

## Boundary exchange processes on and along the Kerguelen plateau

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The Kerguelen Ocean and Plateau compared Study (KEOPS) took place during the austral summer (19 Jan-13 Feb 2005, R/V "Marion-Dufresne", 68°-78°E/ 49°-52°S sector). One of the KEOPS objectives was to determine the mechanisms responsible for the bloom occurring on the Kerguelen plateau. Coupled with physical measurements, a multi-proxy investigation was carried out in order to better constrain the sources of iron, as well as the water mass and particle pathways. REE concentrations and radium isotope activities already indicated that dissolution of basalts from the shelf of Heard Island loads significant amounts of iron into the plateau waters [1, 2]. However surface waters are depleted in dissolved iron [3], making us suspect that in addition to the biological consumption, strong scavenging affects these waters.

Here we present dissolved Nd isotopic compositions, measured at 5 stations on and 4 off the Plateau, expressed as  $\epsilon_{Nd} = [(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{chur} - 1] * 10,000$  where "chur" means a reference. Isotopes bring new insight on the scavenging, mixing and exchange processes at play in this area. At open ocean stations, circumpolar deep waters are characterized by  $\epsilon_{Nd}$  of  $-9.9 \pm 0.2$ , value that increases to  $-8.6 \pm 0.3$  when the same waters flow along the eastern slope of the Plateau, whereas Nd concentration simultaneously drops by a factor  $\sim 2$ . Both the input of radiogenic Nd (explaining the  $\epsilon_{Nd}$  increase) and its obvious subtraction reveal that strong "Boundary Exchange" is acting along the slope. First estimates yield an input of  $5.4 \times 10^8$  for a removal of  $1.7 \times 10^9$  mol/y of Nd, that is a net exchange of  $-1.1 \times 10^9$  mol/y, in favor of removal. On the Plateau, most of the values are above -8, the most radiogenic ones (-4.8) being observed at the station nearby Heard Islands. These radiogenic waters are also characterized by less pronounced Ce anomaly than the non radiogenic ones, clearly confirming the recent dissolution of basaltic particles ( $\epsilon_{Nd} > -2$ ). These different data allow the estimate of input and scavenging rates on the Plateau, results that are compared to the scavenging rates deduced from Th and Pa at the same locations [4].

[1] Zhang *et al.* (in press) *Deep Sea Res. II*. [2] van Beek P. *et al.* (in press) *Deep-Sea Res. II*. [3] Blain S. *et al.* (2007) *Nature* **446**, 1070-1074. [4] Venchiarutti C. *et al.* (in rev.) *Deep Sea Res.*

## Denitrification coupled to pyrite oxidation and changes in groundwater quality at Oostrum, the Netherlands

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Denitrification is the major pathway of nitrate removal from groundwater systems, with organic matter or minerals, primarily pyrite, serving as electron donors. Because pyrite oxidation leads to sulfate production, as well as the release of trace metals and changes in pH, it can significantly affect groundwater quality.

This study focuses on the occurrence and effects of denitrification coupled to pyrite oxidation in a sandy aquifer using detailed geochemical analyses of both sediment and groundwater combined with groundwater age dating (<sup>3</sup>H/<sup>3</sup>He). Our study site is located in cultivated fields and an adjacent forested area at Oostrum, the Netherlands.

Shallow groundwater in the region has high nitrate levels (up to 500 mg/L) due to intense fertilizer application. Nitrate removal from the groundwater below cultivated fields correlates with sulfate production and the release of Fe<sup>2+</sup> and pyrite-associated trace metals (e.g. As, Ni, Zn, Co). These data and the presence of pyrite in the sediment matrix within the nitrate removal zone indicate that denitrification coupled to pyrite oxidation is the main pathway removing nitrate infiltrating into the aquifer. However, the observed increase in sulfate concentrations below the depth of nitrate depletion is about 50% lower than expected from complete oxidation of pyrite to sulfate. Possible explanations include production of elemental sulfur, additional reactions consuming sulfate, or incomplete denitrification. Comparison of regional sulfate and nitrate inputs between 1940 and 2000 to age profiles of sulfate and nitrate in the aquifer for this period confirm significant nitrate loss and sulfate production in the aquifer. The maximum rate of nitrate removal within the reaction zone is estimated at 0.6 mM y<sup>-1</sup>.

Pollutant concentrations (e.g. NO<sub>3</sub>, Cl, As, Ni) in the groundwater of the agricultural areas decreased between 1996-2006, due to decreased fertilizer use. In the downstream forest area, in contrast, pollutant concentrations have increased because of lateral inflow from the adjacent cultivated fields.