

compare ventilation and water mass proxy data (benthic $d^{18}\mbox{O}$ and d¹³C, radiogenic Nd isotopes, benthic foraminiferal distribution and XRF scanning Mn/Ca data) in well-dated, expanded sedimentary sequences from Pacific sites sampling different intermediate to deep water masses. We focus on the middle Miocene interval from 15 to 12.7 Ma, which includes the major Antarctic ice sheet expansion and global cooling step at ~ 13.9 Ma (Shackleton and Kennett, 1975; Savin et al., 1975; Woodruff and Savin, 1991; Wright et al., 1992; Flower and Kennett, 1993, 1995; Abels et al., 2005; Holbourn et al., 2005, 2007; Shevenell et al., 2004, 2008). Integration of new and published data sets from Southeast Pacific Ocean Drilling Program (ODP) Sites 1236 and 1237, western Equatorial Pacific ODP Site 806, central Equatorial Pacific Deep Sea Drilling Program (DSDP) Site 574, Southwest Pacific DSDP Sites 588 and 590, and Southern Ocean ODP Site 1171 allows to closely monitor water mass evolution and changes in the strength of the Pacific MOC following the major Antarctic ice sheet expansion marking the end of the middle Miocene warm period.

2. Pacific Ocean circulation

2.1. Modern oceanography

Today, the deep Pacific basin is mainly fed by Circumpolar Deep Water (CPDW), a mixture of Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW) that originates from the Antarctic Circumpolar Current (Reid, 1986, 1997; Talley, 1993; Tsuchiya and Talley, 1996; Sigman et al., 2010

flux of deep waters from the South into the Pacific Ocean, stimulating

1533 m water depth), Site 590 ($31^{\circ}10.02'$ S, $163^{\circ}21.51'$ E; 1299 m water depth), and Site 591 ($31^{\circ}35.06'$ S, $164^{\circ}26.92'$ E; 2131 m water depth) form a depth transect on the Lord Howe Rise in the Southwest Pacific Ocean, allowing reconstruction of vertical water mass structure and circulation development. These sites were situated ~4° South of their present location and in comparable water depths during the middle Miocene (Flower and Kennett, 1995). ODP Site 1171 ($48^{\circ}29.9971'$ S, $149^{\circ}6.7051'$ E; 2150 m water depth), located at paleolatitudes of 55°S and in paleodepths of ~1600 m during the middle Miocene, provides insights into the properties of CPDW or "Southern Component Water" (Shevenell et al., 2008). ODP Site 761 ($16^{\circ}44.23'$ S, $115^{\circ}32.10'$ E; 2189 m water depth), located on the Wombat Plateau off northwestern Australia, is included for comparison with the eastern subtropical Indian Ocean.

4. Methods

4.1. Stable isotope analysis (ODP Sites 806 and 1236)

Nannofossil chalks in Hole 806B were sampled at $\sim 20~{\rm cm}$ intervals ($\sim 5-6~{\rm kyr}$ resolution, 20 cm³ sample size) between 455.95 and 498.85 mbsf. Nannofossil oozes in Site 1236 were sampled at $\sim 4~{\rm cm}$ intervals ($\sim 7~{\rm kyr}$ resolution, 20 cm³ sample size) from a composite sequence (the so-called splice) in Holes 1236B and C (77.66–96.73 m composite depth). All samples were oven dried at 40 °C and weighed before washing over a 63 μm sieve. Residues were oven dried at 40 °10.02

Ŵ

2007), show a prominent 100 kyr eccentricity rhythm. This is particularly evident between 15 and 14.7 Ma and between 14 and 12.7 Ma, when d¹⁸O and Log(Mn/Ca) varied in anti-phase, indicating that eccentricity-paced carbonate dissolution cycles occurred during warmer intervals (Fig. 6). In contrast, d¹⁸O and Log(Mn/Ca) exhibit only a broad anti-phase variability without any distinct eccentricity beat between 14.7 and 14 Ma, which corresponds to a period of low 100 kyr eccentricity forcing and high amplitude variability in the 41 kyr obliquity cycle (Laskar et al., 2004). The 100 kyr beat is also imprinted on the benthic $d^{13}C$ records (Figs. 3 and 6), supporting that deep water ventilation deteriorated (d¹³C decreases) during warmer periods (d¹⁸O decreases) at high eccentricity (Holbourn et al., 2005, 2007). Other salient features of the Log(Mn/Ca) record are the marked increase in amplitude variations and the shift to substantially lower values during colder intervals (d¹⁸O maxima) between 13.9 and 12.7 Ma, following the major pulse of Antarctic ice expansion and global cooling at \sim 13.9 Ma (Fig. 6).

The total number of benthic foraminifers and the number of Cibicidoides spp. show marked increases in numbers after 13.9 Ma, following an initial transient increase at 14.3–14.2 Ma that coincided with a d¹⁸O increase (Fig. 6). As sedimentation rates approximately doubled after 13.9 Ma (Holbourn et al., 2007), benthic foraminiferal accumulation rates (not shown) exhibit even more pronounced increases between ~13.9 and 12.7 Ma. After

13.9 Ma, for aminiferal abundances display a marked 100 kyr beat, varying in phase with $d^{18}\rm O$ and in antiphase with Log(Mn/Ca), which is consistent with increased bottom water ventilation and an intensified biological pump during colder intervals. The ratios

(Southwest Pacific Ocean) during CM6, implying that this change represents an ocean-wide feature. The divergence in d^{13} C between deeper and shallower sites appears to have started somewhat earlier at ~13.8 Ma in the Southwest Pacific Ocean, in contrast to ~13.6 Ma in the Southeast and Equatorial Pacific Ocean, possibly reflecting asymmetric northward spreading of AAIW. However, the relative timing of the change is difficult to ascertain in the Southwest Pacific Ocean due to the low temporal resolution of the Site 590 isotope record. In contrast, the 1236 and 1237 Nd and d^{13} C data indicate a vertically more homogeneous water mass structure in the Southeast tropical Pacific between 14.3 and 13.6 Ma (Fig. 5).

We attribute the intensified $d^{13}C$ gradient between Pacific intermediate and deep waters to an enhancement of the MOC following the onset of permanent Antarctic glaciation and global cooling after 13.9 Ma (Fig. 7). As a result, the deeper Equatorial and Southeast Pacific sites became increasingly affected by the return southward PCW flow (more depleted d^{13}

hemisphere cooling after 13.9 Ma led to a steeper latitudinal temperature gradient with stronger westerlies promoting intensification of the Antarctic Circumpolar Current. Increased upwelling in the Southern Ocean in turn stimulated formation of deep

Southwest Pacific Ocean is supported by the marked $d^{13}C$ divergence in Sites 588, 590 and 591 (\sim 30–35°S) after 13.8 Ma (Fig. 4; Flower and Kennett, 1995). The gradual increase in the $d^{18}O$ gradient (from 0.9% to 1.2% between \sim 13.8 and 13.1 Ma) between the shallow Site 590, mainly bathed in AAIW, and the deep Site 1237 bathed in PCW further indicates increasing density (cooling) of PCW after 13.8 Ma (Fig. 4).

The 1237 XRF Log(Mn/Ca) and benthic foraminiferal data additionally provide evidence that southern hemisphere cooling after 13.9 Ma promoted an amelioration in Pacific deep water ventilation (Fig. 6). The Log(Mn/Ca) curve exhibits a shift toward more negative values, indicating improved carbonate preservation and deepening of the lysocline after 13.9 Ma, in particular during colder climate phases. Benthic foraminifers, in particular suspension feeders (Cibicidoides spp.), increase markedly in this deep site after 13.9 Ma, supporting more vigorous bottom currents and improved deep water ventilation. Our results suggest that strengthening of the MOC occurred as a direct response to Antarctic glacial expansion after 13.9 Ma, fostering a general improvement in Pacific ventilation with development of a steeper $d^{13}C$ gradient between Pacific intermediate and deep waters during CM6 (Figs. 4 and 6). A plausible scenario is that southern

Secondly, the middle Miocene ice cover over East and West Antarctica was probably less extensive than during the late Pleistocene, and fluctuated considerably between warmer and colder phases, even following the 13.9 Ma glacial expansion (Lewis et al., 2006; Haywood et al., 2008). It is therefore unlikely that extensive ice shelves, which inhibited downwelling and deep water production during the last glacial maximum (Anderson et al., 2009; Sigman et al., 2010), developed around Antarctica

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.01.020.

References

- Abels, H.A., Hilgen, F.J., Krijgsman, W., Kruk, R.W., Raffi, I., Turco, E., Zachariasse, W.J., 2005. Long-period orbital control on middle Miocene global cooling: integrated stratigraphy and astronomical tuning of the Blue Clay Formation on Malta. Paleoceanography 20, PA4012, http://dx.doi.org/10.1029/2004PA001129.
- Albarède, F., Goldstein, S.L., 1992. World map of Nd isotopes in sea-floor ferromanganese deposits. Geology 20, 761–763.
- Albarède, F., Goldstein, S.L., Dautel, D., 1997. The neodymium isotopic composition of manganese nodules from the Southern and Indian Oceans, the global oceanic neodymium budget, and their bearing on deep ocean circulation. Geochim. Cosmochim. Acta 61, 1277–1291.
- Amakawa, H., Sasaki, K., Ebihara, M., 2009. Nd isotopic composition in the central North Pacific. Geochim. Cosmochim. Acta 73, 4705–4719.
- Anderson, R.F., Ali, S., Bradtmiller, L.I., Nielsen, S.H.H., Fleisher, M.Q., Anderson, B.E., Burckle, L.H., 2009. Wind-driven upwelling in the southern ocean and the deglacial rise in atmospheric CO₂. Science 323, 1443–1448.
- Barrat, J.A., Keller, F., Amossé, J., 1996. Determination of rare earth elements in sixteen silicate reference samples by ICP-MS after Tm addition and ion exchange separation. Geostand. Newsl. 20, 133–139.
- Bayon, G., German, C.R., Boella, R.M., Milton, J.A., Taylor, R.N., Nesbitt, R.W., 2002. An improved method for extracting marine sediment fractions and its application to Sr and Nd isotopic analysis. Chem. Geol. 187, 170–199.
- Broecker, W.S., Clark, E., Hajdas, I., Bonani, G., 2004. Glacial ventilation rates for the deep Pacific Ocean. Paleoceanography 19, PA2002, http://dx.doi.org/10.1029/ 2003PA000974.
- Broecker, W.S., Clark, E., Barker, S., 2008. Near constancy of the Pacific Ocean surface to mid-depth radiocarbon-age difference over the last 20 kyr. Earth Planet. Sci. Lett. 274, 322–326.
- Butzin, M., Lohmann, G., Bickert, T., 2011. Miocene ocean circulation inferred from marine carbon cycle modeling combined with benthic isotope records. Paleoceanography 26, PA1203, http://dx.doi.org/10.1029/2009PA001901.
- Carter, P., Vance, D., Hillenbrand, C.D., Smith, J.A., Shoosmith, D.R., 2012. The

- Poore, H.R., Samworth, R., White, N.J., Jones, S.M., McCave, I.N., 2006. Neogene overflow of northern component water at the Greenland–Scotland ridge. Geochem. Geophys. Geosyst. 7, Q06010, http://dx.doi.org/10.1029/ 2005GC001085.
- Reid, J.L., 1986. On the total geostrophic circulation of the South Pacific Ocean:
- Reid, J.L., 1986. On the total geostrophic circulation of the South Pacific Ocean: flow patterns, tracers and transports. Prog. Oceanogr. 16, 1–61.
 Reid, J.L., 1997. On the total geostrophic circulation of the Pacific Ocean: flow patterns, tracers, and transports. Prog. Oceanogr. 39, 263–352.
 Roberts, N.L., Piotrowski, A.M., McManus, J.F., Keigwin, L.D., 2009. Synchronous deglacial overturning and water mass source changes. Science 327, 75–78.
 Robinson, L.F., et al., 2005. Radiocarbon variability in the western North Atlantic during the lact deglaciation. Science 310, 1460, 1472.
- during the last deglaciation. Science 310, 1469-1473.

Rutberg, R.L., Hemming, S.R., Goldstein, S.L., 2000. Reduced North Atlantic Deep