2.7.P05

Non-destructive pre-selection of minimally altered fossil tooth enamel for additional geochemical analysis

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During biomineralization, an organism incorporates into solid form not only the major elements that define the mineral, but also trace elements and isotopic signatures that reflect the geochemical environment during the organism's life. If these signatures are preserved in biological apatite, then archeologists and paleontologists can use trace-element analysis as well as radiogenic and light-stable-isotope analysis to infer, e.g., the grazing range, the type of vegetation (C-3 vs. C-4) consumed, and the climate pertinent to paleontologic samples, as well as the possible homeland/hometown of buried individuals at archeologic sites. It is well recognized that fossil tooth enamel, with its coarser crystallites and low concentration of organic components, re-equilibrates less readily with groundwater and soil moisture than do bone and dentin. However, even though enamel typically is the biological material of choice for geochemical analysis, it also can become chemically altered after burial, as revealed by fluoridation and recrystallization of the apatite. Using a laser Raman microprobe (1-um beam spot), we have made traverses across the exposed crown and a freshly sawn cross-section of a 10,000-year-old horse molar. The chewing surface of a horse's molar is designed to reveal edge-on ribbons of enamel in a matrix of dentin. This structure makes the molar an ideal sample in which to study both 1) the differential response of dentin and enamel to diagenetic processes and 2) the spatial extent of alteration into the interior of the tooth. Raman spectral band positions and widths of the biological apatite reflect the expected mineralogic differences between dentin and enamel, as well as changes due to diagenesis. The sawn cross-section of the interior of the tooth shows the spectral features indicative of more fluoridation and recrystallization in the dentin than in the enamel, as expected. The exposed crown surface, surprisingly, shows the opposite relation, i.e. enamel more fluoridated than dentin. These recorded differences demonstrate the need for careful spatial selection of biological apatites whose compositions and isotopic signatures are used in paleoenvironmental reconstruction. Raman spectroscopy offers a relatively rapid, non-destructive means of evaluating at a few-um scale how well preserved a biological apatite sample is. Spectroscopic monitoring could be used to pre-select the least altered enamel samples for additional (destructive) chemical and isotopic analyses.

2.7.P06

Observations of Si isotope mass fractionation during freshwater diatom blooms

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Understanding the distribution of Silicon (Si) isotopes between different terrestrial reservoirs and thus the Si isotope terrestrial mass-balance is fundamental for the development of Si isotopes as a tracer of biogeochemical cycles. We have investigated the Si isotope composition in freshwater diatoms collected in sediment traps from Lake Lugano, Switzerland. This lake has well-documented seasonal changes in the degree of primary production, with distinct blooms of diatoms in spring that utilise most of the available silicic acid in the surface waters [1, 2]. Hence, we are able to test the natural Si isotope mass fractionation during Si utilisation in a natural environment. The stable Si isotopes of cleaned biogenic silica were measured by high-resolution MC-ICP-MS via a desolvating nebuliser system to obtain both δ^{30}Si and δ^{29}Si isotope values.

We observe seasonal variations in δ^{30}Si and δ^{29}Si between 0.0 and +1.5, and between 0.0 and +0.8, respectively. Over the same time period, concentrations of Si in the surface waters varied from 1.4 ppm Si to less than 0.4 ppm. The highest δ^{30}Si (and δ^{29}Si) values are observed at the end of the spring blooms of diatoms, whilst the surface waters are strongly depleted in Si, and the thermocline is most pronounced. Over the seasonal cycles there is a good correlation between the Si isotope composition and the vertical Si concentration gradient in the lake, corresponding to the biological removal of Si from the surface waters.

The results clearly demonstrate the strong link between the Si isotope composition of biogenic silica and the consumption of Si in aquatic environments. Thus, Si isotopes can be used as indictors of biogenic Si utilisation. During late spring, diatom growth in Lake Lugano appears to be limited by the availability of Si, yet, during the rest of the year growth is limited by other factors.

References

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