AGU PUBLICATIONS

Paleoceanography and Paleoclimatology

Supporting Information for

Baltic Perspective on Early to early Late Ordovician $\delta^{13}C$ and $\delta^{18}O$ Records and its Paleoenvironmental Significance

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Additional Supporting Information (Files uploaded separately)

Introduction

This supplementary text provides background information on the part of the conducted analyses that focus on assessing whether diagenetic alteration may have affected the primary carbon and oxygen isotopic signal in the brachiopod shells studied. These data are presented in figures S1–S3. Dataset S1, which may be downloaded as a separate file, contains all analyzed data in stratigraphical order.

Text S1: Screening of Brachiopod Samples

Although early diagenesis is thought to only have a negligible impact on the isotopic composition of carbonate precipitates because it occurs at temperatures and isotopic compositions similar to those of ambient seawater, meteoric and burial diagenesis can significantly alter the primary isotopic composition of carbonates (Jaffrés et al., 2007; Veizer et al., 1999). In many cases, diagenetic alteration has been reported to be signified by depletion of ^{13}C and ^{18}O in carbonate precipitates (Jaffrés et al., 2007b; Korte et al., 2008a; Swart, 2015). Consequently, a suite of different tests is usually employed to assess the near-primary nature of stable isotope data derived from carbonate rocks and fossils alike.

A combination of optical (Scanning Electron Microscopy), chemical (element/Ca ratios) and statistical methods (correlation between element/Ca ratios and $\delta^{13}C$, $\delta^{18}O$) have been applied to assess the fidelity of the carbon and oxygen isotope data herein presented (see Ullmann & Korte, 2015 for a review).

SEM photomicrographs (Fig. 8, main text) reveal that Ordovician brachiopod shells on Öland range from well preserved (i.e. show no discernible recrystallization features) to partially preserved (i.e. possess both well-preserved and recrystallized sites). Also, no immediately clear correlation is visible between brachiopod shell textural preservation, C and O isotope compositions and element/Ca ratios. However, this disconnect between optical and geochemical observations may be due to differential preservation of shell ultrastructure and the utilization of different shell fragments for optical and geochemical analyses.

Element/Ca ratios are employed as indicators of diagenetic alteration based on the observation that diagenetically altered carbonates usually differ from their near-primary counterparts in their element/Ca ratios (Brand and Veizer, 1980; Schobben et al., 2016; Ullmann et al., 2017) Sr/Ca ratios in biogenic calcite usually decline while Mn/Ca ratios tend to increase with increasing diagenetic influence e.g. from carbonate recrystallization (Brand & Veizer, 1981; Korte et al., 2008a; Steuber & Veizer, 2002), and this is frequently accompanied by the depletion of the heavier isotopes (Korte & Hesselbo, 2011).

Mn/Ca ratios of Ordovician brachiopods from Öland are generally higher than assumed upper limits for well-preserved Phanerozoic brachiopods (e.g. (Bruckschen & Veizer, 1997; Ullmann & Korte, 2015; Veizer et al., 1999). Lithology-driven element/Ca ratio variation can be discounted because there is no discernible correlation between lithological change and element/Ca ratios in the studied brachiopods (Fig. S1). Thus, observed Mn enrichment probably reflects, at least in part, near-primary biogenic Mn uptake, likely owing to the depositional context of the carbonate successions on Öland, which is subsequently discussed.

Sedimentation on Öland was characterized by extremely low accumulation rates (see Section 3 in the main text) (Lindskog et al., 2017; Stouge, 2004). This was coupled with low oxygen conditions (B. W. Rasmussen et al., 2017; Terfelt et al., 2014) as reflected by the common occurrence of glauconite (see Fig. 3). In addition, the frequent disconformity surfaces observable in Lower to Middle Ordovician carbonate successions (Calner et al., 2014; Eriksson et al., 2012; Jaanusson, 1961; Lindström, 1963, 1979, 1984), as well as the presence of phosphatized grains (Stouge, 2004), *point to early seafloor lithification in the relatively proximal Öland area within the paleobasin. This paleobasin configuration likely predisposed the ensuing sediments and chemical precipitates to authigenic mineralization with increased constituent trace metal abundances. Consequently, prevailing conditions during deposition of the Ordovician successions on Öland probably favored early Mn incorporation into sediments and biogenic precipitates. In addition, elevated Mn concentrations in Darriwilian and Sandbian Baltoscandia successions can be attributed to enhanced erosion documented for that time, which resulted in increased Mn influx (Rasmussen & Stouge, 2018) and references therein). Importantly, there is no discernible difference in Mn/Ca vs $\delta^{18}O$ trends during any of the time spans investigated (Floian to Sandbian, Fig. 1), suggesting a perpetual decoupling of Mn concentration and ^{18}O composition of the studied carbonate successions.*

Furthermore, unusual element/Ca ratios (high Mn/Ca and low Sr/Ca) and very light or relatively heavy carbon and oxygen isotope compositions are observed in texturally pristine and partially altered brachiopod shells alike. In many texturally altered brachiopods, a common feature is that their $\delta^{18}O$ value is comparable to or heavier than that of their texturally well-preserved counterparts. For example, sample OLH-98 (Fig. 8D) exhibits recrystallization features but has heavier $\delta^{18}O_{brachiopod}$ (-5.8‰) and Sr/Ca values (1.91 mmol/mol) relative to contemporaneous well-preserved brachiopod samples. In fact, texturally compromised brachiopods exhibit some of the heaviest oxygen isotope values – a trait which is usually associated with well-preserved brachiopod shells (e.g. Korte et al. 2008). In addition, relatively high Mn/Ca ratios exhibit no correlation with $\delta^{18}O_{brachiopod}$, which is considered to be sensitive to diagenetic modification (Shields et al., 2003) (Fig.9). Also, high Mn/Ca ratios are recorded even in samples with comparatively heavy $\delta^{18}O_{brachiopod}$ values, further suggesting that Mn incorporation cannot be solely explained by diagenetic alteration.

This finding is congruent with the observations of (Bergmann et al., 2018), who reported that Ordovician calcitic fossils with elevated trace element (Fe, Mn) concentrations from the Baltic–Ladoga Klint exhibit low clumped isotope temperatures. Conversely, contemporaneous well-preserved fossil brachiopods from the eastern Baltoscandian Paleobasin (Russia) reveal no Mn/Ca enrichment or Sr/Ca depletion (C. M. Ø. Rasmussen et al., 2016) (Fig. 9) even though their C and O isotope trends mirror those observed in this study (Figs. 11; 12). Furthermore, there does not seem to be any discrepancy between element/Ca values from northern Öland samples and those from the Degerhamn Quarry in southern Öland (Figs. 9; 10) even though those samples were probably heated to nearly 90°C as they were buried quite close to the oil window (Tullborg et al., 1995). Moreover, Mn/Ca ratios of up to 0.64 mmol/mol have been reported even for modern articulate brachiopods (e.g. Brand et al., 2003). Consequently, the incongruence of the measured trace element trends in fossil brachiopods within Baltoscandia suggests that elevated Mn concentrations on Öland are local and probably do not reflect on the preservation of near-primary C and O isotope compositions of the carbonate successions (see supplementary information). Therefore, we consider our Öland dataset to dominantly reflect near-primary carbon and oxygen isotope trends.

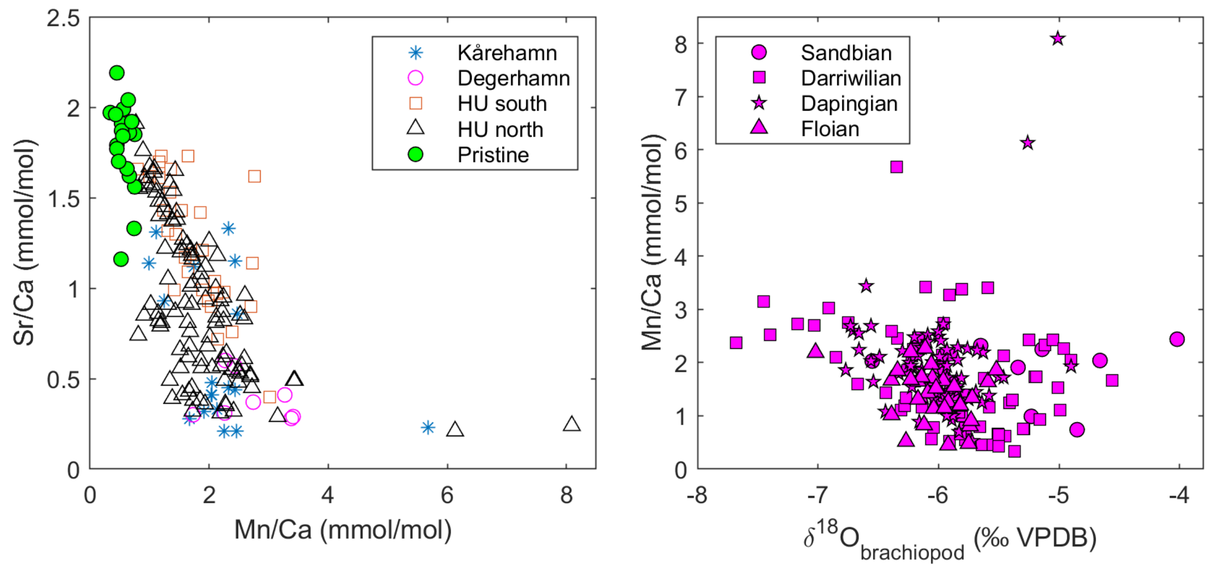
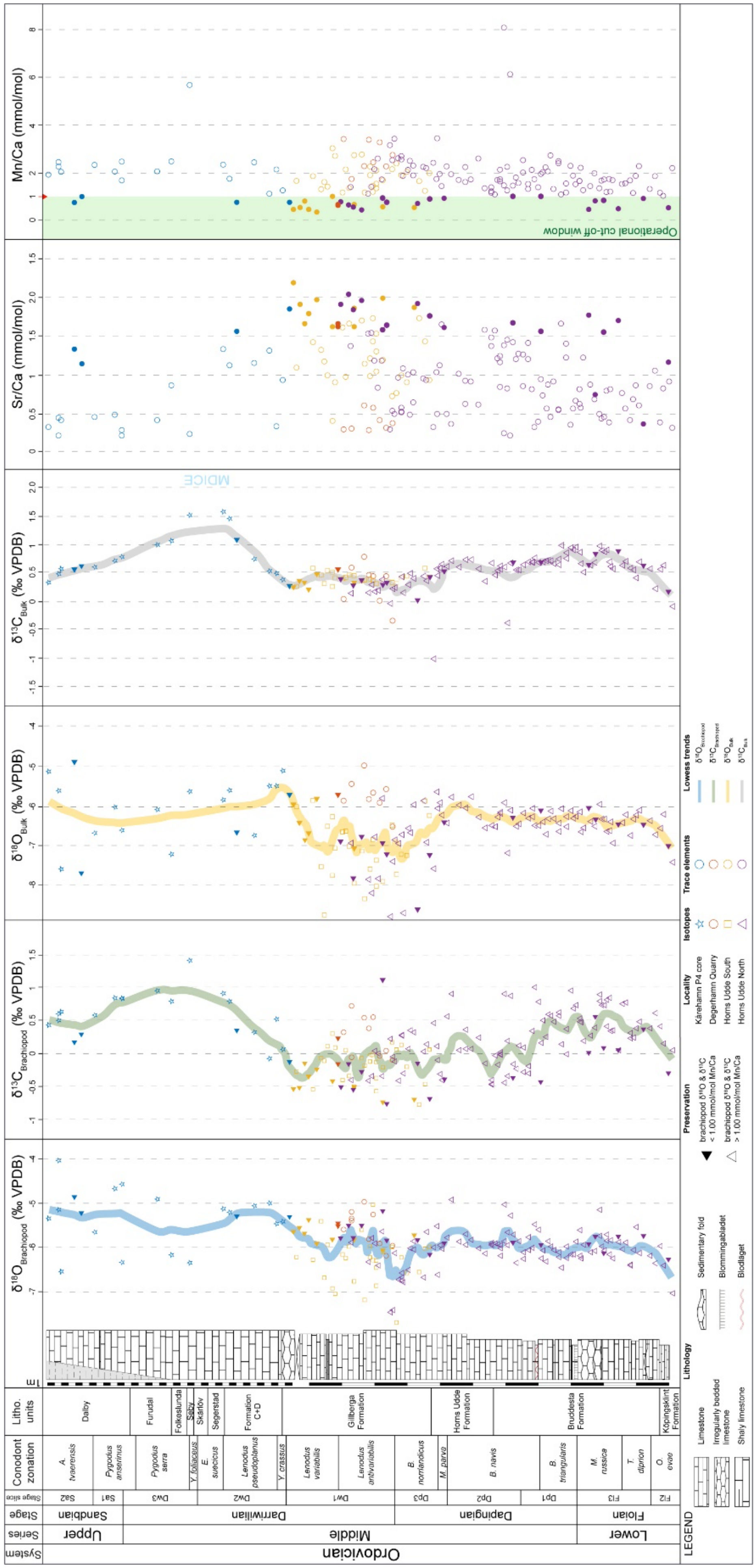


Figure S1: *Scatter plot showing Sr/Ca plotted against Mn/Ca by sample locality (left figure) and Mn/Ca vs brachiopod $\delta^{18}O$ for each investigated Stage (right figure). Element/Ca ratios do not show any correlation to sampling locality as the whole range of element/Ca values are recorded in samples from all localities. However, if all sample localities are taken together as one population, there appears to be a modest overall correlation between Sr/Ca and Mn/Ca (r^2 = 0.4). Note the absence of correlation between Mn/Ca and brachiopod oxygen isotopes during the investigated time intervals (right figure).*

Figure S2 (below): *Overview figure of all oxygen and carbon isotope data, as well as Element/Ca values for bulk carbonate and brachiopods through the studied interval. Note that the dataset is not evenly scaled. The mid-Darriwilian to Sandbian part of the figure is vertically compressed due to reduced sampling resolution in this interval. See legend for details.*



System
Series
Stage
Stage slice
Conodont zonation
Litho. units
Lithology
Ordovician
Lower
Middle
Upper
Floian
Dapingian
Darriwilian
Sandbian
Gillberga Formation
Bruddesta Formation
Horns Udde Formation
Köpingsklint Formation
Dalby
Furudal
Folkeslunda
Segerstad
Skärlöv
Seby
B. navis
B. triangularis
B. norrlandicus
M. parva
M. russica
T. diprion
O. evae
Lenodus variabilis
Lenodus antivariabilis
Lenodus pseudoplanus
Y. crassus
Y. foliaceus
E. suecicus
Pygodus serra
Pygodus anserinus
A. tvaerensis
Mn/Ca (mmol/mol)
Sr/Ca (mmol/mol)
Operational cut-off window
MDICE
LEGEND
Limestone
Irregularly bedded limestone
Shaly limestone
Sedimentary fold
Blommingabladet
Blodlaget
Preservation
Locality
Kårehamn P4 core
Degerhamn Quarry
Horns Udde South
Horns Udde North
Isotopes
Trace elements
Lowess trends

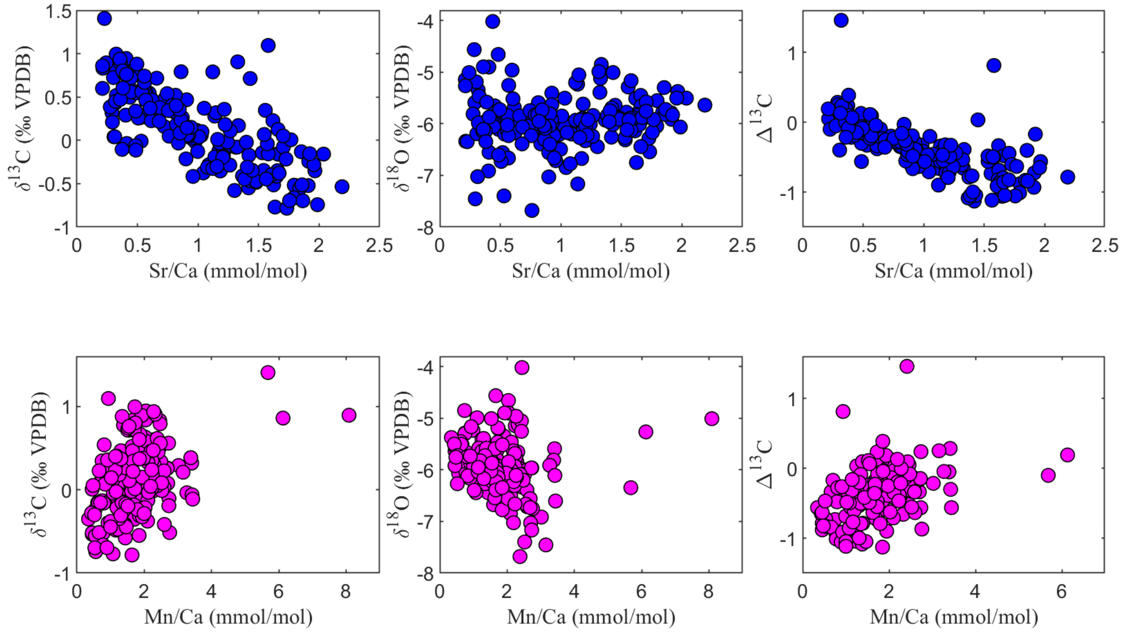


Figure S3: *Scatter plots illustrating the statistical relationship between element/Ca ratios and $\delta^{18}O$ and $\delta^{13}C$ values of investigated brachiopods in the current study. Note the negative correlation between $\Delta^{13}C$ vs Sr/Ca and $\delta^{13}C$ vs Sr/Ca ($r^2 = 0.51$ and 0.54 respectively). This implies that brachiopod $\delta^{13}C$ values decreased in tandem with depletion in Sr/Ca values. No such relationship is distinguishable for Mn/Ca.*

Data Set S1. *Spreadsheet containing all analyzed data discussed in the text.*