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Effects of organic solvents on stable isotopic composition of otolith and abiogenic aragonite

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ABSTRACT

Otoliths are important proxies for climate change and ecological studies and are typically stored in glycerin or ethanol for preservation. This study is the first attempt to assess the isotopic effects of these preservatives on carbon and oxygen isotope ratios of otolith aragonite. Experimental tests from the 4th annulus of dried Pacific halibut otoliths were compared to samples from the same otoliths collected after 30 day storage in either glycerin or ethanol. In addition, isotopic measurements of abiogenic pure aragonite samples soaked in glycerin, ethanol, acetone, dichlorom (DCM), and methanol were compared to the initial values following the same protocol. No $\delta^{18}O$ effect was observed for otoliths stored in glycerin or ethanol; and no isotopic effects (both $\delta^{18}O$ and $\delta^{13}C$) were observed for abiogenic pure aragonite stored in the five organic solvents commonly used in geochemical laboratories. Although there was a significant but very small difference in carbon isotope ratios of halibut otoliths, the shift was of a barely measureable magnitude and the statistically significant difference only in $\delta^{13}C$ values may result from the inhomogeneous composition and structure of otoliths. Thus we concluded that there was no isotopic exchange during organic solvent storage or preservative interference in the isotope ratio measurements.

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1. Introduction

In teleost fishes, otoliths (the solid phase) are formed and suspended with endolymph (the liquid phase) in the auditory canals and function as hearing, balance, and postural control (Carlstrom, 1963; Degens et al., 1969; von Baumgarten and Thumler, 1979). Because of this microenvironment in the natural setting, field-collected otolith samples are often stored in organic solvents for later age determination and/or chemical analyses. For age determination of using otoliths in fisheries science and management (e.g., Chilton and Beamish, 1982; Beamish and McFarlane, 1987; Matta and Kimura, 2012) the effect of organic solvents is not a problem because the process does not change the physical structure of the otoliths. However, when doing stable carbon and oxygen isotope ratio analyses in otoliths (e.g., Devereux, 1967; Mulcahy et al., 1979; Kalish, 1991; Patterson et al., 1993; Gao et al., 2010), concerns may arise over the use of fluid-preserved specimens for reconstructing the past temperature and environment based on the isotopic composition.

A good example of the need for testing the effects of preservatives on otolith isotope chemistry is the historical collections of Pacific halibut *Hippoglossus stenolepis* since the early 1950s. The fishery is managed by the International Pacific Halibut Commission (IPHC) and otolith sampling is a routine task through the harvest seasons. Every year IPHC collects tens of thousands of halibut otoliths for age determination and stock assessment, and uses a glycerin solution (50:50 with water) for storage (IPHC, 1987). Simultaneously, some sampling programs use ethanol (92% rubbing alcohol or higher concentration) to preserve otoliths. Because the halibut otoliths are exceptionally large and the long time series of halibut catch, age, and growth data provides a unique opportunity to evaluate the biological response of Pacific halibut to ocean environmental changes (Gao and Beamish, 2003a,b), it is essential to understand the effects, if any, of storage media on the carbon and/or oxygen isotopic composition of halibut otoliths.

Investigations of the effects of organic solvent treatments have focused on: (1) consolidants and cleaning techniques on bone collagen and hydroxylapatite for archaeological and fossil vertebrate remains (e.g., Moore et al., 1989; Cormie and Schwarcz, 1994; Koch et al., 1997; McNulty et al., 2002; France et al., 2011); (2) formalin fixation and ethanol for blood and tissues of biological samples (Hobson et al., 1997; Bosley and Wainwright, 1999; Edwards et al., 2002; Olin et al., 2014); and (3) chemical treatments for foraminifera shells and aragonite crystals on trace elements and stable isotopes (Ganssen, 1981; Love and Woronow, 1991; Pingitore et al., 1993). For example, Edwards et al. (2002) confirmed that formalin clearly decreases the $\delta^{13}C$ values in preserved fish tissues by either exchanging light isotopes

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for heavy ones or simply adding light carbon isotopes from formalin; however, the magnitude of isotopic variations are quite small compared to dietary shifts that are of interest in ecological studies (about 1‰ in $\delta^{13}C$ and 3-4‰ in $\delta^{15}N$ with each trophic level; cf. DeNiro and Epstein, 1978, 1981; Schoeninger and DeNiro, 1984). Ganssen (1981) reported isotopic analyses of foraminifera shells soaked in solutions of formalin, ethanol, and other solvents. His results showed that for the ethanol treatment no effect is observed in $\delta^{18}O$ values, but a small change (+0.25‰ to +0.39‰) occurs in $\delta^{13}C$ composition. All these investigations indicate that treatment with organic solvents may change the isotopic composition of different specimens.

There are no studies on the isotopic effects of ethanol or glycerin preservation of otoliths to the authors' knowledge. This may be partly because otoliths are well preserved in a fish's skull and have few pores in their crystal structures, so no diagenetic alteration has been found in otolith aragonite (Brand and Veizer, 1981). The analysis of stable isotopes in otoliths, on the other hand, reacts powdered aragonite samples with phosphoric acid to produce CO_2 gas (cf. Epstein et al., 1953). If there is no reaction of organic solvent residues in otoliths with the phosphoric acid to produce CO_2 gas, the contamination question should not be a concern. Nevertheless, little is known about the isotope exchange during the process of otolith storage or interferences during the CO_2 extraction and isotope ratio measurement. A simple comparison between "untreated" and "treated" specimens under the same experimental conditions seems an effective approach for testing these potential effects.

In this study, we report the results of stable carbon and oxygen isotope analyses in Pacific halibut otoliths from the Washington west coast, USA, and a naturally occurring abiogenic "pure" crystalline aragonite from Castile-La Mancha, Spain. The primary goal of the project was to determine if the glycerin and ethanol solvents change the isotopic composition of preserved otoliths by comparing the freshly-dried otoliths (dried sample) to otoliths after organic solvent storage (stored sample). This objective was achieved by repeated microsampling of the same individual otolith and growth ring before and after storage. The second goal of the research was to extend the study to abiogenic pure aragonite soaked in glycerin, ethanol, and other organic solvents (i.e. acetone, dichloromethane (DCM), and methanol). Although the treatments do not embrace a complete list of organic solvents, they represent the most commonly used ones in geochemical laboratories. By statistically analyzing these two data sets (dried sample vs. stored sample) and using two slightly different experimental protocols (natural otolith and abiogenic aragonite), we examined the "usability" of historical Pacific halibut otolith collections and the data derived from isotopic analyses of preserved specimens.

2. Materials and methods

2.1. Otolith sampling and analysis

Sixty-two left-side sagittal otoliths of Pacific halibut were randomly collected from the commercial fisheries off the Washington west coast in 2013, and kept as dried samples. After field collection the otoliths were cleaned in an ultrasonic water bath for about 15 min, and then transferred to a tap-water filled transparent vessel for age determination (Chilton and Beamish, 1982). The surface-aged otolith samples were then rinsed with distilled water three times, and dried at room temperature before further sampling and preparation.

One aragonite powder sample was first taken from the 4th annulus of each freshly-dried otolith using the Dremel method (Gao, 1999). The 4th annulus was chosen because these growth rings are always clear, wide and stable in halibut otoliths. The microsampling was about 100 μm in resolution and at least 50 μg of aragonite powder samples were collected for stable isotope analysis. Once a sub-sample was completed, the otolith and the microsampling bit were cleaned using Aero-Duster gas.

After the 1st-round of microsampling, 31 halibut otoliths were each stored in glycerin and ethanol solutions at room temperature for 30 days. The 2nd-round of microsampling was then conducted with the same procedures. The methods for cleaning and preparing the stored otoliths have been reported elsewhere (Gao and Beamish, 2003a). Briefly, the otolith samples were placed in an aluminium mold and then embedded in a fibreglass resin for hardening. After sectioning and polishing, the otolith surface was thoroughly cleaned with ethanol. The 2nd-round aragonite powder sample was also taken from the 4th annulus of each otolith, very close to the position in the 1st-round of microsampling.

Isotopic analysis of otolith powder samples was performed in the Environmental Isotope Laboratory of University of Arizona in Tucson, USA, using an automated carbonate preparation device (Kiel-III) coupled to a Finnigan MAT 252 mass spectrometer. Powdered samples were reacted with dehydrated phosphoric acid (density >1.92 g/ml) under vacuum at 70 °C. All the isotope ratio measurements are reported in the standard δ notation (‰): $\delta^{18}O = \{[(^{18}O/^{16}O)_A/(^{18}O/^{16}O)_S] - 1\} \times 1000$, for instance, where *A* is otolith aragonite sample and *S* is an international standard (VPDB, Vienna Peedee belemnite). Calibration of isotopic ratios to the VPDB scale is based on daily analysis of NBS-19 (National Bureau of Standards) carbonate and scale compression is corrected by analysis of NBS-18. The analytical precision is better than 0.10‰ for both $\delta^{13}C$ and $\delta^{18}O$ values (1 standard deviation).

2.2. Abiogenic pure aragonite analysis

A sample of a naturally occurring, abiogenic "pure" crystalline aragonite from Castile-La Mancha, Spain, was crushed, passed through a 53 micron sieve and mixed to produce a homogenised powder. The sieved material was analysed by XRD to check mineralogy and purity (Crowley, unpublished data). Six splits were removed from the stock: one split was retained (untreated) as a reference, the other 5 splits were used to prepare 1% w/v mixtures of aragonite and an organic liquid. The organic liquids were analytical grade: glycerin, ethanol, acetone, dichloromethane (DCM), and methanol. The mixtures were sealed in glass vials and left for 30 days at ambient laboratory temperature (about 23 °C). Following treatments the aragonite was recovered by centrifugation and the excess organic liquid was removed with a pipette. For ethanol, acetone, DCM, and methanol any remaining liquid was allowed to evaporate overnight in a fume hood. Excess glycerin was removed by repeated cycles of dilution in distilled water and centrifugation before freeze-drying the cleaned powder.

Isotopic measurement was undertaken following reaction of aragonite with phosphoric acid (specific gravity 1.91-1.92) at 25 °C for about 16 hours using a procedure similar in all aspects to the "sealed vessel" method described by McCrea (1950) and Swart et al. (1991). Isotope ratios of the recovered CO_2 were measured using a VG SIRA10 dual-inlet stable isotope ratio mass spectrometer in the Stable Isotope Laboratory of University of Liverpool, UK. All data are reported relative to VPDB. Replicates of each sample were prepared in 15 batches and the analytical precision is better than 0.10‰ for $\delta^{13}C$ and $\delta^{18}O$ values. Each batch consisted of duplicates aliquots of the untreated (reference)

Table 1
Summary statistics for the isotopic measurements of samples from dried halibut otoliths compared to samples from the same otoliths collected after storage in either ethanol or glycerin for 30 days (sample size: 31 for ethanol and 30 for glycerin).

Isotope	Storage treatment	Mean (‰, VPDB)	Standard deviation	Coef. of variation	Range	
					minimum	max.
$\delta^{13}C$	Dry	-1.896	0.456	24.1%	-2.85	-1.10
	Ethanol	-1.790	0.458	25.6%	-2.67	-1.02
$\delta^{18}O$	Dry	1.402	0.694	49.5%	-0.37	2.66
	Ethanol	1.419	0.727	51.2%	-0.57	3.00
$\delta^{13}C$	Dry	-1.912	0.304	15.9%	-2.44	-1.33
	Glycerin	-1.822	0.299	16.4%	-2.39	-1.22
$\delta^{18}O$	Dry	1.351	0.580	42.9%	0.38	2.56
	Glycerin	1.329	0.610	45.8%	0.27	2.43

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