



Least destructive sampling of human remains using laser drilling for Sr isotope analysis by TIMS

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Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) measured in ancient human remains can be used to reconstruct migration patterns of ancient human populations. This application is based on the fact that different geologic regions have distinct Sr isotope signatures that are cycled through the soils, plants and rivers, and eventually enter the food cycle. Sr isotope ratios measured in skeletal remains (bones and teeth) reflect the average of dietary Sr that was consumed when the tissue was formed, allowing the investigation of human migration between geologically distinct terrains.

The analysis of human remains is always a sensitive topic requiring minimal damage to the sample, while at the same time providing highly precise and accurate results. Samples can be analysed either by solution methods like thermal ionisation mass spectrometry (TIMS), or by in-situ laser ablation MC-ICP-MS.

For TIMS a drill is used to extract a small amount of sample, which is then digested in acid and Sr is separated out using ion exchange chromatography. This technique provides highly precise and accurate results, because any isobaric interferences are removed during chemical separation. The drawback is that drilling may cause visible damage to the sample, restricting access to precious human remains.

LA-MC-ICP-MS analysis is very fast and nearly destruction free. However, the accuracy and precision of LA-MC-ICP-MS is limited by a number of factors including large instrumental mass discrimination, laser-induced isotopic and elemental fractionations and molecular interferences on ^{87}Sr . Its application thus requires rigorous data reduction, which can introduce significant uncertainties into the analysis. This is especially true for samples with relatively low Sr concentrations such as human teeth (e.g., Woodhead et al., 2005; Horstwood et al., 2008; Vroon et al., 2008). In addition, LA-MC-ICP-MS has traditionally required a flat sample surface, thus an unbroken tooth needs to be cut, which is rather destructive.

To evaluate sample strategies which cause minimal damage we have used laser drilling to extract material from the outside of the tooth. Spot sizes between 100-233 μm were used to ablate tooth enamel and collect it in a Teflon beaker. The ablated material was then digested in acids, underwent chemical separation for Sr, and was measured using TIMS. This method minimises sample damage, allows for a large sample throughput and at the same time offers high precision and accuracy. While this method is considerably slower than using conventional LA-MC-ICP-MS, it circumvents the complicated data reduction and its associated uncertainties.

Horstwood, M., Evans, J., & Montgomery, J. (2008). Determination of Sr isotopes in calcium phosphates using laser ablation inductively coupled plasma mass spectrometry and their application to archaeological tooth enamel. *Geochimica et Cosmochimica Acta*, 72(23), 5659–5674. doi:10.1016/j.gca.2008.08.016

Vroon, P. Z., van der Wagt, B., Koornneef, J. M., & Davies, G. R. (2008). Problems in obtaining precise and accurate Sr isotope analysis from geological materials using laser ablation MC-ICPMS. *Analytical and bioanalytical chemistry*, 390(2), 465–76. doi:10.1007/s00216-007-1742-9

Woodhead, J., Swearer, S., Hergt, J., & Maas, R. (2005). In situ Sr-isotope analysis of carbonates by LA-MC-ICP-MS: interference corrections, high spatial resolution and an example from otolith studies. *Journal of Analytical Atomic Spectrometry*, 20(1), 22. doi:10.1039/b412730g