

Sr isotopic composition of pore water of shelf cores from IODP Expedition 317: Canterbury Basin, New Zealand

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We used Sr isotope ratios to investigate diagenetic and sedimentary controls on the chemical composition of pore water in shelf sediments of deep-penetration (>300 m) cores recovered by Integrated Ocean Drilling Program Expedition 317 at three sites on a landward-to-basinward transect in the Canterbury Basin off New Zealand (sites U1353, U1354, and U1351, Fig. 1).

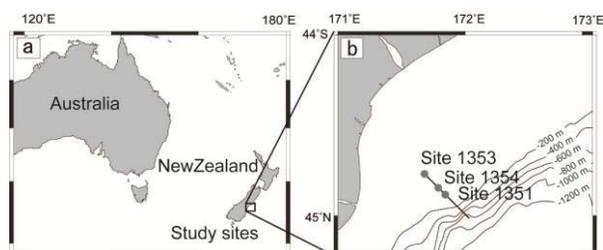


Figure 1: Map showing the locations of drilling sites of IODP Expedition 317: Canterbury Basin, New Zealand.

In general, the pore-water Sr concentration increased as $^{87}\text{Sr}/^{86}\text{Sr}$ values decreased in the shelf environment. Such Sr enrichment accompanied by rapid decreases of $^{87}\text{Sr}/^{86}\text{Sr}$ reflect the diagenetic release of Sr from reactive minerals such as biogenic carbonate and silicate minerals (e.g., plagioclase, mica). The degree of Sr enrichment was less and $^{87}\text{Sr}/^{86}\text{Sr}$ was higher in the pore water of the core from the most nearshore site (U1353) compared with the other two cores. Moreover, molar ratios of major cations remained constant throughout most of the U1353 core. These results suggest that the site U1353 sediments underwent less diagenesis. In addition, a less saline lens was observed in the uppermost 150 m only at site U1353. $^{87}\text{Sr}/^{86}\text{Sr}$ values in the less saline lens were uniform, and the plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ showed no significant mixing trend related to salinity changes. The $^{87}\text{Sr}/^{86}\text{Sr}$ data suggest that the less saline lens can be explained by the introduction of freshwater in the past in association with sea-level fluctuations. The repeated freshwater intrusion during periods of emergence followed by seawater replenishment after submergence that probably accompanied Pleistocene to Holocene sea-level changes would have homogenized $^{87}\text{Sr}/^{86}\text{Sr}$ values and caused some pore water to be discharged into the ocean. Moreover, no hydrocarbons were detected at site U1353 and sulfate concentrations were close to the seawater value. We propose that during sea-level lowstands, climate-driven flushing of pore water was accompanied by the inhibition of methane generation in the fine-grained sediments.

Fate of nitrogen during oxic submarine groundwater discharge into Stony Brook Harbor, New York

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A combination of electrical resistivity surveys, porewater sampling and ultrasonic seepage meter measurements were used to investigate nitrogen attenuation in a subterranean estuary STE in Stony Brook Harbour, an embayment with direct connection to Long Island Sound. Nitrogen loading calculations for Long Island Sound assume conservative transport of nitrogen during submarine groundwater discharge through the subterranean estuary (STE) [1]. However, the STE is increasingly recognized as a potential nitrogen sink due to rapidly changing redox conditions at the freshwater/saltwater interface. To minimize cesspool and lawn fertilizer derived nitrogen inputs to coastal waters, municipal land planners require better estimates of nitrogen attenuation in the STE.

Coupled land-sea electrical resistivity profiles show distinct shallow saline tidal recirculation cells overlying a 9m thick freshwater zone in the coastal aquifer. STE porewater was sampled in two perpendicular to shore piezometer transects 75m apart. Each transect consisted of 5 piezometer wells, sampled at intervals of 0.5m to a maximum depth of 7.6m. Ultrasonic seepage meters were placed offshore to record discharge during STE porewater sampling. A combination of N_2/Ar and $\delta^{15}\text{N}-\text{NO}_3^-$ are used to determine extent of denitrification in the shallow saline transition zone. This approach is used in traditional groundwater denitrification studies [2] but this study is the first to employ this method in a STE.

The shallow saline transition zone, where salt water from tidal oscillations penetrates into discharging fresh water, is the most geochemically active portion of this STE. Dissolved oxygen concentrations were above 70% saturation throughout the freshwater portion of the STE. Where dissolved oxygen concentrations were less than 2mg L^{-1} , nitrate concentrations were less than $50\mu\text{M L}^{-1}$ and salinity was 20ppt or greater, but no NH_4^+ is present. Along one transect, NO_3^- concentrations decreased seaward to 5mg L^{-1} over a distance of 26 meters. Anammox, coupled nitrification-denitrification or dilution of nitrate in the shallow saline zone may account for this removal of nitrogen.

In STEs where groundwater is oxic, nitrate concentrations remain high but may be diluted during transport, as evidenced by silica and sulfate porewater distributions. Nitrogen attenuation occurs in the shallow saline transition zone, where saltwater derived dissolved organic carbon drives microbial reactions. Combined N_2/Ar and $^{15}\text{N}-\text{NO}_3^-$ elucidate attenuation mechanisms in the shallow saline transition zone.

[1] Scorca, M and Monti, J (2001) *U.S. Geological Survey Water-Resources Investigations Report 00-4196*, 29 [2] Singleton et al (2007) *Environmental Science and Technology* **41** (3), 759-765