

## Groundtruthing the nitrogen isotopic composition of planktonic foraminifera as a paleobiogeochemical proxy

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The nitrogen isotopic composition of the organic matter trapped within the calcite shells of planktonic foraminifera (FB- $\delta^{15}\text{N}$ ) has been explored as a new proxy in ocean sediment records to reconstruct past changes in the marine nitrogen cycle, but information on its generation and preservation is so far minimal. In this study, we report measurements of the  $\delta^{15}\text{N}$  of foraminiferal biomass from Sargasso Sea net tow material and shell-bound N from shallow sediments collected in different open ocean regions. The annual average biomass  $\delta^{15}\text{N}$  of three euphotic zone dwelling species, *G. ruber*, *G. sacculifer*, and *O. universa* in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate  $\delta^{15}\text{N}$ , as well as their shell-bound  $\delta^{15}\text{N}$  in the surface sediment. We observe large seasonal variations in the biomass  $\delta^{15}\text{N}$ .  $\delta^{15}\text{N}$  is lowest in fall to winter, followed by a  $\delta^{15}\text{N}$  rise during the spring bloom. Our global data set of FB- $\delta^{15}\text{N}$  from surface sediments in the oligotrophic regions shows a strong correlation between FB- $\delta^{15}\text{N}$  and changes in the subsurface nitrate  $\delta^{15}\text{N}$ , which is the dominant source of new N to the euphotic zone. In the subarctic North Pacific and the eastern equatorial Pacific, where nitrate is abundant at the surface, FB- $\delta^{15}\text{N}$  in the surface sediment closely tracks changes in surface nitrate  $\delta^{15}\text{N}$  and is thus anticorrelated with nitrate concentration. These results are strong evidence that FB- $\delta^{15}\text{N}$  is a reliable proxy for tracing the  $\delta^{15}\text{N}$  of the N supply to surface waters in oligotrophic regions and for reconstructing surface nitrate utilization in high-nutrient regions. We will also examine the interspecies differences in terms of depth habitat and trophic level.

## Heavy metal availability in contaminated soils: complementary insights from isotopic exchange, DMT, and sequential extractions

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Contaminated calcareous topsoils were sampled from paddy fields around a lead/zinc mine in Lechang, Guangdong Province, South China. The soil pH was 7.8, total heavy metal contents were 768 mg Pb kg<sup>-1</sup>, 715 mg Zn kg<sup>-1</sup>, 58.7 mg Cu kg<sup>-1</sup> and 22.6 mg Ni kg<sup>-1</sup>.

Donnan membrane technique (DMT) and stable isotopic exchange kinetic (SIEK) technique were performed to determine the concentration of free metal ion (FMI) in soil solution and the available metal pool (isotopically exchangeable metal, *E* value) in soil. Traditional sequential extractions were also used to assess the metal distribution among the geochemical compartments of soil solid phase.

DMT results showed that quite few FMIs were presented in the soil solutions. At soil:solution ratio = 100 g L<sup>-1</sup>, the total dissolved Pb, Zn, Cu, Ni were only 0.91, 3.29, 3.34, 0.07 µg L<sup>-1</sup>, while large proportion of Pb, Cu and Ni were complexed. A good agreement was found between the FMIs concentration measured by experiments and calculated by NICA-Donnan model.

However, multi-SIEK results indicated that the isotopically exchangeable pool of Pb, Cu and Zn were large. After 12-day equilibrium,  $E_{\text{Pb}}$ ,  $E_{\text{Cu}}$ , and  $E_{\text{Zn}}$  value were 302, 13, and 106 mg kg<sup>-1</sup>, which were up to 39%, 22% and 15% of metal total content, respectively. In contrary,  $E_{\text{Ni}}$  value was only 1 mg kg<sup>-1</sup> (i.e. 1.5% of total Ni).

Combined with the metal distribution in solid phases given by sequential extractions, the larger Pb available pool may be attributed to the high carbonate-bound and Mn oxides-bound fractions. A large proportion of Ni in the so-called residual fraction (i.e. 75% of total Ni) may explain the lower  $E_{\text{Ni}}$ .

Therefore, such combination of different techniques can give a more comprehensive insight into the heavy metal availability, thus it can provide implications to risk assessment and long term remediation.