Tracing Antarctica's terrigenous sediment contributions to the Southern Ocean

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The Southern Ocean is known to play an important role in Earth's climate system. It is most likely the major contibutor to the glacial to interglacial changes in atmospheric pCO_2, and the presence of a circum-polar current effectively isolates Antarctica from the heat pump effect of the surface ocean gyres. The vigor of the Antarctic Circumpolar Current is regulated by the position and strength of the westerly wind belt. The positions of fronts within the Antarctic Circumpolar Current and the details of deep-water formation processes are also likely influenced by the westerly winds.

Constraints on the sources of terrigenous sediment can lead to constraints on the position and vigor of the Antarctic Circumpolar Current and its fronts. We have a campaign to characterize the regional sediment provenance signals around the perimeter of Antarctica using combined geochemical approachs including Ar-Ar ages of detrital hornblende and biotite grains, and radiogenic isotopes of Nd, Sr, Hf and Pb. The major ice catchments around the Antarctic perimenter can be identified by this combined approach, and we seek to identify past changes in ice sheet dynamics by applying provenance tracer approaches. By combining these approaches with stratigraphic evidence of changes in sediment delivery and grain size sorting, we can link climatic changes in Antarctica with changes in the Southern Oceans. The same provenance characterization will lead to a better understanding of the deep-water fingerprint that would be imparted from Antarctic sources.

First-principles simulations of Boron XANES with implications for determining B coordination in glasses and melts

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Borosilicate glass is proposed by many countries as the candidate encapsulation material for the long term storage of high level radioactive waste. Of particular importance to the stability of these glasses is the ratio of $^{[3]}B/^{[4]}B$. The formation of $^{[4]}B$ is dependent upon the availability of charge compensators such as Na. Alkali and alkaline-earth cations may act as network modifiers and depolymerise the borosilicate network, but in the presence of $^{[4]}B$ they act as charge compensators for the excess charge on BO_4, without depolymerization of the network. We have been investigating the stability of borosilicate glasses using B K-edge XANES and in particular the coordination of B. However, the XANES spectra are complex with the energy region due to $^{[4]}B$ being overlapped with peaks due to $^{[3]}B$ making extraction of quantitative $^{[4]}B$ values difficult [1]. Furthermore, several mineral reference spectra exhibit splitting of the main $^{[3]}B$ peak at ~194 eV, as well as, splitting of peaks in the higher energy envelope (~198-208 eV). The splitting of the ~194 eV peak occurs principally in borates containing OH and appears to be related to hydrogen bonding in the structure. The higher energy splitting seeems to be related to the B-O bond length and next nearest neighbour as suggested previously (Fleet and Muthupari [2]. To better understand the spectra we have investigated several borate and borosilicate reference minerals using first-principles calculations. Ongoing analysis of the results indicate that the ~194 eV splitting is due to contributions from O 2P states that are influenced by the hydrogen bonding.

[1] Fleet and Muthupari (1999) *J. Non-crystalline Solids*, **255**, 233-241. [2] Fleet and Muthupari (2000) *Am. Mineral* **85**, 1009-1021.