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The climate of the Late Cretaceous: New insights from the application of the carbonate clumped isotope thermometer to Western Interior Seaway macrofossil

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ABSTRACT

We apply the carbonate clumped isotope thermometer (Δ_{47}) to macrofossils from the *Baculites compressus* (~73.5 Ma) and the *Hoploscaphites nebrascensis* (~67 Ma) ammonite zones of the Western Interior Seaway (WIS) of North America, and nearby coeval terrestrial and open marine environments. The carbonate clumped isotope thermometer is based on a single-phase isotope exchange equilibrium that promotes the 'clumping' of two heavy isotopes together within a single carbonate molecule as temperature decreases. Due to the thermometer's isotopic independence from water, coupled measurements of Δ_{47} and the bulk oxygen isotopic composition of a carbonate ($\delta^{18}O_c$) enable the reconstruction of both paleotemperature and the isotopic composition of the water in which the organisms grew. Before applying the technique to the aragonite shells of fossil marine organisms (mostly ammonites, but also some gastropods, bivalves, and one belemnite), we measure the clumped isotopic composition of modern nautilus and cuttlefish, two of the nearest living relatives to the Cretaceous ammonites. Modern cephalopods exhibit disequilibrium isotope effects with respect to Δ_{47}, but not $\delta^{18}O_c$, therefore a simple correctional scheme is applied to the Late Cretaceous macrofossil data before reconstructing paleotemperatures. Diagenesis is also assessed by visual preservation and previously measured Sr concentrations (Cochran et al., 2003). Temperatures reconstructed for the Late Cretaceous Western Interior Seaway range from 16.4 ± 3.5 °C for an offshore Interior Seaway environment from the *H. nebrascensis* zone to 24.2 ± 0.4 °C for the *B. compressus* ammonite zone. The seaway itself has an isotopic composition of approximately −1‰ (relative to VSMOW), the expectation for an ice-free global ocean average, while a nearby freshwater environment has an isotopic composition approaching −20‰. We compare the attributes of the reconstructed climate to predictions based on Late Cretaceous climate models and previous reconstructions of the seaway, and also assess the sensitivity of our results to the modern cephalopods correction by comparisons to suitable modern analogs. Finally, our clumped isotope data are consistent with cooling between the Late Campanian and Maastrichtian, as also seen in benthic foraminfera $\delta^{18}O$.

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1. Introduction

Geochemical proxies (e.g., Barrera and Savin, 1999; Barron, 1983; Douglas and Savin, 1975; Huber et al., 2002), the geographic extent of climatically sensitive terrestrial and marine flora and fauna (Habicht, 1979; Markwick, 1998) and studies of leaf physiognomy (Davies-Vollum, 1997; Herman and Spicer, 1997) suggest the Cretaceous was a 'greenhouse' world marked by higher temperatures, a reduced equator-to-pole temperature gradient (Barron, 1983; Hay, 2008; Sloan and Barron, 1990) and elevated CO_2 concentrations (Arthur et al., 1985; Barron, 1985; Berner et al., 1983; Royer et al., 2001). A significant feature of the warmer world was the presence of large epicontinental seaways (Barron, 1983; Hancock and Kauffman, 1979), such as the Western Interior Seaway (WIS) of North America. At its greatest extent the WIS connected the boreal Arctic ocean with the Gulf of Mexico and covered the foreland basin of the western Cordillera (Miall et al., 2008) with seaway depths of about 200 m, with a possible maximum of 300 m (Hancock and Kauffman, 1979; McDonough and Cross, 1991). This sea level high coincided with the peak in Cretaceous greenhouse temperatures between about

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100 to 85 Ma (Huber et al., 1995, 2002), after which global cooling proceeded until the end of the Cretaceous (Barrera and Savin, 1999; Clarke and Jenkyns, 1999; Huber et al., 1995, 2002). By the Late Campanian and Maastrichtian (from approximately 75–65 Ma), the WIS had receded significantly, was situated between 40° and 50°N, and had a maximum depth of about 100 m (Kauffman, 1984; Kennedy et al., 1998; Miall et al., 2008).

Reconstructing temperatures and paleoceanography, e.g., the circulation and connectivity to the open-ocean, of semi-enclosed epicontinental seaways can be challenging using traditional oxygen isotope paleothermometry. A primary reason for this is that the hydrological conditions of a seaway, e.g., local salinity and the oxygen isotopic composition of the water ($\delta^{18}O_w$), are difficult to constrain given their dependence on the balance of evaporation to precipitation and sources of freshwater. Assuming there is no long term change in the budget of oxygen isotopes in the hydrosphere, and for an ice-free world such as the Late Cretaceous, the global ocean average isotopic composition of seawater is expected to be about -1‰ on the VSMOW scale (Cramer et al., 2011; L'Homme, Clarke, 2005; Shackleton and Kennett, 1975), or -1.27‰ relative to the VPDB scale (Bemis et al., 1998; Hut, 1987; Shackleton and Kennett, 1975). Using this ice-free value, open-ocean paleotemperature reconstructions are possible given assumptions for meridional gradients in surface water $\delta^{18}O_w$ (e.g., Poulsen et al., 1999; Zachos et al., 1994). In contrast, the complex, and often unknown, hydrography and circulation of semi-enclosed basins make differentiating between changes in temperature and changes in $\delta^{18}O_w$ more difficult. This is especially important when sea level fluctuations are globally synchronous and forced by changes in ice volume, which will alter the isotopic composition of seawater temporally.

The carbonate clumped isotope thermometer is a valuable tool for reconstructing temperatures in such settings due to its independence from the isotopic composition of the water from which a carbonate precipitates. The thermometer is based on a single-phase, thermodynamically controlled, mass dependent isotope exchange reaction that orders ^{13}C and ^{18}O atoms into bonds with each other within a carbonate mineral lattice. As the formation temperature of the carbonate mineral decreases, the 'clumping' of these heavy isotopes into a single carbonate ion is promoted (Guo et al., 2009; Schauble et al., 2006; Wang et al., 2004). It is quantified using the parameter Δ_{47}, which measures the deviation in mass 47 CO_2 (mostly comprised of $^{13}C^{18}O^{16}O$, a 'clumped' isotopologue) from that expected given the sample's abundance of O and C isotopes, and it has an inverse relationship with temperature (Eiler, 2007; Eiler and Schauble, 2004; Wang et al., 2004). In the case of carbonate thermometry, the CO_2 is derived from acid digestion of a carbonate mineral, and Δ_{47} should reflect the temperature at which isotope exchange last occurred, likely in the carbonate or bicarbonate phase and at the water temperature at the time of mineral formation. Empirical calibrations using synthetic carbonates grown at controlled temperatures and modern natural carbonates have been shown to conform to the thermodynamic principle expected for clumped isotopologues of carbonate (Eiler, 2007, 2011; Ghosh et al., 2006, and the references therein), although some discrepancies between calibrations remain (Dennis et al., 2011; Dennis and Schrag, 2010), and some natural carbonates do not conform to synthetic carbonate calibrations (Affek et al., 2008; Daëron et al., 2011) suggesting disequilibrium isotope effects may be important for some carbonates.

Although the WIS has been studied in the past (e.g., Coulson et al., 2011; Slingerland et al., 1996), details about the paleotemperature and paleosalinity are difficult to infer using only oxygen and carbon isotopes in carbonates. For example, although assuming $\delta^{18}O_w = -1$‰ leads to reasonable temperature estimates for most cephalopods, other organisms, particularly inoceramid bivalves record temperatures in excess of 35 °C (Tourtelot and Rye, 1969). Explanations of these data have focused on either 'vital' effects[1] (Rye and Sommer, 1980; Tourtelot and Rye, 1969), or temperature and salinity stratification coupled to regional variability in the oxygen isotopic composition of the seaway (He et al., 2005; Wright, 1987). Unfortunately, these hypotheses cannot be tested without additional insight into the oxygen isotopic composition of the Seaway.

Another study by Cochran et al. (2003), examined the mixing of freshwater and seawater in the Maastrichtian WIS by measuring Sr isotopes in a variety of paleoenvironments. They found that the variation in $^{87}Sr/^{86}Sr$ between the open ocean and a brackish environment could not be explained by simple mixing between the freshwater and seawater end-members. Instead they hypothesized that submarine groundwater discharge could balance the Sr isotope budget, adding a further complexity to the hydrography of the Seaway. The successful application of clumped isotopes to the WIS would enhance our understanding of the temperature and $\delta^{18}O_w$ of the WIS, thereby improving our knowledge of (i) spatial variability in water properties, (ii) water column stratification, and (iii) the circulation of the Seaway.

By applying carbonate clumped isotope thermometry to a suite of macrofossils (also studied by Cochran et al., 2003), we seek to improve our understanding of paleosalinity and paleotemperature gradients in the Late Cretaceous WIS. Before doing so, we measure several modern shelled cephalopods, relatives of the Cretaceous ammonites, from known growth environments to assess if their $CaCO_3$ shells align with previous calibrations of the clumped isotope thermometer. Given evidence for disequilibrium precipitation, a correction is applied to the Late Cretaceous macrofossils before reconstructing temperatures and the isotopic composition of the shallow seaway. The climatic significance of our results is assessed by comparing them to (i) predictions based on Late Cretaceous climate models, (ii) previous reconstructions of the seaway and coeval terrestrial and open marine environments, and (iii) suitable analogs in the modern world. In addition, we compare our reconstructions from the Maastrichtian to the Late Campanian.

2. Materials and methods

2.1. Modern cephalopods

Modern cephalopods that grew at known temperatures were used to assess if their carbonate shells precipitated with the same dependence between temperature and Δ_{47} as synthetic carbonates (Table 1). Samples were loaned from the American Museum of Natural History (AMNH Loan number 512), the University of Tokyo via the AMNH (Loan number 509), and the Alfred Wegener Institute (AWI).

We selected to study modern nautilus because of their morphological similarities to Cretaceous ammonites, with both precipitating external, chambered shells. In addition, the chambered shell, which is comprised of aragonite, precipitates in oxygen isotopic equilibrium with water (Landman et al., 1994; Oba et al., 1992). Modern nautilus (*Nautilus pompilius, N. belauensis* and *N. macromphalus*) were either captured in the wild and moved to a temperature controlled aquarium (samples 1/8-6, 1/10-2, 1/10-3), raised in an aquarium (sample 89-39) or were wild for their entire lives (samples MN-1, AX and AR). The growth

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[1] A vital effect is a generic term that reflects isotopic disequilibrium precipitation by an organism, possibly due to photosynthetic and/or metabolic activity (Epstein et al., 1951; Erez, 1978; Urey et al., 1951).

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