Mid–late Pleistocene deep-water circulation in the Southwestern Subtropical Pacific

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The modern $\delta^{13}C_{DIC}$ distribution in the deep-waters of the southwestern subtropical Pacific is consistent with a regional mixing regime between deep-waters of open-Pacific and Tasman Sea origin (Fig 1). Comparison of a down-core record of benthic foraminiferal (*C. wuellerstorfi*) $\delta^{13}C$ from site MD06-3018, New Caledonia Trough (2500m water depth), with a similar record from the Pacific deep western boundary current region shows that the relative influence of open-Pacific deep-waters on the mixing regime is reduced during glacial in comparison to interglacial stages over the past 1100ka. This offset arises from the continued presence of mid-depth deep-waters of southern Atlantic origin in the glacial Tasman Sea whereas the glacial southern Pacific is dominated at the same depths by waters from the Southern Ocean.

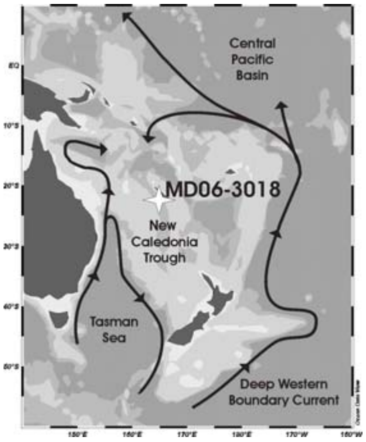

Figure 1: Schematic diagram of regional deep-water flow.

Molecular paleoclimatology

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The geological investigation of global change phenomena is becoming increasingly dependent on a better molecular level understanding of key geochemical processes that record the characteristics of ancient atmospheric and oceanic reservoirs. Many of these processes involve the uptake of stable isotopes of elements such as carbon, boron, and iron into minerals that form over geological timescales in soils and ocean floors in contact with these reservoirs. Effective use of these tools of climate reconstruction depends critically on input at the molecular level.

The isotopic composition of boron trapped in calcite is used to estimate the pH of seawater in the geologic past. Recent work [1] has clearly shown that the low value of 1.019 (25°C) for the equilibrium constant (K_{34}) for the reaction $^{11}B(OH)_3+^{10}B(OH)_4^-=^{10}B(OH)_3+^{11}B(OH)_4^-$ results from misassignment of the vibrational spectrum of $B(OH)_4^-(aq)$ [2]. Our interpretation of 20 million years of earth history thus depended on a simple missasignment of the asymmetric stretching vibration of $B(OH)_4^-(aq)$. Despite definitive experimental determination of the equilibrium constant at 1.028 [3], controversy surround K_{34} with many groups claiming that the erroneous value for K_{34} is in better agreement with geological observations.

The $Fe(CO_3)OH$ proxy uses the isotopic composition of CO_2 dissolved in goethite [$CO_2(m)$] to estimate the PCO_2 of the atmosphere. Here, computational studies [4] indicate the possibility of heterogeneous isotopic signatures for $CO_2(m)$, ranging from -20 to +7 per mil, with respect to $CO_2(g)$, most of which appear to be inconsistent with geological evidence pointing to a value of ~ +2.5 [5]. Paleoclimate science is becoming increasingly dependent on precise knowledge of the structure and isotopic fractionation associated with the chemical species that record climate. These problems have immense importance in setting environmental policy, and deserve our best molecular-level tools. It is already clear that computational methods will play an important role in the molecular transformation of paleoclimatology.

[1] Rustad & Bylaska (2007) *J. Am. Chem. Soc.* **129**, 2222. [2] Kakihana *et al.* (1977) *Bull. Chem. Soc. Japan* **50**, 158. [3] Klochko *et al*. (2006) *Earth Planet. Sci. Lett.* **248**, 276. [4] Rustad & Zarzycki (2008) *Proc. Nat. Acad. Sci. USA* **105**, 10297. [5] Yapp & Poths (1996) *Earth Planet. Sci. Lett.* **137**, 71.