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Bromine in teeth and bone as an indicator of marine diet

Alexis E. Dolphin [a,*], Steven J. Naftel [a], Andrew J. Nelson [a], Ronald R. Martin [b], Christine D. White [a]

[a] Department of Anthropology, The University of Western Ontario, 1151 Richmond Street, London, ON N6A 5C2, Canada
[b] Department of Chemistry, The University of Western Ontario, London, ON N6A 5C2, Canada

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ABSTRACT

Nitrogen isotope ratios in tissues are often used to aid in the reconstruction of the marine component of diets in past populations. Elevated $\delta^{15}N$ values normally found with high trophic level marine resource consumption can, however, also be mimicked by physiological conditions (breastfeeding, pathological states affecting nitrogen balance), climate (aridity), and anthropogenic environments (manuring). This paper presents a pilot study testing whether bromine concentrations can provide a tool for teasing apart possible causes of variation in nitrogen isotope ratios. Blind analyses of bromine in archaeological samples correctly identified individuals derived from coastal vs. inland regions and high vs. low marine consumption time periods. Thus, bromine can provide an important supplement to other isotopic analyses of diet.

1. Introduction

Stable isotope ratios are widely used to reconstruct the palaeodiets, ecological shifts and mobility patterns of ancient humans and non-humans alike. Nitrogen isotope ratios ($\delta^{15}N$) derived from bone collagen provide information regarding the trophic level of consumers and, when combined with $\delta^{13}C$ values, can be used to determine the relative amount of marine vs. terrestrial protein in diets (Ambrose, 1993; DeNiro and Epstein, 1981; Schwarcz, 1991; Schwarcz and Schoeninger, 1991). An individual or population demonstrating enriched $\delta^{15}N$ values is most commonly linked to a high protein diet and/or consumption of marine resources (Richards and Hedges, 1999). Such a linkage relies on the assumption that one's $\delta^{15}N$ values are primarily a reflection of their diet and that metabolic processes determining fractionation are relatively constant throughout the lifecourse (Warinner and Tuross, 2010). In reality, while healthy adult organisms do experience a homeostatic balance between nitrogen synthesis and loss, at some point(s) during their lifespan they may fall out of equilibrium for a variety of reasons. For example, when experiencing nutritional or disease related stress, organisms tend to lose lean muscle mass, which results in a net catabolic state (Fuller et al., 2005; Minagawa and Wada, 1984). As a result the organism enters a negative nitrogen balance which, in turn, results in elevated $\delta^{15}N$ values (Habran et al., 2010). Gestation and lactation, and the associated need for protein synthesis, however, result in decreased maternal $\delta^{15}N$ values due to a positive nitrogen balance (net anabolic state) (Fuller et al., 2004; Kurle, 2002). Several researchers have documented relationships between $\delta^{15}N$ data and variables affecting the physiological states of organisms, such as: pregnancy (Fuller et al., 2004), wasting disease (Katzenberg and Lovell, 1999), anorexia/starvation (Focken, 2001; Gaye-Siessegger et al., 2003, 2004; Hobson et al., 1993; Mekota et al., 2006), trauma/disease (Olsen et al., 2010), water availability (Ambrose and DeNiro, 1987), dietary quality (Hobson and Clark, 1992; Robbins et al., 2005); and growth (del Rio and Wolf, 2005; Trueman et al., 2005).

For those using $\delta^{15}N$ values to help identify the degree of marine resource consumption by members of past populations it is necessary to consider all possible factors causing variation in their datasets. One way of approaching this issue would be to utilize complimentary chemical techniques that can aid in the detection of marine values in ancient tissues. Sulphur isotopes have recently been successfully used for this purpose (Nehlich et al., 2010, 2011; Richards et al., 2001) but sulphur isotopic compositions of plant foods can be confounded in coastal regions by a sea spray effect, which limits the ability to detect marine resource consumption in some contexts. As an alternative, the trace element bromine (Br), which is most commonly found in foods of marine origin, might be used to cross-check the nitrogen isotope ratio data. The preliminary research presented here tests the hypothesis that Br concentrations

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[*] Corresponding author. Tel.: +1 519 636 1564; fax: +1 519 661 2157.
E-mail addresses: adolphin@uwo.ca (A.E. Dolphin), snaftel@uwo.ca (S.J. Naftel), anelson@uwo.ca (A.J. Nelson), rrhm@uwo.ca (R.R. Martin), white2@uwo.ca (C.D. White).

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in archaeological hard tissues (bones and teeth) can provide a reliable additional line of evidence that identifies the degree of marine resource consumption by humans.

2. Bromine as a dietary indicator

Although there has been a considerable amount of research regarding variation in the concentration of other essential halogens (e.g. Cl, I, F) in humans, there is uncertainty regarding the physiological role of Br in the human body. Some animal studies have suggested that Br is an essential element (e.g. Br deficiency linked to depressed growth and fertility in goats; Br supplements alleviating growth retardation in mice [van Leeuwen and Sangster, 1987]), but there is currently no consensus on whether Br is required for maintaining good nutrition or healthy human function (Nielsen, 1998; Ziegler and Filer, 1996).

Bromine is widely available in the environment, with 99% of the world's stock found in sea waters (van Leeuwen and Sangster, 1987; Winnek and Smith, 1987). The Br content of river water and in the earth's crust is considerably lower. As such, several researchers have explained Br variation in human tissues as being indicative of the relative proportion of marine foods consumed (Carvalho et al., 2004; Dixon, 1935; Pinheiro et al., 1999). Rose et al. (2001) assessed the Br concentrations of 20 commonly consumed foods in the United Kingdom, noting that nuts (26.0 ppm), fish (6.7 ppm), and meat products (5.6 ppm) had the highest levels of Br, while the lowest were found in beverages (0.1 ppm), fruits (0.7 ppm), potatoes (1.8 ppm) and sugars (1.8 ppm). While there are very few studies of the Br intake of contemporary peoples, it does appear that there can be considerable variation between populations. For example, Shiraishi et al. (1999) found that the daily intake for a Ukrainian sample (3.47 ± 2.12 mg) was lower than that of a Japanese sample (11.4 ± 2.4 mg) who, the authors noted, consumed significant amounts of seaweed. Observation of the diets of adults from Japan, China and Korea by Kawai et al. (2002) linked the consumption of algae, fish, and shellfish to the Br concentrations of participants' urine samples. More specifically, the Chinese members of the study demonstrated relatively lower Br values – likely because, as argued by Kawai and colleagues, their water-derived foods came from rivers and lakes instead of from the sea as was the case for the Korean and Japanese study members.

In general, although links between the Br content of various tissues and marine food consumption has been identified in several studies, it is important to note that Br concentrations should be interpreted with caution when it is known that nuts, with their high Br content may have contributed significantly to the diets of individuals being sampled. When examining contemporary data linking diets and concentrations of Br in the human body it is important to also consider that the fumigation of crops is well known to elevate the Br content of soils, the plants that grow in them, and the animals who consume them (Kawai et al., 2002; Kishi et al., 1991; Miyahara and Saito, 1994).

It is also necessary to consider that Br of marine origin could possibly enter the human body via different pathways. The consumption of marine foods themselves, or of terrestrial plants and/or animals living in proximity to a marine source of Br the consumption, could be responsible for elevated Br levels in human tissues. Research examining the Br content of Norwegian spruce tree needles (Wyttenbach et al., 1997) has shown that soil contamination with Br does not result in elevated Br concentrations in the needles themselves. Proximity to a polluted or marine environment does increase the surface contamination of the needles, however, and the surface contamination is correlated with the endogenous Br content of the needle itself. In this case it appears that plants growing in marine environments are not gaining their Br from the soil, but getting a boost in Br through sea spray and halogenated organic gases coming from the sea (Wyttenbach et al., 1997). Thus, any reconstruction of paleodiets utilizing Br data would benefit from considering whether the human tissue concentrations of Br examined will reflect direct consumption of marine plants, or perhaps the fact that the terrestrial plants consumed were grown within a certain distance of a coastline (within the range of sea spray, for example), or both.

The mean concentrations of Br in samples of contemporary and archaeological human dental and bone samples, as determined by several researchers, are presented in Table 1. The published Br concentrations vary considerably, possibly due to dietary differences among groups, but this is difficult to determine due to the application of differing analytical techniques and sampling strategies (e.g. whole tooth, enamel only, dentine only, etc.). Despite these confounding factors, the few researchers evaluating the presence of Br in hard tissues have argued that dietary factors, particularly consumption of marine foods (for example, Carvalho et al., 2004), provide the best means for explaining inter- and intra-group variation in Br concentrations. These assertions, however, have not been tested systematically with samples where other lines of evidence have been used to verify the source of Br in the diet. The research presented here will examine the Br content of tooth and bone samples from three archaeological regions (one coastal, one land-locked, and one represented by both coastal and

Table 1
Summary of published determinations of the Br content of human hard tissues. All values are in ppm.

Reference	Root Dentine	Crown Dentine	Enamel	Cementum	Bone	Origin of sample
Soremark and Samsahl, 1961	–	–	4.6	–	–	Modern
Soremark and Samsahl, 1962	–	4.2	–	–	–	Modern
Hardwick and Martin, 1967	–	100–1000	10–100	–	–	Modern
Retief et al., 1971	–	114	33.79	–	–	Modern, South Africa
Losee et al., 1974	–	–	1.12 (0.32–2.6)	–	–	Modern
Rasmussen, 1974	–	–	0.87–7.3	–	–	Neolithic, Denmark
Rasmussen, 1974	–	–	1–4.4	–	–	Modern, Sweden
Curzon et al., 1975	–	–	1.0	–	–	Modern, USA
Curzon et al., 1975	–	–	3.4	–	–	Modern, New Zealand
Curzon and Crocke, 1978	–	–	4.54 (0–33.2)	–	–	Modern, USA and NZ
Molokhia and Nixon, 1984	3.53 ± 2.51	2.28 ± 1.91	0.26 ± 0.16	–	–	Modern
Hancock et al., 1989	–	–	–	–	17.9 ± 1.1	12th c., France
Hancock et al., 1989	–	–	–	–	110 ± 55	Modern, Canada
Pinheiro et al., 1999	5.7 (5.0–7.1)	8.0 (5–10)	2.7 (1–4.5)	–	–	Modern, Portugal
Carvalho et al., 2000	30 (13–48)	15 (7–21)	1 (1–2)	–	69 (62–75)	Chalcolithic, Portugal
Carvalho et al., 2004	10 ± 3	6 ± 3	2.2 ± 0.7	–	–	Neolithic, Portugal
Martin et al., 2007	–	–	–	1	–	Inca, Peru