In situ $^{87}Sr/^{86}Sr$ LA-MC-ICPMS on biogenic apatites: a matrix-matched standard correction approach

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Strontium isotope ratios are a strong tool to study ancient hominin and animal migrations, hence the increasing need to have a simple, fast and micro-destructive analytical technique to obtain accurate and precise $^{87}Sr/^{86}Sr$ ratios of precious tooth enamel and bone tissue. The traditional analysis by the TIMS or MC-ICPMS tecniques requires sample dissolution; therefore, several LA-MC-ICPMS methods have been developed to prevent sample destruction, particularly for prehistoric human teeth. Instrumental calibration on human enamel is difficult because of the typical low-Sr concentration and analytical interferences. In fact, the methodology for data reduction of *in situ* Sr isotopes of biogenic apatite is largely debated in the literature [e.g. 1, 2]. While monoatomic interferences (Kr, Rb, REE^{2+}) are routinely corrected, the correction of polyatomic interferences (CaCa, CaAr and $^{40}Ca^{31}P^{16}O$) are challenging. In particular, the CaPO molecule strongly interferes on mass 87, hindering the achievement of precise and accurate $^{87}Sr/^{86}Sr$ ratios. Following on the work of Horstwood *et al*. (2008), we developed a method based on the concurrent analyses of multiple matrix-matched standard materials. We show how the linear regression of $^{87}Sr/^{86}Sr$ accuracy vs. $1/^{88}Sr$ of at least three standards allows correction of this interference. During each analytical session, we analyse our four in-house matrix-matched standards (a human tooth, a bovine tooth, a swine tooth and a shark tooth) covering a wide range of Sr concentrations (from *c.a*. 100 ppm of the human tooth to the 1000 ppm of the shark tooth). A daily CaPO model is then built to predict the expected accuracy of the analysis. This correction gives an external reproducibility to the 4th decimal digit (e.g. 2σ-human enamel = 0.00047; *c.a*. 100 ppm) and an accuracy between the 4th and the 5th decimal digit when applied to analyses with a laser spot sizes of 100μm and a linear dynamic ablation pattern. Monitoring of the CaPO molecule formation during analysis is also achieved by performing several high resolution mass scans.

[1] Horstwood *et al*. (2008) *Geochim. Cosmochim. Ac*. **72**, 5659-5674. [2] Müller and Anczkiewicz (2016) *J. Anal. At. Spectrom*. **31**, 259-269.