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Spatial resolution, precision, accuracy and matrix effects of bio-apatite Sr isotopic composition measurements by laser ablation MC ICP-MS

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The high abundance and compositional diversity in the natural environment has made Sr isotopes one of the most important tools in palaeoenvironmental studies of mammals. Dental enamel, as the hardest and most durable tissue, is particularly well suited to recover the in vivo uptake of trace elements and their isotopic composition, reflecting the animal's habitat, diet and mobility. The prolonged, sequential mineralisation of dental tissues requires high spatial resolution techniques, such as laser ablation (LA) MC ICPMS, to decipher temporal variations hindered by bulk analysis. The quest to analyse a minimum sample volume with maximum precision has led to the development of different strategies in terms of hardware, instrumental parameters and data reduction. Apart from technological improvements such as the collision/reaction cell capable of eliminating problematic isobars, or the use of special geometry cones to increase instrument sensitivity, the tuning conditions have been identified as an important factor in reducing or eliminating effects impeding the accuracy of LA MC ICPMS measurements. Although bioapatite, best approximated as hydroxyapatite $Ca_5(PO_4)_3(OH)$ with CO_3 substitutions, is flexible in incorporating a wide range of elements, bio-mineralisation imposes some limitations. The absence of doubly charged REE isobars makes it particularly suitable for quantifying matrix effects such as Ca-argide and dimer or $^{40}Ca^{30}P^{16}O$ formation, whose influence on the accuracy of Sr isotope measurements is debated. An additional factor comes from the use of high sensitivity cones, which together with the increased ion beam modify isotopic fractionation, mass bias and oxide production. In this study we quantify the influence of matrix effects, isotopic fractionation and instrumental mass bias, on precision, accuracy and long-term reproducibility of Sr isotope measurements by LA MC ICPMS under various plasma conditions. We present >10-year long record of analyses conducted by MC ICPMS *Neptune* and compare it with the data obtained by *Neoma*. Additional experiments were carried out utilising high sensitivity cones and 10^{13} Ω amplifiers. The LA data are compared with long-term record of solution-based analyses under wet and dry plasma conditions. We showcase high precision analyses wth increased spatial resolution in a histomorphometric context applied to woolly mammoth and human dental enamel.