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# Conodont (U-Th)/He thermochronology: A case study from the Illinois Basin



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#### ABSTRACT

Acquisition of thermochronologic data in carbonates and shales has traditionally been elusive owing to the paucity of dateable minerals in these lithologies. Conodont apatite (U-Th)/He (CAHe) thermochronology has the potential to fill this need. We acquired 50 (U-Th)/He dates for conodonts with CAI values  $\leq$ 1.5 from seven Pennsylvanian shale and limestone samples from two drillcores in the Illinois Basin. We also obtained X-Ray microcomputed tomography (MicroCT) results for 8 conodonts to evaluate the accuracy of alpha-ejection corrections. The simplified geometric corrections yield corrected dates within 5% of those derived from 3D characterization using MicroCT. Nearly all of the conodont CAHe dates are substantially younger than their depositional age, indicating that maximum post-depositional temperatures of  $\leq$  90 °C caused He loss over geologic timescales. The youngest and most reproducible dates consist of whole platform elements from shales, and may record a regional Late Cretaceous–early Tertiary cooling and erosion event. The remainder of the data exhibit strong negative date-U and date-Th correlations, characterized by higher and more variable Th/U than the conodonts with reproducible dates. These patterns are best explained by U loss, with more limited Th loss. The results suggest that whole platform elements and higher U-Th conodont materials are the most promising targets for CAHe analysis.

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#### 1. Introduction

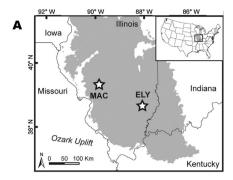
Apatite (U-Th)/He (AHe) thermochronology is one of the major tools used to resolve the thermal history of rocks in the upper kilometers of the Earth's crust. The technique is based on the radioactive decay of trace U and Th to He in apatite crystals. It is sensitive to temperatures from  $\sim$ 30-90  $^{\circ}$ C, and can provide detailed temporal constraints on geologic processes such as burial, unroofing, and topographic development (e.g., Reiners and Ehlers, 2005, review volume). It also is used to predict hydrocarbon maturation in basins through the reconstruction of time-temperature paths (e.g., Ketcham, 2012). However, AHe thermochronology is limited to rocks in which high-quality apatites occur. While apatites are common in granitoid, some metamorphic, and coarse clastic sedimentary rocks, carbonates and shales contain neither apatites nor any other established thermochronometer. Thus, the thermal evolution of vast areas dominated by these lithologies, including cratonic settings, basinal sedimentary sequences, and some areas of high-relief mountain belts, commonly cannot be constrained using thermochronologic methods.

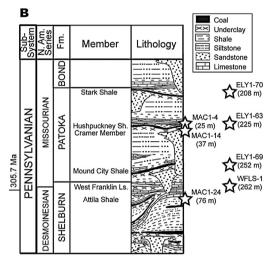
Here we address this problem by exploring the potential of conodonts as low-temperature thermochronometers. Conodonts are bioapatite microfossils that are common in Paleozoic through early Mesozoic marine sedimentary rocks. They are well-known to the petroleum industry through use of their color alteration index (CAI) as a semi-quantitative indicator of peak temperature (e.g., Epstein et al., 1977). The only published (U–Th)/He study of conodonts showed intriguing promise (Peppe and Reiners, 2007). That work acquired conodont <sup>4</sup>He diffusion data, reported conodont (U–Th)/He data from seven different localities, and suggested that conodont apatite retains He across the same temperature range as abiotic apatite (Peppe and Reiners, 2007).

In this study we present (U-Th)/He dates for a suite of conodonts extracted from Pennsylvanian marine black shale, calcareous shale, and limestone samples collected from two Illinois Basin drillcores (Fig. 1). The maximum temperatures of these samples were ≤90 °C based on the CAI values of the studied conodonts (Rosenau et al., 2014). The close spacing of the samples within each drillcore allows us to evaluate the reproducibility of data for samples that experienced the same thermal history. We additionally acquired MicroCT data for 8 conodonts to evaluate the accu-

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**Fig. 1.** A) Map of the study area adapted from Rosenau et al. (2013). The extent of Pennsylvanian units in the Illinois Basin is shaded in gray. Stars mark the MAC and ELY core locations. B) Sample locations on a generalized stratigraphic column for the Illinois Basin, adapted from Rosenau et al. (2013).

racy of simplified geometric alpha-ejection corrections. We use the results to consider the temperature sensitivity of the conodont AHe (CAHe) system and the significance of the CAHe data patterns for conodont open-system behavior. Our work displays both the potential of this tool and the outstanding questions that remain in its development.

#### 2. Conodont apatite

Conodont elements are tooth-like biomineralized structures that are parts of the feeding apparatus of a class of nektobenthonic or pelagic soft-bodied chordates that existed from Cambrian through Triassic time (Sweet and Donoghue, 2001). Their diversity and ubiquity have made conodonts a key biostratigraphic indicator. As conodonts are subjected to temperatures from ~50 to 600 °C, they irreversibly change color from pale yellow to amber, light brown, dark brown, black, white and clear (Epstein et al., 1977; Rejebian et al., 1987). The conodont color alteration index (CAI) was established by Epstein et al. (1977) as a measure of organic metamorphism based on this color progression. The CAI is well-documented as a peak temperature indicator, although there is significant overlap in the temperature ranges of adjacent CAI values and the CAI imposes no timing constraints on thermal histories.

Conodont elements vary in size from <0.05 to 3 mm and are characterized by ornate morphologies corresponding to taxa and function (Sweet and Donoghue, 2001). The element geometries correspond to their position in a complex feeding apparatus that varies by order and genus. Platforms, cones, blades and bars are common conodont morphologic terms used in the lit-

erature (e.g., Rejebian et al., 1987; Murray and Chronic, 1965), which we also employ in this study. Conodont chemical composition ranges from hydroxyapatite to carbonate fluorapatite and is generally given as  $(Ca_5Na_{0.14}(PO_4)_{3.01}(CO_3)_{0.16}F_{0.73}(H_2O)_{0.85})$ . Three different types of mineralized conodont tissues vary in crystallinity, permeability, and U-Th content (e.g., Trotter and Eggins, 2006; Trotter et al., 2007). Minor and trace element analyses demonstrate that dense, low-permeability albid tissue is formed by single apatite crystals up to 250 µm in size, with U and Th concentrations generally <1 ppm. Albid tissue grades into microcrystalline hyaline tissue, which is typified by higher permeability, <10 ppm U, and <100 ppm Th. The majority of preserved conodonts are crown structures, which are composed of a mix of albid and hyaline tissue. Nanocrystalline basal tissue is rarely preserved within crown structure cavities but can contain up to 100 pm U and 1000 ppm Th where present. Trace elements are incorporated during early diagenesis and may be subjected to protracted alteration after that time (e.g., Trotter and Eggins, 2006).

Attempts to date conodonts radiometrically using U-Pb and fission track have been variably successful, depending on U concentration and possible diagenetic alteration histories (e.g., Sachs et al., 1980; Ueki and Sano, 2001; Jolivet et al., 2008). Perhaps the most promising of these previous conodont dating studies was that of Peppe and Reiners (2007), in which a suite of conodonts from seven samples, all from different locations, were dated using CAHe. Conodonts from four samples displayed reproducible CAHe dates consistent with local cooling histories. Of the remaining three samples, two displayed significant dispersion while one yielded only geologically unreasonable dates. The four samples with reproducible dates were characterized by CAI values from 1-5, suggesting that CAI does not have a major effect on conodont He systematics. Instead, the authors suggested that open-system behavior of U and/or Th in different tissue types was the probable cause of the observed dispersion. Two conodont <sup>4</sup>He diffusion experiments suggested that conodonts are characterized by <sup>4</sup>He diffusivities similar to that of the well-studied Durango igneous apatite standard, thus implying that the CAHe system has a similar temperature sensitivity range to abiotic apatite (Peppe and Reiners, 2007). Their results also suggested that the conodont itself was the diffusion domain, with a correlation between conodont size and closure temperature estimated from the diffusion experiment. No further work has been published on the CAHe system.

### 3. Geologic setting and samples

The intracratonic Illinois Basin of the North American midcontinent contains up to 7 km of Cambrian through Permian strata (Burgess, 2008) (Fig. 1). It is bounded by the Ozark Uplift to the southwest and the Cincinnati and Kankakee Arches to the southeast and northeast, respectively. Pennsylvanian strata in the basin represent mixed terrestrial and shallow marine deposition (Burgess, 2008). In the north-central basin, conodont CAI values of  $\leq$ 1.5 indicate maximum temperatures of  $\leq$ 90 °C for the Pennsylvanian section, consistent with temperature estimates based on coal rank measurements (e.g., Damberger, 1991), smectite to illite transformations (e.g., Grathoff et al., 2001), and sphalerite fluid inclusion study (Cobb, 1981). In the southern basin, maximum temperatures estimates are up to ~175 °C (e.g., Harris, 1979; Damberger, 1991; Grathoff et al., 2001). Estimates of post-Pennsylvanian burial in the Illinois Basin based on the above constraints vary from  $\sim$ 1500 m in the north-central basin to  $\sim$ 3 km in the southern basin, with an interval of magmatism and fluid flow in the southern basin invoked to explain the higher temperatures estimated there (Harris, 1979; Grathoff et al., 2001; Rowan et al., 2002). Two unconformities broadly suggest times when the additional overburden was eroded. First, at the south-

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