Diagenetic stability of Ca, Mg, Zn, and Sr isotopes in teeth – an in vitro alteration experiment of biogenic apatite in isotopically enriched tracer solution

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Stable isotope ratios and trace element concentrations of fossil bones and teeth are important geochemical proxies for the reconstruction of diet and past environment in archaeology and palaeontology. However, since diagenesis can significantly alter in vivo incorporated isotope signatures and elemental compositions, it is important to understand alteration processes. Here, we present the results of in vitro alteration experiments of dental tissues from a modern African elephant molar in aqueous solutions at 30 °C and 90 °C for 4 to 63 days each. Dental cubes with ≈3 mm edge length, comprising both enamel and dentin, were placed into 2 ml of an acidic (HNO_3) aqueous solution (pH ≈1) enriched with different isotopes (^{25}Mg, ^{44}Ca, ^{67}Zn, ^{86}Sr). Element and isotope distribution profiles across the different dental cubes were measured with LA-(MC-)ICP-MS and EMPA, while potential changes of the bioapatite crystal structure were characterised by Raman spectroscopy. Isotope ratios measured by LA-(MC-)ICP-MS revealed an alteration of the outer ≈200-300 µm of the enamel in all experiments. Dentin was fully altered after one week (at 90 °C) and the tracer solution started to penetrate through the dentin even into the innermost enamel. However, the central part of the enamel remained unaltered. The Raman spectra suggest a strong recrystallization in the dentin and in the outer ≈40 µm of the enamel and a partial demineralisation of the outer rim of the cubes. Our results indicate that independent of time, temperature or low initial pH, enamel apatite shows a high resistance against the experimental alteration in structure and isotopic composition, in contrast to dentin apatite.