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d^2H measurements with various EA-IRMS techniques : a review. New application to archaeological mineralised tissues

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Hydrogen is the simplest element but its physical and chemical properties are often used to resolve complex scientific questions. Before, scientists used off–line systems based on complex vacuum lines, to prepare hydrogen samples for analysis IRMS in dual–inlet mode. Starting with waters mass spectrometry techniques allowed applications to analyses of organic matter. Various reduction techniques (U, Cr, V) were used. More recently, along with the development of continuous flow techniques, elemental analyser pyrolysis online with Isotopic Ratio Mass Spectrometry (EA-Py-IRMS) was developed for hydrogen analyses. Different types of reactors were developed to cover various types of hydrogen isotopic analyses. Fine chromium reagent better known as “ChromHD” was adopted mainly for water analyses with liquid injectors connected to elemental analysers producing excellent accuracy and precision. Glassy carbon reactors were used for both solid and liquid samples, to measure O and H isotopes. Then for samples presenting significant halogen contents, large radius chromium reagent was used for $^2H/^1H$ measurements. Examples of applications for those techniques are shown. A recent illustration of the improvement for those techniques deals with analyses of δ^2H from bone collagen (δ^2H_{coll}), δ^2H of tooth enamel (δ^2H_{enamel}) and δ^2H of bulk bone material (δ^2H_{bone}) measured on specimens of humans, bovids, horses and a pig from the archaeological site of Thézy-Glimont, France. All samples have been previously studied using other isotopic proxies: $\delta^{18}O$ of bone hydroxy-apatite and tooth enamel $\delta^{13}C$ of tooth enamel and $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ of bone collagen. We show that similar interpretations can be achieved from the hydrogen isotope analysis of mineral tooth enamel (δ^2H_{enamel}), with the possibility of interpreting supplementary information about child feeding practices. Moreover, hydrogen isotope signature of bulk bone material (δ^2H_{bone}) records a similar signal as bone collagen but seems more influenced by diet than climate.

These results open new prospects in a variety of research topics. Dietary and climatic signals can be interpreted from archaeological/prehistoric populations, where collected remains contain degraded collagen without the need to use expensive techniques. Mineral body tissue δ^2H is now a useful proxy associated to the already-used panel of isotopic tools.