

Precise analysis of Ca isotope natural variations in biological and igneous apatites using LA-MC-ICPMS

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Laser Ablation (LA) is of great potential regarding the understanding of Ca isotopes variations in modern and fossil tooth enamel (~ 40 wt.% Ca), because this technique enables increased spatial resolution and is almost non-destructive.

We developed a strategy based on matrix-matched (including hardness and Sr content) sample/standard bracketing using an Excite 193 nm Excimer Photon Machines LA system coupled to a Neptune *plus* MC-ICPMS.

A series of 5 crystalline igneous apatites and 6 modern tooth enamel samples were first micro-sampled using micromill device, producing holes of about 400 μm of diameter. High precision $\delta^{44/42}\text{Ca}$ solution mode analyses were proceeded according to procedure described in [2]. We then sintered by means of SPS technique bone ash SRM1400 standard, and two synthetic apatites (doped or not with Sr) using the method described in [3]. The Ca isotope compositions in LA mode were obtained using rasters along 600x85 μm profiles and bracketed with SRM1400. Typical sensitivity was ~ 5 V on ^{44}Ca and each profile generated 60 integrations in average.

The $\delta^{44/42}\text{Ca}$ isotopic values ranged evenly between - 0.60 and + 0.60 ‰ (amu). We obtained a very good agreement between solution and LA modes, *i.e.* $\delta^{44/42}\text{Ca}_{\text{LA}}$ vs $\delta^{44/42}\text{Ca}_{\text{Solution}}$ slope of 0.950 ± 0.047 ($R^2 = 0.979$) and null offset at origin (0.010 ± 0.020). For all samples, residual values to the 1:1 slope were ≤ 0.1 ‰ (amu). An unexplained but constant 0.13 ‰ offset occurred when considering $\delta^{43/42}\text{Ca}$ suggesting an uncorrected LA isobaric interference on ^{43}Ca .

We also noticed that the doubly charged Sr interference correction is of crucial importance for accurate matching between solution and laser measurements. In solution mode, Sr is chemically discarded leading to typical 43.5/44 ratios of 10^{-5} to 10^{-6} . In LA, this ratio can exceed 10^{-3} . We show that the $^{87}\text{Sr}/^{86}\text{Sr}$ value used for correction is of importance, and that optimized residuals to the 1:1 slope are obtained using a Sr correction that takes into account a mass fractionation factor for doubly charged Sr distinct from that of Ca.

[1] DePaolo (2004) *Reviews in Mineralogy and Geochemistry* **55**, 255-288. [2] Tacail *et al.* (2014) *JAAS* **29**, 529. [3] Balter & Lécuyer (2004) *GCA* **68**, 423-432.