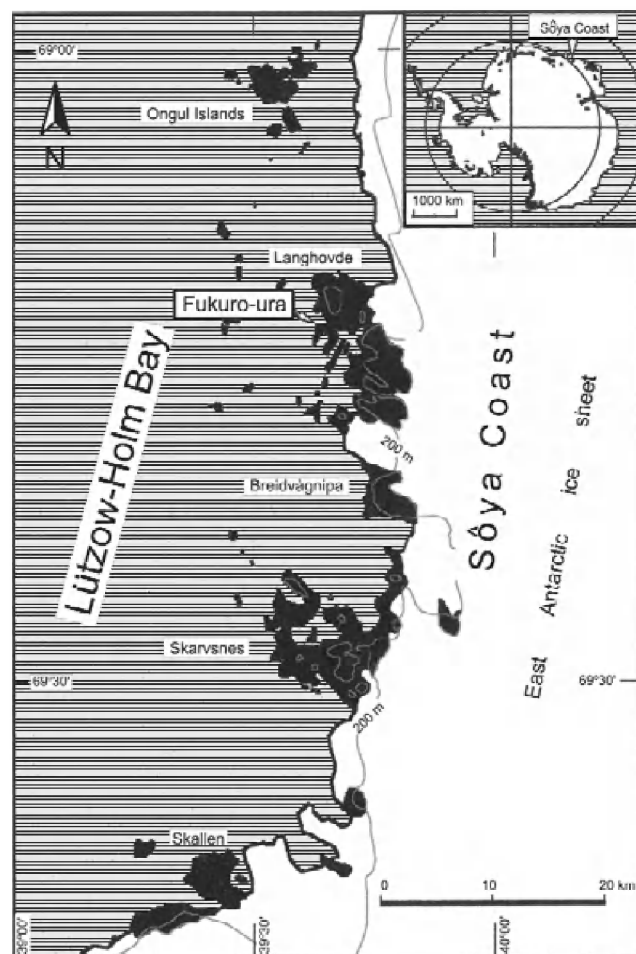
Fig. 2. Sampling locality of the shell of *L. elliptica* on Fukuro-ura Beach in Langhovde, the northern part of the Sôya Coast. The hatched zones indicate positions of seas.

Results

The δ^{18}O values of the shell analysed range from +2.66 to +4.79‰, and distinctly show a periodic fluctuation with 10 peaks (Fig. 3), in contrast to the δ^{18}O profile of Brey & Mackensen (1997). They required a better resolution to recognise the distinct wave pattern of δ^{18}O values from the *L. elliptica* shell; our sampling resolution satisfies their requirement. The δ^{18}O cycle lengths during the earlier periods of shell growth are longer than during the later ones. Brey & Mackensen (1997) also observed a similar change in the δ^{18}O wave lengths. This change in the δ^{18}O periodicity suggests that the shell growth rates of *L. elliptica* gradually decrease during ontogeny. The amplitudes of the δ^{18}O variations are almost constant during early growth. During later growth, however, the most positive values of each period are lower than that of the early growth.

The two main factors controlling the oxygen isotope composition of marine bivalve shells are temperature and the δ^{18}O value of the ambient seawater. In Lützow-Holm Bay, bottom seawater temperature is almost constant

throughout a year, ranging from -1.37 to -1.91°C, with an annual average of -1.76°C (Fukuchi *et al*. 1985, Watanabe *et al*. 1986, Matsuda *et al*. 1987). In this study, we use the marine molluscan aragonite shell palaeo-thermometry relationship from Grossman & Ku (1986):

$$T\,(°C) = 21.8 - 4.69\,[\delta^{18}O_{arag} - (\delta^{18}O_W - 0.2)] \qquad (1)$$

where T is the reconstructed seawater temperature, $\delta^{18}O_{arag}$ represents the stable oxygen isotope ratio of the molluscan shell aragonite, and $\delta^{18}O_W$ is $\delta^{18}O$ value of the local seawater vs Standard Mean Ocean Water (SMOW). Since measurements of the seawater oxygen isotope compositions are not available, we use a local mean $\delta^{18}O$ value, -0.11‰ SMOW, of Antarctic sea surface water sampled from south of 60°S (data from www.giss.nasa.gov). Calculated seawater temperatures range from -0.75 to 9.49°C based on the analysed shell $\delta^{18}O$ values. However, the actual seawater temperatures near the sampling locality are much lower and are in a narrower range than the calculated sea-surface temperatures. Therefore we must turn to seasonal change in the $\delta^{18}O$ value of seawater to explain the $\delta^{18}O$ variation in the shell.

Discussion

In Antarctica, freshwater inflow to the sea is composed mainly of water derived from melted sea ice, snow, and glacial ice. Antarctic snow and terrestrial ice are extremely depleted in ^{18}O (Craig 1961, Johnsen *et al*. 1972, Lorius *et al*. 1979, 1985). The $\delta^{18}O$ values of the ice sheet in the Langhovde area is *c*. -30‰ vs SMOW (Matsubaya *et al*. 1979). Thus, the influx of a significant amount of water derived from melted ice and snow should cause a shift in the oxygen isotope composition of seawater ($\delta^{18}O_W$). The $\delta^{18}O_W$ values can be calculated from Eq. (1) assuming that T is the mean annual seawater temperature in the Lützow-Holm Bay, -1.76°C (Fukuchi *et al*. 1985, Watanabe *et al*. 1986, Matsuda *et al*. 1987). From the calculated $\delta^{18}O_W$ values, we can calculate the seawater salinity values from the following equation, assuming the salinity values of seawater and meltwater are 35 and 0 Practical Salinity Units (PSU) respectively:

$$\delta^{18}O_W = (\delta^{18}O_{seawater} - \delta^{18}O_{melt})/35 \times S + \delta^{18}O_{melt} \qquad (2)$$

where $\delta^{18}O_{seawater}$ represents the mean oxygen isotope composition of local seawater (*c*. -0.11‰ SMOW, data from www.giss.nasa.gov), $\delta^{18}O_{melt}$ is the $\delta^{18}O$ value of meltwater in the Langhovde area (*c*. -30‰ vs. SMOW, referenced from Matsubaya *et al*. 1979), and S is the salinity value of the seawater. The calculated salinity values range from 32.6 to 35.1 PSU. Measured salinities of Antarctic sea-surface water range from 32 to 35 PSU (Railsback *et al*. 1989, Barrera *et al*. 1994, Ahn & Shim 1998, Mackensen 2001). In Lützow-Holm Bay, summer seawater salinity ranges from 33 to 34 PSU (Ishii *et al*. 1998). Our calculated
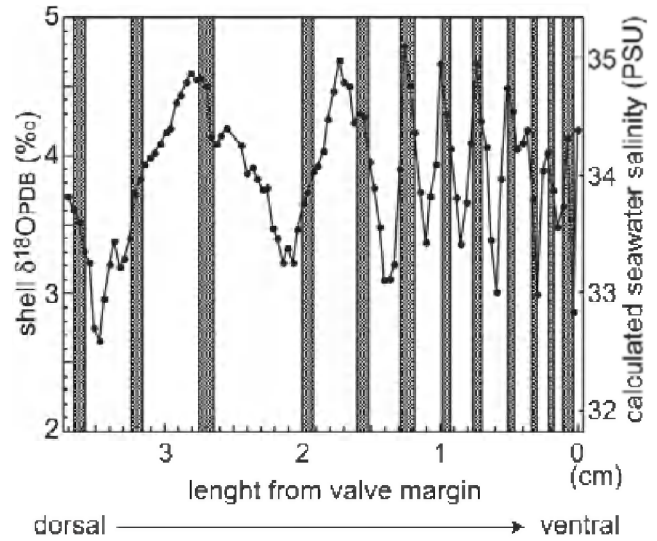

Fig. 3. Stable oxygen ($\delta^{18}O$) isotope profile for the specimen of *Laternula elliptica* examined (SUM-HM-W0007). The hatched zones indicate positions of crests observed on the shell surface of this specimen.

salinity in the summer season is a maximum of 1.4 PSU lower than the measured values by Ishii *et al*. (1998). This difference can be explained by possible salinity variation within the day. *Laternula elliptica* is widely distributed in the onshore area of the bay. On the other hand, Ishii *et al*. (1998) measured salinity of surface water in the offshore area of Lützow-Holm Bay. Since the $\delta^{18}O$ values of nearshore seawater are more easily affected by meltwater than those of offshore seawater, the calculated salinity values may reflect a real gradient in salinity from the nearshore to the offshore values (ranging from 33 to 34 PSU) reported by Ishii *et al*. (1998). Therefore, we conclude that the $\delta^{18}O_{arag}$ profiles observed in the shell of *L. elliptica* are most likely driven by seasonal fluctuations in meltwater inflow to Lützow-Holm Bay.

All of the positive isotope peaks in the $\delta^{18}O$ profile correspond to protrusions or crests observed on the shell surface (Figs 1 & 3). Two crest bands, correlative with negative isotope peaks (Fig. 3), probably represent spawning breaks in the shell of this specimen. Brey & Mackensen (1997) realised that the crest and trough patterns identified on the shell surface of this species correspond to the internal growth bands in the ligamental portion, and suggested furthermore that they are formed annually, as has been observed in other bivalve species (Jones & Allmon 1995, Jones & Quitmyer 1996, Goodwin *et al*. 2001, Schöne *et al*. 2003), because the $\delta^{18}O$ values of the crest samples were significantly different than those of the trough samples. Our high resolution shell isotopic analysis strongly supports the interpretation of Brey & Mackensen (1997). If we assume that no meltwater flowed into the sea during winter, we can calculate the winter seawater temperature from the most positive shell $\delta^{18}O$ value. We obtain a winter

temperature value, *c*. -2.0°C, using local temperature values from higher latitudes (> 60°S) provided by NASA (www.giss.nasa.gov). This value is consistent with the measured winter temperature value of -1.91°C (Fukuchi *et al*. 1985, Watanabe *et al*. 1986, Matsuda *et al*. 1987). Our calculated winter temperature suggests that *L. elliptica* grow throughout the year. Ahn & Shim (1998) suggested that *L. elliptica* survive for several months without food supply during winter by maintaining very low metabolic rates. Our calculated winter temperatures from the shell $\delta^{18}O$ values support the inference of Ahn & Shim (1998). In later ontogeny, the winter temperature values calculated from the positive peaks of the shell $\delta^{18}O$ values are slightly warmer, ranging from -0.6 to +1.5°C. These values may suggest that *L. elliptica* interrupts its own growth during winter in late ontogeny. During late ontogeny, however, the time resolutions of successive analyses are becoming lower than those from the younger part of the shell, and the samples collected from the winter layers might have included not only the winter layers but also some of the summer ones.

We calculated the volume of meltwater inflow to Lützow-Holm Bay during the summer by following the method described in Berkman (1994). He estimated the volume of meltwater into the sea with following equation:

$$V_{melt} \times \delta^{18}O_{melt} + V_{seawater} \times \delta^{18}O_{seawater} = (V_{melt} + V_{seawater}) \times \delta^{18}O_W \quad (3)$$

where the volumes (V) and oxygen isotopic compositions ($\delta^{18}O$) of the meltwater streams (melt) and seawater (seawater) are mixed (W). As mentioned above, the measured mean $\delta^{18}O$ values of the meltwater and seawater in this area are *c*. -30‰ (Matsubaya *et al*. 1979) and -0.11‰ (www.giss.nasa.gov), respectively. As $\delta^{18}O_W$, we use the most positive shell $\delta^{18}O$ values on each cycle of the shell $\delta^{18}O$ profile. The study area at Fukuro Cove was estimated to be 1 km wide and 1.5 km across. In this study, we assumed the maximum water depth of our *L. elliptica* habitat as *c*. 10 m. The summer meltwater volume is estimated as ranging from $0.6 \times 10^6 \, m^3$ to $1.0 \times 10^6 \, m^3$ at the highest. This estimation correlates well with that by Berkman (1994), who calculated the volume of glacial meltwater runoff into summer Explorers Cove as ranging from $0.59 \times 10^6 \, m^3$ to $0.95 \times 10^6 \, m^3$. And our calculated range is valid for the observed summer freshwater volume of the Onyx River in the adjacent Dry Valleys ($3.78 \pm 3.49 \times 10^6 \, m^3$, data from 1968 to 1988), the largest meltwater stream in Antarctica (Chinn 1993).

Our calculated volume of meltwater, however, may be unreliable in the absence of various parameters; e.g. a density gradient between seawater and meltwater, detailed information of sea bottom topography, accurate positions of *L. elliptica* habitats and meltwater streams, the volume of groundwater seep (a part of meltwater), etc. We need better constraints on these parameters to precisely estimate the meltwater volume.

Conclusions

Because this modern shell of *L. elliptica* records the seasonal variation of seawater salinity caused by inflowing meltwater as fluctuations in the oxygen isotope ratio, we can estimate the amount of inflowing meltwater into the Antarctic nearshore environment from the $\delta^{18}O$ values of *L. elliptica* shell. This species is widely distributed in the Antarctic nearshore water (Ahn & Shim 1998) and is one of the most common macrofossils of Antarctic Quaternary and Tertiary sediments (Berkman 1991). Therefore, $\delta^{18}O$ values of fossil shells of *L. elliptica* can be used as a quantitative indicator for estimating seasonal change in salinity of the ancient nearshore water and thereby the palaeo-record of ice-melt events in Antarctica.

Acknowledgements

References

AHN, I.-Y. & SHIM, J.H. 1998. Summer metabolism of the Antarctic clam, *Laternula elliptica* (King and Broderip) in Maxwell Bay, King George Island and its implications. *Journal of Experimental Marine Biology and Ecology*, **224**, 253–264.

BARRERA, E., TEVESZ, M.J.S., CARTER, J.G. & McCALL, P.L. 1994. Oxygen and carbon isotopic composition and shell microstructure of bivalve *Laternula elliptica* from Antarctica. *Palaios*, **9**, 275–287.

BERKMAN, P.A. 1991. Holocene meltwater variations recorded in Antarctic coastal marine benthic assemblages. *In* WELLER, G., WILSON, C.L. & SEVERIN, B.A.B., eds. *International Conference on the Role of the Polar Regions in Global Changes*. Fairbanks: University of Alaska, 440–449.

BERKMAN, P.A. 1994. Geochemical signatures of meltwater in mollusc shells from Antarctic coastal areas during the Holocene. *Memoirs of National Institute of Polar Research Special Issue*, **50**, 11–33.

BREY, T. & MACKENSEN, A. 1997. Stable isotopes prove shell growth bands in the Antarctic bivalve *Laternula elliptica* to be formed annually. *Polar Biology*, **17**, 465–468.

CHINN, T. 1993. Physical hydrology of the Dry Valley lakes. *Antarctic Research Series*, **59**, 1–52.

CRAIG, H. 1957. Isotopic standards for carbon and oxygen and correction factors for the mass spectrometric analyses of carbon dioxide. *Geochimica et Cosmochimica Acta*, **12**, 133–149.

CRAIG, H. 1961. Isotopic variations in meteoric waters. *Science*, **133**, 1702–1703.

EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H.A. & UREY, H.C. 1953. Revised carbonate–water isotopic temperature scale. *Bulletin of Geological Society of America*, **64**, 1315–1326.

FUKUCHI, M., TANIMURA, A., OHTSUKA, H. & HOSHIAI, T. 1985. Marine biological data of BIOMASS programme at Syowa Station in the 1982 winter (JARE-23). *JARE Data Reports, Marine Biology*, **6**, 1–113.

GOODWIN, D.H., FLESSA, K.W., SCHÖNE, B.R. & DETTMAN, D.L. 2001. Cross-calibration of daily growth increments, stable isotope variation, and temperature in the Gulf of California bivalve mollusc *Chione cortezi*: implications for paleoenvironmental analysis. *Palaios*, **16**, 387–398.

GROSSMAN, E.L. & KU, T.-L. 1986. Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. *Chemical Geology*, **59**, 59–74.

ISHII, M., INOUE, H.Y., MATSUEDA, H. & TANOUE, E. 1998. Close coupling between seasonal biological production and dynamics of dissolved inorganic carbon in the Indian Ocean sector and the western Pacific Ocean sector of the Antarctic Ocean. *Deep-Sea Research I*, **45**, 1187–1209.

JOHNSEN, S.J., DANSGAARD, W., CLAUSEN, H.B. & LANGWAY JR, C.C. 1972. Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature*, **235**, 429–434.

JONES, D.S. & ALLMON, W.D. 1995. Records of upwelling, seasonality and growth in stable-isotope profiles of Pliocene mollusc shells from Florida. *Lethaia*, **28**, 61–74.

JONES, D.S. & QUITMYER, I.R. 1996. Marking time with bivalve shells: oxygen isotopes and season of annual increment formation. *Palaios*, **11**, 340–346.

KHIM, B.-K., YOON, H.I., KIM, Y. & SHIN, I.C. 2001. Late Holocene stable isotope chronology and meltwater discharge event in Maxwell and Admiralty bays, King George Island, Antarctica. *Antarctic Science*, **13**, 167–173.

KING, P.P. & BRODERIP, W.J. 1831. Description of the Cirripeda, Conchifera and Mollusca, in a collection formed by the officers of HMS *Adventure* and *Beagle*. *Zoological Journal*, **5**, 332–349.

LORIUS, C., MERLIVAT, L., JOUZEL, J. & POURCHET, M. 1979. A 30 000-year isotope climate record from Antarctic ice. *Nature*, **280**, 644–648.

LORIUS, C., JOUZEL, J., RITZ, C., MERLIVAT, L., BARKOV, N.I., KOROTKEVICH, Y.S. & KOTLYYAKOV, V.M. 1985. A 150 000-year climatic record from Antarctic ice. *Nature*, **316**, 591–596.

MACKENSEN, A. 2001. Oxygen and carbon stable isotope tracers of Weddell Sea water masses: new data and some paleoceanographic implications. *Deep-Sea Research I*, **48**, 1401–1422.

MATSUBAYA, O., SAKAI, H., TORII, T., BURTON, H. & KERRY, K. 1979. Antarctic saline lakes-stable isotopic ratios, chemical compositions and evolution. *Geochimica et Cosmochimica Acta*, **43**, 7–25.

MATSUDA, O., ISHIKAWA, S. & KAWAGUCHI, K. 1987. Oceanographic and marine biological data based on the routine observations near Syowa Station between February 1984 and January 1985 (JARE-25). *JARE Data Reports, Marine Biology*, **10**, 1–21.

MCCREA, J.M. 1950. On the isotopic chemistry of carbonates and paleotemperature scales. *The Journal of Chemical Physics*, **18**, 849–857.

MIURA, H., MAEMOKU, H., SETO, K. & MORIWAKI, K. 1998. Late quaternary east Antarctic melting event in the Soya Coast region based on stratigraphy and oxygen isotopic ratio of fossil molluscs. *Polar Geoscience*, **11**, 260–274.

MURAYAMA, H. 1987. Reports of visual observations on penguins, peals and other seabirds near Syowa Station, Antarctica, by the JARE-26 in 1985. *Antarctic Record*, **31**, 67–76. [In Japanese with English abstract].

RAILSBACK, L.B., ANDERSON, T.F., ACKERLY, S.C. & CISNE, J.L. 1989 Paleoceanographic modeling of temperature–salinity profiles from stable isotopic data. *Paleoceanography*, **4**, 585–591.

SCHÖNE, B.R., TANABE, K., DETTMAN, D.L. & SATO, S. 2003. Environmental controls on shell growth rates and the $\delta^{18}O$ of the shallow-marine bivalve mollusk *Phacosoma japonicum* in Japan. *Marine Biology*, **142**, 473–485.

WADA, H., FUJII, N. & NIITSUMA, N. 1984. Analytical method of stable isotope for ultra-small amounts of carbon dioxide with MAT 250 mass-spectrometer. *Geoscience Reports of Shizuoka University*, **10**, 103–112. [In Japanese with English abstract].

WATANABE, K., SATOH, H., KANDA, H. & TAKAHASHI, E. 1986. Oceanographic and marine biological data from routine observations near Syowa Station between February 1983 and January 1984 (JARE-24). *JARE Data Reports, Marine Biology*, **9**, 1–22.