



Effects of extraction protocols on the oxygen isotope composition of conodont elements



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ABSTRACT

Oxygen isotopic measurements of conodont elements can provide important paleoclimatic, paleoecological, and paleoenvironmental information. However, preparation techniques are often cited as a potential, albeit poorly constrained, source of error. Prior to isotopic measurements, conodont elements are typically liberated from a calcium carbonate matrix using dilute solutions of acetic or formic acid. These extraction techniques are well established for paleontological studies, but the protocols were established before conodonts became a common target for isotopic analyses. Whereas concerns are often raised about the possibility of bias introduced through phosphate leaching, especially with stronger acid, empirical observations regarding error in isotopic measurements introduced due to the preparation techniques used are limited and generally anecdotal.

This study was designed to constrain the effects different types of acids used for carbonate digestion have on the measured oxygen isotopic compositions of bioapatite (specifically, conodont elements and brachiopod shells). We performed parallel analyses on splits from seven Late Ordovician samples that were processed with both buffered and unbuffered solutions of acetic and formic acid. In addition, to further assess the potential for $\delta^{18}\text{O}$ alteration related to partial apatite dissolution, we forced partial dissolution of isolated conodont elements by placing them in an unbuffered formic solution for varying intervals of time prior to analysis. Measured $\delta^{18}\text{O}$ values from conodont elements and brachiopod shell fragments show no statistically significant differences related to processing technique, but isolated conodont elements with visible evidence of partial dissolution due to prolonged exposure to unbuffered formic acid record consistently offset $\delta^{18}\text{O}$ values. Such partially dissolved elements should be avoided in geochemical studies. If specimens exhibiting apparent etching are avoided, though, we conclude that standard digestion protocols for conodont element extraction from carbonates do not introduce a bias (either a systematic offset or an increase in variance) on measured $\delta^{18}\text{O}$ values from phosphate-bound oxygen in bioapatite above the limits of the resolution of this study.

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1. Introduction

Conodont elements (Figs. 1 and 2) are teeth-like structures from the feeding apparatus of the conodont animal, an extinct group of marine organisms. Typically only isolated or, more rarely, assemblages of conodont elements are preserved in the rock record because the elements are the only mineralized tissue of the conodont animal. Due to the high preservation potential of the highly crystalline bioapatite [$\text{Ca}_5\text{Na}_{0.14}(\text{PO}_4)_{3.01}(\text{CO}_3)_{0.16}\text{F}_{0.73}(\text{H}_2\text{O})_{0.85}$] (Pietzner et al., 1968) of

which these elements are composed, conodonts have an extensive fossil record that spans the Cambrian through the Triassic. This record combined with their well-resolved taxonomy has led to conodonts being used extensively for biostratigraphic purposes. They are also increasingly being used in paleoclimatic studies. The $\delta^{18}\text{O}$ values of conodont bioapatite are more resistant to diagenetic alteration than $\delta^{18}\text{O}$ values in carbonate (e.g., Kolodny and Luz, 1991; Wenzel et al., 2000; MacLeod, 2012), and improvements in analytical techniques have allowed this characteristic to be exploited for paleotemperature estimates (e.g. Joachimski et al., 2009; Sun et al., 2012; Trotter et al., 2015).

Although conodont elements are commonly found in Paleozoic marine deposits, their abundance in most samples is low (typically 100's of elements or less per kg of total rock). Standard procedures for isolating and concentrating these elements from carbonate lithologies typically involve dissolution of much of the host carbonate using either dilute

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Fig. 1. Isolated mixed conodont elements whitened and etched by soaking in a 10% unbuffered formic solution for ~2 h. The elements are, clockwise from top, *Oulodus serratus* P, *Drepanoistodus suberectus* P, and an *Oulodus serratus* S element).

acetic or formic acid (e.g. Harris and Sweet, 1989; Jeppsson, 2005; MacLeod, 2012). Acetic and formic acid solutions buffered using calcium phosphate or sodium acetate were shown to result in relatively little dissolution of original phosphate (Jeppsson, 2005). However, solutions with a pH < 3.4 may result in significant surface pitting and etching of recovered elements (Fig. 1, Jeppsson, 2005). In fact, it is recommended to avoid the use of unbuffered acids, especially formic acid, as complete and/or partial dissolution of elements results in significantly lower conodont element yields (e.g. Jeppsson and Anehus, 1995; Jeppsson, 2005; Griffin et al., 2015).

Partial dissolution of bioapatite during extraction, possibly accompanied by isotope exchange and/or reprecipitation of secondary phosphate phases, has been suggested as a source of error that could shift the measured $\delta^{18}\text{O}$ value away from the initial value that best reflects paleoenvironmental conditions (Wheley et al., 2012). However, empirical observations and theoretical calculations addressing the influence various acid pretreatments and digestion protocols can have on phosphate $\delta^{18}\text{O}$ values are limited and yield divergent conclusions (e.g. Wheley et al., 2012; Trotter et al., 2015).

This study aims to constrain the potential magnitude and direction (if any) of biases due to different rock digestion protocols and to address this uncertainty empirically. We measured conodont $\delta^{18}\text{O}$ values from splits of the same samples processed using a variety of standard digestion solutions (i.e., both unbuffered and buffered solutions of both acetic



Fig. 2. *Polyplacognathus ramosus* platform elements isolated from a carbonate matrix using (clockwise from top left) buffered acetic, buffered formic, unbuffered formic, and unbuffered acetic.

and formic acid) to test for offsets in measured $\delta^{18}\text{O}$ values that correlate with different digestion protocols. We also measured $\delta^{18}\text{O}$ values of linguliform brachiopod shell fragments. Brachiopod bioapatite is more porous and is generally thought to be more susceptible to alteration than conodont elements (Wenzel et al., 2000). As such, results from brachiopod shells should provide an extreme case of potential $\delta^{18}\text{O}$ modification related to processing. Combined, our results provide important empirical constraints on potential artifacts introduced by the use of acetic and formic acid.

2. Previous studies

Concerns about biases introduced into geochemical studies by standard fossil processing techniques (e.g., acid pretreatments of fossil bone, chemical pretreatments for organic matter removal, acid digestion for microfossil liberation) are based on observations of alteration within different mineral phases and isotope systems (Koch et al., 1997; Grimes and Pellegrini, 2012; Hellawell and Nicholas, 2012; Wheley et al., 2012). Koch et al. (1997) found that common pretreatment techniques (e.g., NaOCl, H₂O₂, and acetic acid) used to remove secondary mineral phases and/or organic matter from bone and dentin may result in significant variability in carbonate oxygen and carbon isotopic measurements. Similarly, Grimes and Pellegrini (2012) documented increased oxygen isotopic variability from the phosphate-bound oxygen in bone and dentine related to pretreatment techniques used to remove trace organic matter. Hellawell and Nicholas (2012) suggested that systematic variation observed in the stable carbon and nitrogen isotopic composition of trace organic matter in fish bone when using acetic acid was the result of the preferential release of the heavier isotope into the acetic solution. The increased variability and progressive modification of stable isotopic ratios observed in these studies has led to the suggestion that even the use of weak acids can significantly alter stable isotopic compositions (e.g. Koch et al., 1997; Grimes and Pellegrini, 2012; Hellawell and Nicholas, 2012). Of these studies, only one (Grimes and Pellegrini, 2012) measured phosphate-bound oxygen isotopes. However, the very different crystallinity and structure of the material they studied complicate the extrapolation of their conclusions to oxygen isotopic studies of conodont elements. Still, the conclusions of these studies motivate concerns about processing biases in conodont oxygen isotope studies.

Conodont elements are highly crystalline (low permeability), and the strong P–O bond analyzed in oxygen isotopic studies is relatively resistant to alteration (e.g., Wenzel et al., 2000, Joachimski et al., 2009). Bone and to a lesser extent dentine, in contrast, have relatively low crystallinity and a relatively high susceptibility to recrystallization and alteration (Kohn and Cerling, 2002). For this reason, the isotopic composition of phosphate-bound oxygen measured in conodont apatite may not be as susceptible to error introduced through acid pretreatments as are oxygen isotopic values of bone.

The study that most closely accomplished the goal of relating processing techniques to sources of bias in oxygen isotopic studies of conodont elements is Wheley et al. (2012). Using secondary ion mass spectrometry (SIMS), Wheley et al. (2012) measured $\delta^{18}\text{O}$ values of individual conodont elements that had been processed using formic acid and acetic acid. They showed increased variability of oxygen isotopes in conodont elements that had been processed with formic acid. That observation led Wheley et al. (2012) to suggest that use of formic acid could result in significant oxygen isotopic alteration and recommended samples processed using formic acid should be avoided in geochemical studies. However, these results may be specific to SIMS measurements. While the high temperature reduction IRMS (isotope ratio mass spectrometry) techniques that are routinely employed in conodont oxygen isotope studies only analyze the chemically separated phosphate-bound oxygen, *in situ* SIMS measurement represent a weighted $\delta^{18}\text{O}$ average of all the oxygen bearing phases (PO₄³⁻, CO₃²⁻, and H₂O). Therefore, the variability in measured $\delta^{18}\text{O}$ values using SIMS might be the result of 1) differences in fractionation and diagenetic

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