



LA-ICP-MS chemical analysis of archaeological otoliths as a tool for seasonality and site catchment studies



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ABSTRACT

Analysis of the trace element chemistry of otoliths via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) has become common in fisheries-related work, allowing biologists to trace connectivity between habitats over the life cycles of fish. For archaeological specimens, elements from the outer edges of archaeological otoliths have the potential to provide information on site seasonality complementary to oxygen isotope data; they also may inform on place of capture of fish, thus elucidating exploited ranges and/or social and economic links between settlements. Adopting this method will require careful consideration of a number of complicating factors related to metabolic processes affecting otolith production, analytical procedures peculiar to LA-ICP-MS, and diagenesis, in addition to the usual complications of species identification and assessment of sample adequacy. Here, we review such factors as they affect the utility of the method for sourcing and seasonality research with archaeological otoliths, using the results of a pilot study of specimens from two Woodland-period sites in coastal Alabama, southeastern USA, to illustrate the potential and the current limitations of the method for archaeological research.

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1. Introduction

The last quarter-century has seen an explosion of fisheries-related work using otolith (fish “earstone”) chemistry (e.g., Hamilton and Warner, 2009; López-Duarte et al., 2012; Ramsay et al., 2011; Thorrold et al., 1998; Weber et al., 2002). Such work is predicated upon several useful properties of otoliths relative to other biological structures: 1) otoliths begin growing during the larval stage and growth continues throughout the life of the fish; 2) growth is expressed in incremental bands representing short-term (even daily) periods; 3) otoliths are acellular and metabolically inert, meaning that, once formed, they are not resorbed or otherwise chemically altered via biogenic processes (e.g., Ramsay et al., 2011); and 4) otolith chemistry represents, to some degree, the chemical composition of the waters in which fish live over the

course of their lives. These characteristics combine to make otoliths particularly useful structures for determining fish natal habitats and connectivity, the exchange of individuals over habitat patches over time (López-Duarte et al., 2012), and such information lends itself to range-scale management practices.

For archaeology, information on otolith chemistry can be applied in two ways: 1) as a method of determining site seasonality that is complementary to O isotope and other traditional forms of seasonality assessment (Andrews et al., 2003; Saunders et al., 2005); and 2) establishing catchment, or the geographic range over which fish were harvested in the past (Disspain et al., 2015). Before either of these applications can be realized, however, the many variables affecting otolith chemistry and those arising from different analytical methods must be recognized (Disspain et al., 2015) and formal procedures established to control for those variables as much as possible. In this paper we discuss such variables, using data from a pilot study of otoliths from two coastal sites in the southeastern USA to illustrate both the promise of otolith chemical data for archaeology and the complications that analysts will face

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as they try to obtain such data and put them to use.

2. Sources of variation in otolith chemistry

The basis for both modern and archaeological applications of otolith chemistry is the assumption that environmental differences over space are reflected in different elemental concentrations in water bodies, which in turn are reflected in otoliths, yielding information on spawning locales, point of capture, and any seasonal movement between. In a word, chemical “fingerprinting” of individual fish and/or species. In practice, there are a large number of factors that influence the incorporation of major (1 wt. % or more), minor (>100 ppm) and trace (<100 ppm) elements in otoliths, so the relationship between water chemistry and otolith chemical composition is not a direct one. [Disspain et al. \(2015\)](#) have recently published a valuable overview related to this topic; we refer readers to their article for additional coverage of this topic and some interesting site-specific examples.

Otoliths are structures within the inner ear of vertebrates that function to help maintain balance (motion and orientation to gravity). In bony fishes, otoliths “float” behind the brain, at the back of the fish's cranium. They are surrounded by a fluid called the endolymph. Elements are incorporated into otoliths as they crystallize. There are three kinds of otolith: the sagitta, the lapillus, and the asteriscus. Sagittae are preferentially used for time-dependent environmental tracking and paleoclimatic work due to larger size and formation at an early life stage (e.g., [Hoff et al., 1997](#)). All otoliths are calcium carbonate; asteriscii are vateritic, while the other two kinds are aragonitic. An important constituent is protein, which comprises from 1 to 8% of otoliths depending on species, with around 3–4% being a common amount ([Campana, 1999:265](#)). Water-insoluble proteins (a.k.a. “otolin” – [Degens et al., 1969](#)) make up about half the protein present and provide the “structural framework” for calcification, while calcification rate is partly regulated by the remaining, water-soluble proteins ([Campana, 1999:265](#)) and by temperature. The full effects of temperature on otolith formation are incompletely understood, but elements known to be affected include Mg, U, Na, K, Mn, Zn and Fe ([Campana, 1999](#)). While some authors have seemingly detected a correlation between temperature and Sr incorporation in otoliths (e.g., [Bath et al., 2000](#)), [Campana \(1999:273\)](#) reviewed a large number of case studies and found no consistent relationship in this regard, except in very cold (<10 °C) water. Sr concentrations are, however, affected by salinity ([Campana, 1999:267, 274](#); see also [Kalish, 1989](#)).

Elemental impurities in the otolith matrix can occur “within the crystal lattice as a [ionic] substitute for calcium, as an inclusion in the interstitial spaces, or in association with the proteinaceous matrix” ([Campana, 1999:266](#)). Precipitation of other carbonates, such as SrCO₃, is a less likely source of elemental inclusion than is ion substitution, which favors Sr, Mg, and Ba ions that have the same charge as Ca (2+) and ionic radii deviating from Ca by less than 25% ([Campana, 1999:266](#); [Ramsay et al., 2011:831](#); [Gaetani and Cohen, 2006: 4617](#)) and that are consequently bound into the crystal lattice. Among these elements, Sr has the most similar radius to Ca, while Mg and Ba are smaller and larger, respectively. On the other hand, elemental inclusions in interstitial spaces such as the “micro-channels” typical of otolith architecture are relatively poorly bound, so that elements such as Na, Cl, Zn and K are easily leached out ([Campana, 1999:266](#)).

A major consideration in understanding the relative availability of elements for inclusion in otoliths is bioregulation ([Bath et al., 2000:1705](#); [Campana et al., 1994:1949](#); [Kalish, 1991](#)). Fish take up elements via the gills; these are then passed into the blood plasma, from there into the endolymph, and from there into the crystallizing otolith ([Campana, 1999:266–267](#)). There are various

complicating factors in this process. For one, blood plasma chemistry can vary seasonally with temperature ([Kalish, 1991](#)), a factor that likely is species-specific. Another complicating factor is osmoregulation, the maintenance of water levels in an organism. In fish, osmoregulatory processes “level out” the concentrations of elements such as Ca, Na, K, Mg, Cl, P, Cu, and S, even between fresh and saltwater environments ([Campana, 1999:268–269](#)). Accordingly, “it is clearly unrealistic to expect the otolith content of physiologically regulated elements to reflect environmental abundance” ([Campana, 1999:269](#)). Elements found in otoliths that are relatively unregulated, and therefore expected to more closely reflect environmental loads, include Sr, Zn, Pb, Mn, Ba and Fe ([Elsdon and Gillanders, 2003](#); [Campana, 1999:269](#); [Hamilton and Warner, 2009](#); see also [Disspain et al., 2012](#)). [Campana \(1999:269–270\)](#) also mentions Li, Cd, Ni and the “less abundant” elements as possibly falling into this category, although he notes that, with the exception of Sr, element:calcium ratios in blood plasma will be higher than in the otolith, “indicating that the otolith composition is not merely a passive reflection of plasma composition, even if correlated.” Some elements are then barred or taken up selectively from the blood plasma into the endolymph, “resulting in an endolymph concentration which is depleted in all major ions other than K” ([Campana, 1999:267](#)). The otolith thus reflects the chemical composition of the endolymph more so than that of the aquatic environment.

Beyond uptake via the gills, some elemental contributions to otoliths come from drinking water (especially marine fish, which drink continually) and from food, although this contribution appears to be relatively low (e.g., ca. 10–20% of Ca and Sr for freshwater fishes – [Campana, 1999:267](#)). Obviously, this can vary by species, and may vary seasonally by sex; for example, [Mendoza-Carranza \(2003\)](#) found that during the rainy season, male gafftopsail catfish (*Bagre marinus*) in near-shore waters consumed significantly more prey fish than did females.

Sr is recognized as the best marker for source (e.g., [Ludsin et al., 2006](#); [Pontual et al., 2000](#)), especially for anadromous fish ([Campana, 1999](#); see also [Disspain et al., 2015](#)), because: 1) it is the least-regulated element; 2) there is a purported lack of a temperature effect on Sr uptake ([Campana, 1999](#)); and 3) differences in concentration between fresh and salt water (lower Sr:Ca in the former – [Hale and Swearer, 2008](#); [Pontual et al., 2000](#)) can be quite abrupt, ([Hamilton and Warner, 2009](#)), reflecting the 30–35% difference in salinity between the two environments. However, differences in Sr:Ca ratios between species, even those habitually occupying the same areas, may be expected, as will be an increase in Sr:Ca with the age of the fish ([Campana, 1999](#); [Hamilton and Warner, 2009](#)). This latter effect probably is related to the rate of protein synthesis ([Kalish, 1989](#)), which in turn affects the rate of crystallization of the otolith ([Campana, 1999:2740](#)), which generally slows with age ([Chang et al., 2012](#)). [Ramsay et al. \(2011\)](#) were able to correct for the effects of otolith size via regression analysis, with data showing linear relationships; however, [Thorrold et al. \(1998:258\)](#) found “lower levels of most elemental and isotopic variables with increasing otolith weight,” an age-related effect that was not systematic enough to allow for mathematical correction. Such differences between studies likely reflect species-level variability. Elemental differences also can be expected with major ontogenetic phase shifts, such as the period of larval metamorphosis into juvenile stage ([Hamilton and Warner, 2009:242](#); [Mugiya and Satoh, 1995](#); [Swearer, 2000](#)).

Environmental variability, while the very basis for how otoliths can be used in sourcing studies, is at the same time another area of concern. Major differences between marine and freshwater systems are primarily found in the common marine salts ([Campana, 1999:271](#)). However, Sr (or any other chemical) loads are not

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