Application of a nanoEA-IRMS system for $\delta^{13}C$ measurement of biomineral-bound organics in samples of diatom opal with nanomolar quantities of C

Ana Méndez-Vicente, Luz María Mejía-Ramírez, and Heather Stoll
Departamento de Geología, Universidad de Oviedo, Spain (anamendez@geol.uniovi.es)

We describe the isotopic measurement of $\delta^{13}C$ in very small samples of diatom opal (nanomolar quantities of C) both from fossil sediments and cultures. We use a nano-EA system composed of a combustion elemental analyzer (EA3000 series, Eurovector), with standard 18 mm diameter quartz oxidation-reduction reactors and an ash removal device that aids in removal of uncombusted opal and ensures a long reactor lifetime. This is coupled to a custom designed trapping and chromatography system (Nano-CF, Nu Instruments Ltd.) which cryogenically removes CO$_2$ generated by sample combustion and introduces the gas into a low-flow helium carrier stream to the mass spectrometer (Nu Perspective IRMS instrument, Nu Instruments Ltd.).

This technique allows for an important reduction in the minimum sample requirements for analysis compared to a typical EA, however the need to reduce the contribution of the blank to the measured values becomes all the more critical. Blank from the capsules can be minimized through specific protocols including cleaning with solvents and reducing the size of the capsule by cutting it to a smaller size, attaining blanks as low as 13.75±2.15 nmol C. Under these conditions we can accurately measure both standards and diatom reference materials in the range of 100 to 330 nmol C, with a precision of $2\sigma < 1\%$. The measured $\delta^{13}C$ is independent of sample size in this range for standards or samples with $\delta^{13}C < -11\%$ which is the compositional range expected for natural diatom samples. Furthermore, no memory effect is observed in samples with an isotopic $\delta^{13}C$ value differing by $> 10\%$ analysed in sequence.

Applied to measure biomineral-bound organics in cleaned diatom samples from sediments, the low sample size requirements of this technique allows us to analyse multiple size fractions within one sample, and explore isotopic fractionation patterns between them. We have analysed samples from sediments of both centric and pennate diatoms typically in the range of 200 to 1300 $\mu$g of cleaned opal. Analysis of culture samples of Thalassiosira pseudonana of 20 to 150 $\mu$g of cleaned opal, allows us to evaluate if there is covariation of the whole cell particulate organic carbon (POC) and diatom-bound $\delta^{13}C$ values. Initial results suggest that diatom-bound $\delta^{13}C$ is more depleted than POC.