Stable Calcium isotope ratios ($\delta^{44/42}$Ca) in bones and teeth for the detection of dairying by ancient humans

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The transition to agriculture and pastoralism from hunting and gathering is considered one of the pivotal points in human development, leading to profound changes in society, economy, nutrition, and ultimately our modern way of life. Geochemical techniques, particularly stable isotope analysis, can be used to provide information not available from traditional archaeological techniques, and offer the possibility of greater insight into the timing and breadth of the adoption of new foods and their relationship to the "Neolithic revolution".

Dairy products offer advantages of more efficient land use, improved nutrition, and more reliable and constant access to protein, so that understanding the adoption of dairy and its timing is key to developing a fuller understanding of the Neolithic.

We have measured stable calcium isotope ratios ($\delta^{44/42}$Ca) of bones and teeth for the direct detection of dairy consumption by prehistoric humans. Dairy products have lower $\delta^{44/42}$Ca than other dietary calcium inputs [1], and this results in lower $\delta^{44/42}$Ca of the dairy consumer. We have measured the $\delta^{44/42}$Ca of human and animal bones from a range of archaeological sites by MC-ICP-MS with standard bracketing. Results from pre- and post-agricultural times at the key Near Eastern site of Abu Hureyra, Syria (11,100 –7,300 BP) show a $\delta^{44/42}$Ca signal attributable to dairy consumption by ancient humans, with a changing pattern through time. Work on intra- and inter-tooth $\delta^{44/42}$Ca variability is in progress as this material is expected to form a robust archive of in vivo isotope ratios.

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Optimization of a ^{46}Ca-^{43}Ca double-spike to study radiogenic and stable isotope variations

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While Ca isotopes are relatively heavy compared with traditional stable isotopes such as H, C and O, studies have clearly demonstrated the existence of mass-dependent fractionation between stable calcium isotopes (e.g. 40, 42 or 44). The usual notation used for reporting Ca isotope composition is the δ^{44}Ca notation which is defined as variations of the ^{44}Ca/^{40}Ca ratio of a sample compared to a standard in part per thousand (‰). However, the β-decay of ^{40}K produces ^{40}Ca (half life = 1.28 Ga and a branching ratio of 89% [1]) that can lead to easily detectable ^{40}Ca isotope anomaly in biotites and granitic rocks [e.g. 2]. In order to separate radiogenic anomalies from stable isotope variations, the stable isotopes variations must be determined without using ^{40}Ca, and isotope variations need to be expressed relative to ^{42}Ca.

Here we present the optimization of a ^{46}Ca-^{43}Ca double-spike which can be used to determine both the stable and radiogenic isotope variations. This spike is distinct from earlier work [3, 4]. We strive for an improved analytical precision available through the carefully selected double-spike and utilization of the TRITON thermal ionization mass spectrometer (TIMS). It was found that previous spike-sample mixtures, whilst minimizing error propagation of the spike ratios, had small intersection angles of the natural and measured fractionation lines. This angle was optimized in the choice of available spike compositions to provide more orthogonal geometries at low spike-sample ratios ($\theta > 60^{o}$). This optimization is required to separate the instrumental fractionation from estimates of the unspiked natural fractionation factor, and thus minimise error propagations.

The application of the double spike technique is also applicable to high-resolution MC-ICPMS for the determination of stable Ca isotope variations. Initial results documenting its applicablity and comparing TIMS and MC-ICPMS results will be shown.

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