Amino acid ratios in reworked marine bivalve shells constrain Greenland Ice Sheet history during the Holocene

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ABSTRACT

Reconstructions of ice sheet fluctuations during the Holocene, which encompassed cooler and warmer conditions than those that are captured in the historic record, help to elucidate ice margin sensitivity to climate change. We used amino acid geochronology to constrain the history of the western Greenland Ice Sheet margin during intervals of relative warmth in the middle Holocene. We measured the extent of amino acid racemization in 251 ice sheet-reworked marine bivalve shells from three locations spanning western Greenland. A significant relationship between shell age and the ratio of aspartic acid (Asp) isomers (Asp D/L) was revealed using Bayesian model fitting on 20 radiocarbon-dated shell fragments. The range of Asp-inferred bivalve ages at each site corresponds well with independent records of early Holocene ice retreat and late Holocene ice advance. Furthermore, the frequency of Asp-inferred bivalve ages from the three widely separated locations is nearly identical, with most ages between 5 and 3 ka, coinciding with optimum oceanic conditions. Because ice margin changes in western Greenland are tightly linked with oceanographic conditions, the distribution of reworked bivalve ages provides important information about relative ice margin position during smaller-than-present ice sheet configurations. This approach adds a new chronometer to our toolkit for constraining smaller-than-present ice sheet configurations and may have wide applicability around Greenland.

INTRODUCTION

Pronounced ongoing changes of the Greenland Ice Sheet have important ramifications for global climate and sea-level change (Alley et al., 2010). Predicting future Greenland Ice Sheet change is challenging, however, because the spatial and temporal patterns of recent and ongoing ice sheet response to Arctic warming are highly variable (e.g., Joughin et al., 2010). Reconstructions of past ice margin changes can constrain the spatial expression of Greenland Ice Sheet response to climate variability on longer time scales (Long, 2009). The Holocene is an important period over which to evaluate ice margin response to climate change because the temperature history is relatively well known and includes conditions that were warmer than the 20th century during the Holocene thermal maximum (e.g., Kaufman et al., 2004). The overall pattern of ice sheet retreat during early Holocene warming followed by ice sheet advance during late Holocene cooling is generally known from field and modeling results (e.g., Funder et al., 2011). However, reconstructing the timing of maximum ice sheet retreat during warm times in the Holocene is challenging because the geologic record of former ice margins is mostly obscured by subsequent ice advances during the late Holocene Neoglacial period (Kelly, 1980; Long et al., 2009).

Varieties of approaches have been used to reconstruct past glacier change, but few tools are available for reconstructing smaller-than-present ice extents. Sediments in adjacent marine and lake basins have been used successfully to reconstruct past ice margin changes, but ideal sites are sparse (e.g., Briner et al., 2010; Colville et al., 2011; Larsen et al., 2011). Numerical models driven by paleoclimate reconstructions offer insight into interglacial ice sheet extent (e.g., Simpson et al., 2009), but these are often poorly constrained by geologic data. Additional evidence for the former extent of smaller-than-present ice margin positions can be gleaned from marine faunal remains that have been reworked by glaciers that readvanced across marine sediment, as has been described for the Greenland Ice Sheet during the late Holocene (e.g., Tarr, 1897; Weidick and Bennike, 2007; Bennike, 2008). Radiocarbon dating of reworked shells and bones of marine animals has been used to date the time of smaller-than-present ice sheet extent (e.g., Weidick et al., 2004; Weidick and Bennike, 2007).

The great abundance of reworked marine fossils in deposits that fringe much of the Greenland Ice Sheet attests to both the extent and timing of former ice-free marine environments. However, radiocarbon dating is a cost-limiting method for generating the large number of ages needed to determine the age-population distribution for the plethora of reworked material. Here we report a new approach to dating a large suite of reworked bivalve shells collected from around Greenland’s perimeter to constrain ice margin positions through the Holocene (Fig. 1). The cost-effective technique is based on the enantiomeric composition of amino acids preserved in mollusk shells. We used a mathematical procedure to model the relationship between the extent of aspartic acid (Asp) racemization and radiocarbon age from three different sites spanning western Greenland. We then compare the populations of Asp-inferred shell ages with independent climate and ice margin reconstructions and discuss how amino acid geochronology can be used to constrain the ice margin history of western Greenland.

Figure 1. A: Greenland and three ice margin locations where we collected reworked marine bivalve shells from historical moraines. B–D: Illustrations showing how advances of Greenland Ice Sheet into marine settings can rework fossiliferous marine sediment into Neoglacial moraines.
AMINO ACID GEOCHRONOLOGY

We measured enantiomeric (D-isomers and L-isomers) separations of amino acids from 251 shell fragments of the bivalve *Mya truncata* that were reworked into the historical moraines (which mark the late Holocene maximum ice sheet position) from three different ice margin sites in western Greenland (Fig. 1). Building from Weidick and Bennike (2007), wherein radiocarbon ages from seven reworked shell fragments from the historical moraine in Jakobshavn Isfjord were presented (Fig. 1; Table DR1 in the GSA Data Repository1), we made additional collections of bivalve fragments from the same location (69°7.500′N, 50°3.525′W). In addition, we collected bivalve fragments from a site where a Bowhead whale (*Balaena mysticetus*) bone was reworked into the historical moraine in Melville Bugt (Bennike, 2008; 74°43.841′N, 56°54.756′W), and made collections from historical moraines on two islands in Upernavik Isfjord (72°49.537′N, 54°31.983′W; 72°58.559′N, 54°46.161′W). We collected hundreds of bivalve fragments (many of which are *Mya truncata*) along hundreds of meters of the moraine surface at each sample location.

Subsamples from each *M. truncata* specimen were prepared for analysis by pretreating with bleach to isolate the intracrystalline fraction of amino acids according to procedures described by Penkman et al. (2008). The powdered and bleached shells were hydrolyzed in 6 M HCl under N2 at 110 °C for 6 h and measured by reverse phase, high-performance liquid chromatography (Kaufman and Manley, 1998); analytical precision was <1%. We focus on Asp due to its relatively fast rate of racemization, which provides the most resolving power (Kaufman, 2003), especially for application to millennial time scales in the Arctic (Goodfriend et al., 1996). Because asparagine (Asn) is transformed to Asp during laboratory hydrolysis (Zhao et al., 1989), the Asp values that we report may contain a minor component of Asn (Kaufman and Manley, 1998).

To evaluate the relationship between Asp D/L (D is D-aspartic acid, L is L-aspartic acid) values and age, we selected 20 specimens that span the range of D/L values for radiocarbon dating. Subsamples of the same *M. truncata* fragments used for amino acid analysis were dated at the National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institution (Massachusetts, USA). We calibrated all radiocarbon ages using CALIB version 6.0 (http://calib.qub.ac.uk/calib/) with the Marine09 data set and ΔR = 0 for an updated version of CALIB, see Stuiver et al., 2013), and report the mean age as the midpoint of the two standard deviation age range (Table DR1).

To quantify the radiocarbon age–D/L relationship, we used a Bayesian model fitting approach to evaluate the relative fit of three potential age functions and two uncertainty distributions following Allen et al. (2013). Of the Bayesian models explored, the time-dependent-rate kinetic model had the best fit, and the gamma distribution yielded the best uncertainty estimates for the predicted ages (Allen et al., 2013; Fig. 2); however, all models yielded similar inferred age distributions, and model choice does not change our conclusions (Fig. DR1 in the Data Repository). Quantile uncertainty (2.5%–97.5%) of the inferred ages ranges from 50% to 85%, with a median of 63%.

Asp D/L values in shells from the three study sites overlap, and were aggregated to form a single calibration data set (Table DR2; Fig. 2). We dated four to five individual *M. truncata* fragments of each sample collection, and found that the relationship between Asp D/L values and radiocarbon age from each site overlap within errors. Thus, we combine Asp D/L values and radiocarbon ages from all sites to generate a single calibration data set. Following the methods in Kosnik and Kaufman (2008), we examined the concentration of amino acid isomers to identify specimens with potentially unreliable D/L values. Concentrations of [D-Asp] and [L-Asp] had symmetrical variance, but [L-Asp] versus Asp D/L and [D-Asp] versus Asp D/L relations had notably asymmetrical variance; based on this four shells were excluded from our data set. We used the Asp D/L versus radiocarbon age calibration curve to transform the Asp D/L values into Asp-inferred ages for the individual *M. truncata* fragments. Bayesian model averaging was used to determine the best age estimate for each specimen. We generated histograms of Asp-inferred bivalve age in 1000 yr bins (comparable to calculated uncertainty; Fig. 2) to show the age distribution of *M. truncata* fragments for each of our three ice margin locations (Fig. 3).

DISCUSSION

The main factors that influence Asp D/L of a *M. truncata* shell are time and temperature history of a specimen since death. Some of the scatter within our calibration curve could be due to varying temperature histories of the marine deposits prior to ice sheet reworking. For example, due to *M. truncata* living at various water depths and combined with a complex ocean thermal structure in coastal western Greenland (cold surface waters and warmer Atlantic water at intermediate depth; e.g., Rignot et al., 2010), the specimens probably did not have the same temperature history. Furthermore, because the ocean temperature of western Greenland changed through the Holocene, the time when the mollusk died is an additional variable in its postdepositional temperature history. Nonetheless, the strong relationship between Asp D/L and time implies that specimen age is the largest determinant of its Asp D/L value.

We compare the oldest and youngest Asp-inferred bivalve ages with previous results at each sample location. The oldest Asp-inferred bivalve ages correspond well with independent chronologies for deglaciation at each site. At Jakobshavn Isfjord, where numerous radiocarbon ages from basalt lake sediments and cosmogenic 10Be exposure ages indicate deglaciation ca. 7.5 ka (Weidick and Bennike, 2007; Young et al., 2013), our oldest Asp-inferred bivalve ages are between 7 and 6 ka (Fig. 3). Similarly, in Melville Bugt, a previously published radiocarbon age from a reworked whale bone is 9.2 ka (Bennike, 2008), consistent with our oldest Asp-inferred bivalve ages that date to around that time. The youngest Asp-inferred bivalve ages also compare well with independently derived maximum ages for the ice sheet advance leading to the deposition of the historical moraines. For example, at Jakobshavn Isfjord, radiocarbon ages from proglacial threshold lakes reveal that Jakobshavn Isbrae approached its historical position as early as 2.3 ka, and finally reached it between ca. 600 and ca. 200 calibrated (cal.) yr B.P. (Briner et al., 2010, 2011). This ice margin history is consistent with only one Asp-inferred bivalve age between 2 and 1 ka, and only one Asp-inferred bivalve age younger than 1 ka (Fig. 3). In Upernavik Isfjord, radiocarbon ages from proglacial threshold lake sediments that provide maximum ages for Upernavik Isstrøm’s approach to the historical moraine of ca. 650

![Figure 2. Relation between aspartic acid (Asp) D/L (D—D-aspartic acid, L—L-aspartic acid) and inferred age fit using Bayesian model averaging procedure (see Allen et al., 2013; for model details, see the Data Repository [see footnote 1]). Each small circle is inferred age; gray error bars indicate 95% confidence interval. Black squares are radiocarbon-dated specimens used to fit models; error bars are smaller than symbols.](geology.gsapubs.org.geology.png)
The timing of highest frequency of shell ages from 5 to 3 ka. Thus, we wonder if the lack of Asp-inferred bivalve ages older than ca. 7 ka (Fig. 3). Further south, the ice sheet margin was stable, and advanced between ca. 9 and 8 ka when it deposited the Fjord Stade moraines (Young et al., 2013). The Fjord Stade moraines span ~600 km in southwestern Greenland, but are absent at our northern two sites because the present ice sheet margin is on landscapes deglaciated prior to this interval (Funder et al., 2011). However, ice margin fluctuations during this interval likely occurred behind the present ice position, and fjords currently occupied by the ice sheet might not have been ice free with thriving populations of *M. truncata* until after ca. 8–7 ka. Thus, we wonder if the lack of Asp-inferred bivalve ages dating to the early Holocene at our two northern sites indicates that the ice margin was not far from its current location.

We compared the distribution of Asp-inferred bivalve ages with independent records of climate change in western Greenland. Despite differing ice sheet histories at our three sampling locations, all three populations show the largest number of Asp-inferred bivalve ages from 5 to 3 ka. The timing of highest frequency of shell ages coincides with some, but not all, independent records of relative warmth from western Greenland. For example, chironomid-inferred temperature records from lakes in the Disko Bugt region indicate that the warmest millennia occurred 6–4 ka (Axford et al., 2013). However, other studies suggest 8–6 ka as the time of maximum warmth (e.g., Bennike et al., 2010). The difference in the timing between these estimates of maximum Holocene warmth likely relates to where the proxy data come from, and what the different types of proxy data record. For example, coastal areas are thought to have been chilled by ice sheet meltwater well into the Holocene, and therefore thermal maximum conditions were delayed in relation to maximum Northern Hemisphere insolation (Kaufman et al., 2004; Renssen et al., 2009). Marine sediment records from the Disko Bugt region indicate the warmest marine conditions from 5.5 to 3.5 ka (e.g., Perner et al., 2012) and studies of a marine core offshore northwest Greenland indicate warmer conditions than present from 6.4 to 3.6 ka (Levac et al., 2001). There is increasing evidence that oceanographic conditions play an important role in controlling the position of calving tidewater glaciers (e.g., Lloyd et al., 2011). Thus, minimum extent of western Greenland ice in coastal reaches likely occurred in the middle Holocene, coinciding with the period with the largest number of Asp-inferred bivalve ages. The timing of minimum ice extent might also lag the maximum thermal conditions; there is evidence in western Greenland for lagged ice sheet response to Little Ice Age cooling and 20th century warming (Kelley et al., 2012).

CONCLUSION

The distribution of Asp-inferred bivalve ages is consistent with what is known about the climate and ice margin history of western Greenland. However, it is possible that this interpretation is complicated by additional factors. For example, some combination of marine productivity and temporally varying sedimentation rates might have resulted in a higher frequency of ages from ca. 5–3 ka, and therefore the distribution of ages is controlled not only by ice sheet extent. In addition, the distribution of ages may be influenced by variable ice sheet scouring of fjord-bottom sediments, and thus the sections of historical moraines that we sampled only contain a portion of the fjord-bottom sediment section. Despite these potential complications, we note that the distribution of ages shows a similar pattern at all three locations. Furthermore, times with relatively few ages (early and late Holocene) and times with many ages (middle Holocene) are known intervals of extensive and limited ice margin position, respectively. The time with the most ages coincides with the oceanographic optimum on the western Greenland shelf.

Racemization of Asp in *M. truncata* shells occurs fast enough in western Greenland to yield robust radiocarbon-based calibration curves for Holocene chronologies. Asp D/L values can aid in selecting the oldest and youngest reworked specimens for radiocarbon dating, and provide ages for a complete population of bivalves reworked into moraines. The great abundance of locations where Greenland ice advanced over marine deposits, encompassing the majority of Greenland’s perimeter, implies that this approach could have wide applicability. Amino acid geochronology adds a new chronometer to our toolkit used to determine when coastal glaciers were smaller than present.

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