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$\delta^{13}C$ chemostratigraphy in the upper Tremadocian through lower Katian (Ordovician) carbonate succession of the Siljan district, central Sweden

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Abstract. Based on $\delta^{13}C$ data from two drillcores recovered from the Siljan district, we present a first continuous carbon isotope record of the upper Tremadocian–lower Katian limestone succession of central Sweden. New names for some isotopic carbon excursions from the Cambrian–Ordovician boundary through the basal Darriwilian are introduced. The Mora 001 core from the western part of the Siljan impact structure ranges through the Lower–Middle Ordovician, whereas the Solberga 1 core from its eastern part ranges through the Middle–lower Upper Ordovician. Upper Tremadocian and Floian units are extremely condensed and include extensive stratigraphic gaps. Multiple hardgrounds, sometimes with minor karstic overprint, imply recurrent periods of erosion and/or non-deposition. Like in other parts of Sweden, the Dapingian and Darriwilian succession is characterized by a relatively complete sedimentary record and low sedimentation rates.

Key words: Sweden, Siljan impact structure, Ordovician, carbon isotope stratigraphy, MDICE, GICE, Kope.

ORDOVICIAN $\delta^{13}C$ CHEMOSTRATIGRAPHY

Over the last two decades, the strong potential of the $\delta^{13}C$ record for regional and global correlation of ancient marine sediments has become more and more evident (see Saltzman & Thomas 2012 for a summary). Bergström et al. (2009) compiled a generalized $\delta^{13}C$ curve for the Ordovician System, which serves as a good overview of the period (Fig. 1). The several strong excursions in the late Middle and Upper Ordovician are coupled with climatic changes and have been rather well studied in many parts of the world. The less pronounced excursions in the Early Ordovician have received far less attention.

These smaller excursions seem to occur on more than one palaeocontinent and may thus serve for global correlation of strata as well. Bergström et al. (2009) used the curve by Buggisch et al. (2003) for the compilation of a global standard for the Ordovician $\delta^{13}C$ record, and for many years, no other detailed curves were available for the Lower Ordovician. Our goal is to study the Lower to Middle Ordovician carbon isotope record in Baltoscandia for comparison. A first standard reference section for southern Sweden, the Tingskullen-1 core on northern Öland, was recently published by Calner et al. (2014), which marks the beginning of our effort. In this paper, we present $\delta^{13}C$ data from two overlapping core sections, which could serve as a future $\delta^{13}C$ standard for central Sweden. We also pay attention to the negative carbon isotope excursions of the Lower-Middle Ordovician. Negative carbon isotope excursions in the Phanerozoic often reflect short-term events and their causes and significance are debated, because this would require a fast and volumetrically substantial input of isotopically light carbon into the ocean-atmospheric system. Different sources have been discussed for younger Phanerozoic events, including quick release of methane from dissociation of clathrates, rapid heating of organic matter by volcanic intrusions, or a combination of different factors (for references see Saltzman & Thomas 2012). The Ordovician record seemingly includes similar negative anomalies but more studies are needed in order to evaluate these short-term events. Three short-term and pronounced negative shifts in the Early through Middle Ordovician are termed LTNICE, BDNICE and LDNICE in this study (Fig. 1).

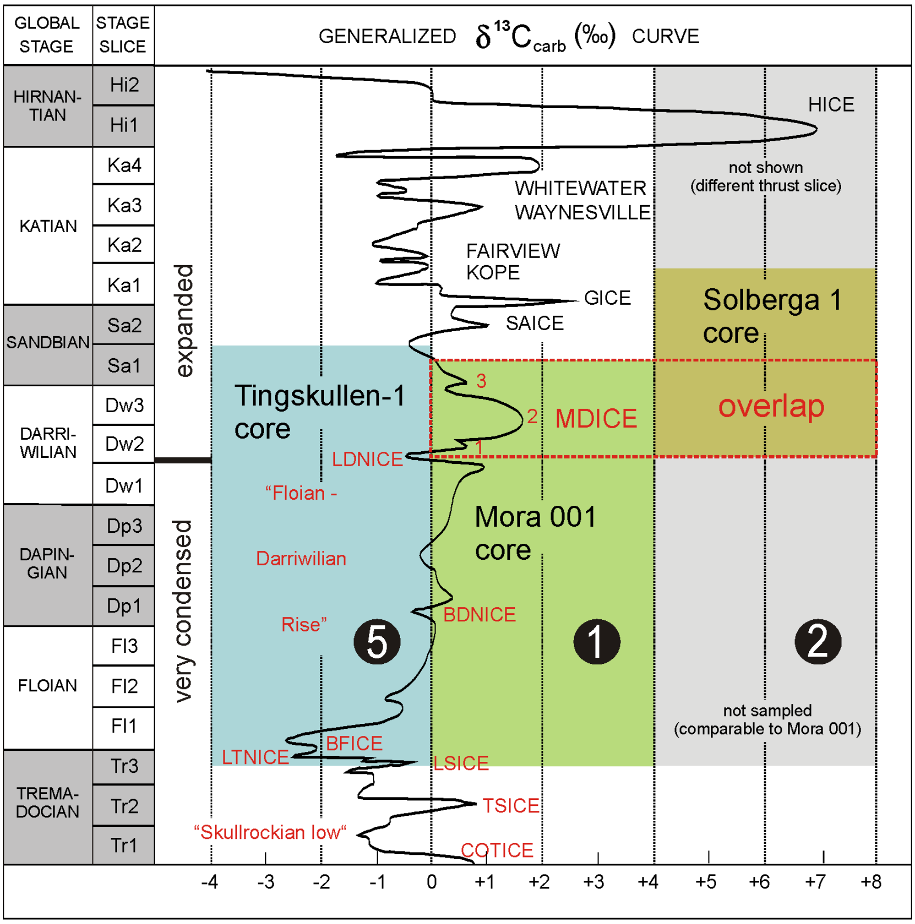

Fig. 1. Generalised $\delta^{13}C$ curve for the Ordovician System. Modified from Bergström et al. (2009, fig. 2) by the addition of the SAICE (Leslie et al. 2011), and the $\delta^{13}C$ events named in the present paper (COTICE, TSICE, LSICE, TNICE, BFICE and DNICE). The MDICE is characterised by a tripartite subdivision indicated by numbers 1–3 for the individual smaller peaks. The informal terms 'Skullrockian Low' and 'Floian–Darriwilian rise' is mentioned in the text. The three coloured blocks show the stratigraphic range of the sedimentary record in the Tingskullen-1, Mora 001 and Solberga 1 cores (the lower part of the succession in Solberga, which is comparable to that in the Mora section, was not sampled for this study and is indicated in grey), the encircled numbers refer to the corresponding location numbers shown in Figure 3.

The Tremadocian and Floian sedimentary succession of Baltoscandia is extremely condensed and virtually displays more gaps than record, which is also reflected by the data presented in this study. We therefore use data from the Argentine Precordillera published by Buggisch et al. (2003, fig. 6; Fig. 2), shown in the lower part of the Ordovician $\delta^{13}C$ standard compiled by Bergström et al. (2009), to name some of the Lower Ordovician events (see Fig. 1; without rescaling of the events in relation to the stage slices). This helps to discuss the possible presence of some of the younger peaks in Swedish sections.

Here we introduce and formally define the following names for significant isotopic carbon excursions (the age frame for the Tremadocian and Floian in terms of conodont faunas studied by Lehnert (2001) and correlated by Lehnert in Buggisch et al. (2003, figs 6, 8) to North American and Baltic conodont zones; Fig. 2):

COTICE: Cambrian–Ordovician Transition Isotopic Carbon Excursion, upper *Cordylodus intermedius* through *C. angulatus* zones, this positive excursion of more than 1‰ is followed by a low ('Skullrockian low') in $\delta^{13}C$ through the upper *Rossodus manitouensis* Zone. This interval displays minor variations and more detailed sampling is needed to clearly detect smaller-scale excursions.

TSICE: Top Skullrockian Isotopic Carbon Excursion, upper/top part of the *R. manitouensis* Zone, significant and most prominent Tremadocian positive excursion of ≥2‰, followed by an excursion in the

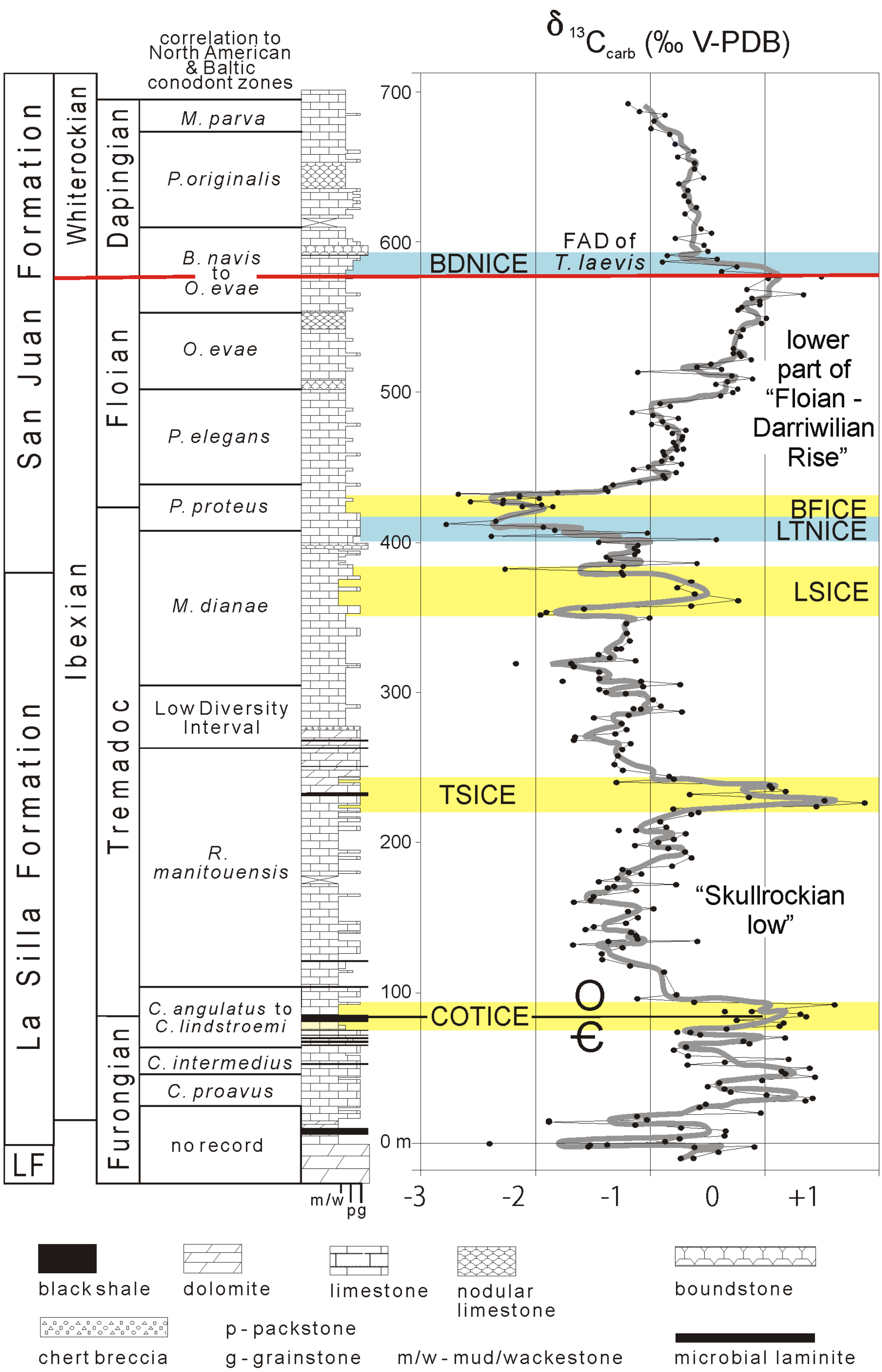

Fig. 2. Stratigraphic levels of $\delta^{13}C$ events defined in this study (COTICE, TSICE, LSICE, LTNICE, BFICE, BDNICE) and plotted on a modified version of fig. 6 of Buggisch et al. (2003) showing the $\delta^{13}C$ record in the Cerro La Silla section of the Argentine Precordillera (topmost La Flecha Formation through the upper San Juan Formation; late Furongian through Dapingian succession; LF – La Flecha Formation). The FAD of *T. laevis* marks the base of the Middle Ordovician in the succession (Albanesi et al. 2006), indicating that the BDNICE starts just at the base of the Dapingian.

Low Diversity Interval and basal *Macerodus dianae* zone of about 1‰, and followed by two or three excursions (depending if an internal peak morphology is suggested) in the *M. dianae* Zone. However, these minor shifts in $\delta^{13}C$ need additional sampling and confirmation from other areas and/or palaeoplates to justify the naming of additional events.

LSICE: Late Stairsian Isotopic Carbon Excursion of about 1.5‰, the upper *M. dianae* Zone.

LTNICE: Late Tremadocian Negative Isotopic Carbon Excursion, strong negative excursion in $\delta^{13}C$ in the topmost *M. dianae* Zone to a level coeval to the upper *Paroistodus proteus* Zone. The negative shift from the maximum of the LSICE to the minimum of the TNICE is about 2.8‰ (Buggisch et al. 2003).

BFICE: Basal Floian Isotopic Carbon Excursion, small positive excursion of less than 1‰ in an interval following the TNICE and correlated to the *P. proteus* Zone by Buggisch et al. (2003). However, the faunal composition of this part of the Precordilleran succession (*Acodus*? *deltatus*–*Paroistodus proteus* Assemblage Zone of Lehnert 1995) can be correlated to the upper *P. proteus* Zone and taxa indicative of three lower subzones of the *P. proteus* Zone are missing in the tropical fauna of Lehnert's (1995) *Parapanderodus striatus*–*Colaptoconus quadraplicatus* Assemblage Zone. Bergström et al. (2004) defined the base of the Floian defined by the first appearance of the graptolite *Tetragraptus approximatus*. The boundary between the uppermost subzones, the *P. gracilis* and the *Oelandodus elongatus*–*Acodus deltatus deltatus* subzones, is slightly below the base of the GSSP. Therefore, the small excursion of Buggisch et al. (2003) in this level presumably is basal Floian in age. After this minor event when values are as low as the minimum of the TNICE, $\delta^{13}C$ values continuously increase from the topmost *P. proteus*/basal *P. elegans* zones to the lower Darriwilian ('Floian–Darriwilian rise').

BDNICE: Basal Dapingian Negative Isotopic Carbon Excursion, strong negative shift in $\delta^{13}C$ in the basal Dapingian in an interval which was correlated to the *Baltoniodus navis* Zone by Buggisch et al. (2003). This shift is observed just above the first appearance date of *T. laevis* in the carbonate platform succession of the Argentine Precordillera (Albanesi et al. 2006), indicating the base of the Dapingian (Wang et al. 2009; Fig. 2). This significant negative shift in $\delta^{13}C$ has also been observed in the basal Dapingian Dikari Member of the Volkhov Formation in the Leningrad area of the East European Platform (Zaitsev & Pokrovsky 2014: fig. 2, *B. navis* Zone).

LDNICE: Darriwilian negative isotopic carbon excursion, strong negative $\delta^{13}C$ shift in the lower Darriwilian (lower Kunda), BC1–BC2 carbon isotope zonal boundary of Ainsaar et al. (2010), observed in the lower regressive interval of the regionally conspicuous facies unit 'Täljsten interval' (Eriksson et al. 2012) and equivalent units in Baltoscandia (Meidla et al. 2004).

REGIONAL BACKGROUND AND THE STUDY INTERVAL

The general aspects of the Lower–Middle Ordovician sedimentary succession of Baltoscandia have been dealt with in numerous publications. Aspects on its origin in temperate water environments within a slowly subsiding, shallow epicontinental basin located at middle palaeolatitudes were briefly summarized by Calner et al. (2014). In central Sweden, marine sediments of this age have been preserved from erosion in a ring-like depression around the ~30 km wide plateau (central uplift exposing the Precambrian basement) of the Siljan impact structure (Ebbestad & Högström 2007). This structure, with a present-day diameter of about 52 km (Grieve 1988; see Juhlin et al. 2012 for references to recent discussions of the original crater diameter), is of late Devonian age (e.g. Jourdan et al. 2012) and is of particular palaeogeographical significance since it preserves marine Ordovician–Silurian strata in a region dominated by Precambrian basement rocks (Lehnert et al. 2012, 2013).

The Lower Palaeozoic successions in the new deep drillings Mora 001 and Solberga 1 (Fig. 3) have recently been documented by Lehnert et al. (2012). In this paper, we describe the results of Tremadocian through Katian carbon isotope analysis of the rocks.

There are only minor differences in sedimentary facies in the lower portions of the two cores. Therefore, there was no need of duplicating the $\delta^{13}C$ sampling of the lower part of the Solberga 1 core after studying the Lower/Middle Ordovician succession through the upper Holen Limestone in the Mora 001 core. In this paper, we therefore document the record in the Solberga 1 core (WGS 84 coordinates: N 60°59.296, E 15°12.735; Fig. 3B), which has a clear and significant overlap with Mora 001 (WGS 84 coordinate system: N 60°58.855, E 14°31.870; Fig. 3B) up to the base of a major thrust zone 4.84 m above the base of the Slandrom Formation (Fig. 4). Both cores were drilled by the Swedish private company Igrene AB for exploration of geothermal energy and natural gas.

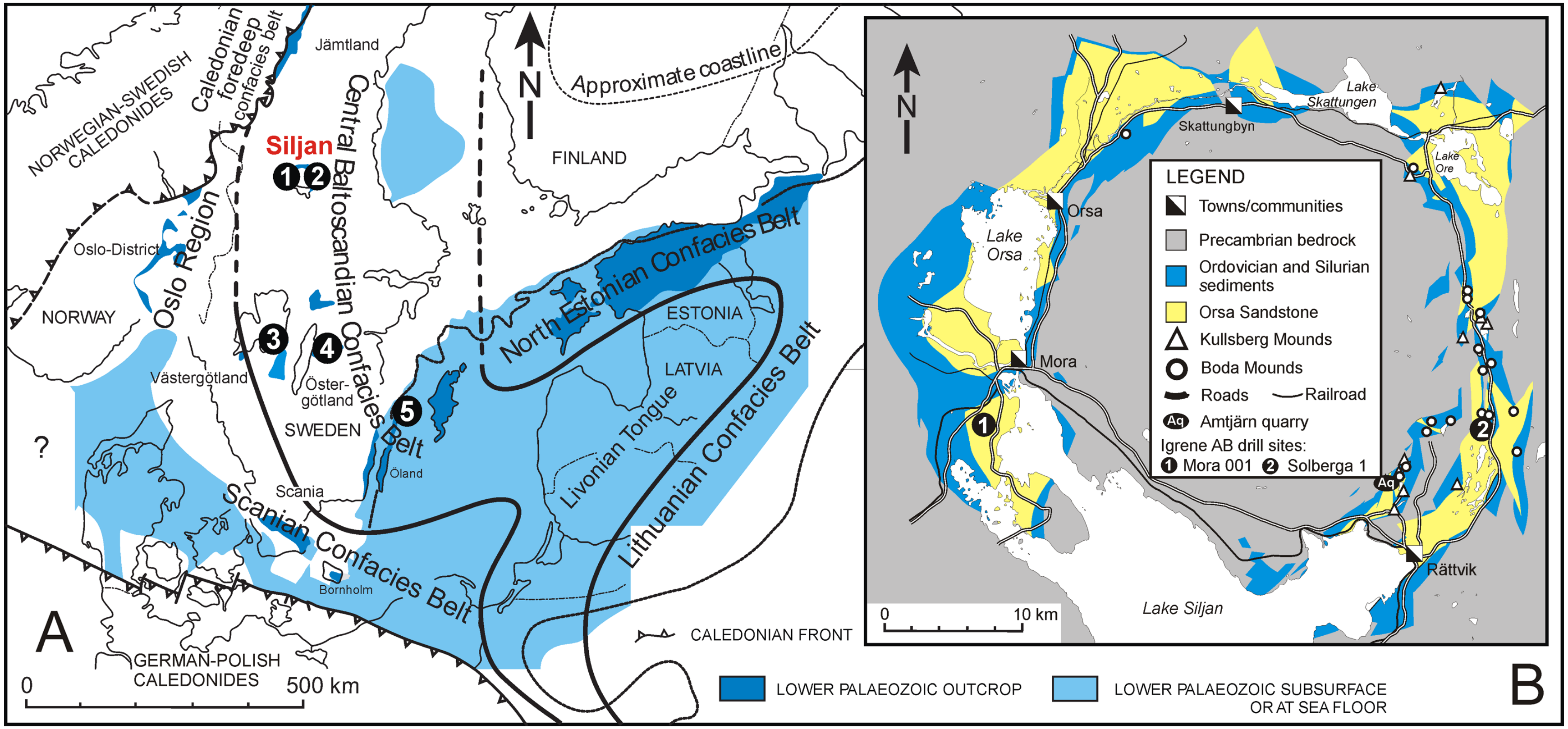

Fig. 3. A, Swedish core and outcrop locations mentioned in the text and shown on a map of Baltoscandia modified from Pärnaste et al. (2013) and J. Bergström et al. (2013), showing their modified concept of regional confacies (bio-lithofacies) belts: 1, Mora 001 core; 2, Solberga 1 core; 3, Hällekis and Skövde, Västergötland; 4, Borenshult 1 core, Östergötland; 5, Tinkgskullen drillcore, Öland. **B**, drill hole location of the cores studied for the Ordovician $\delta^{13}C$ record in the Siljan district, Dalarna, central Sweden: 1, Mora 001; 2, Solberga 1.

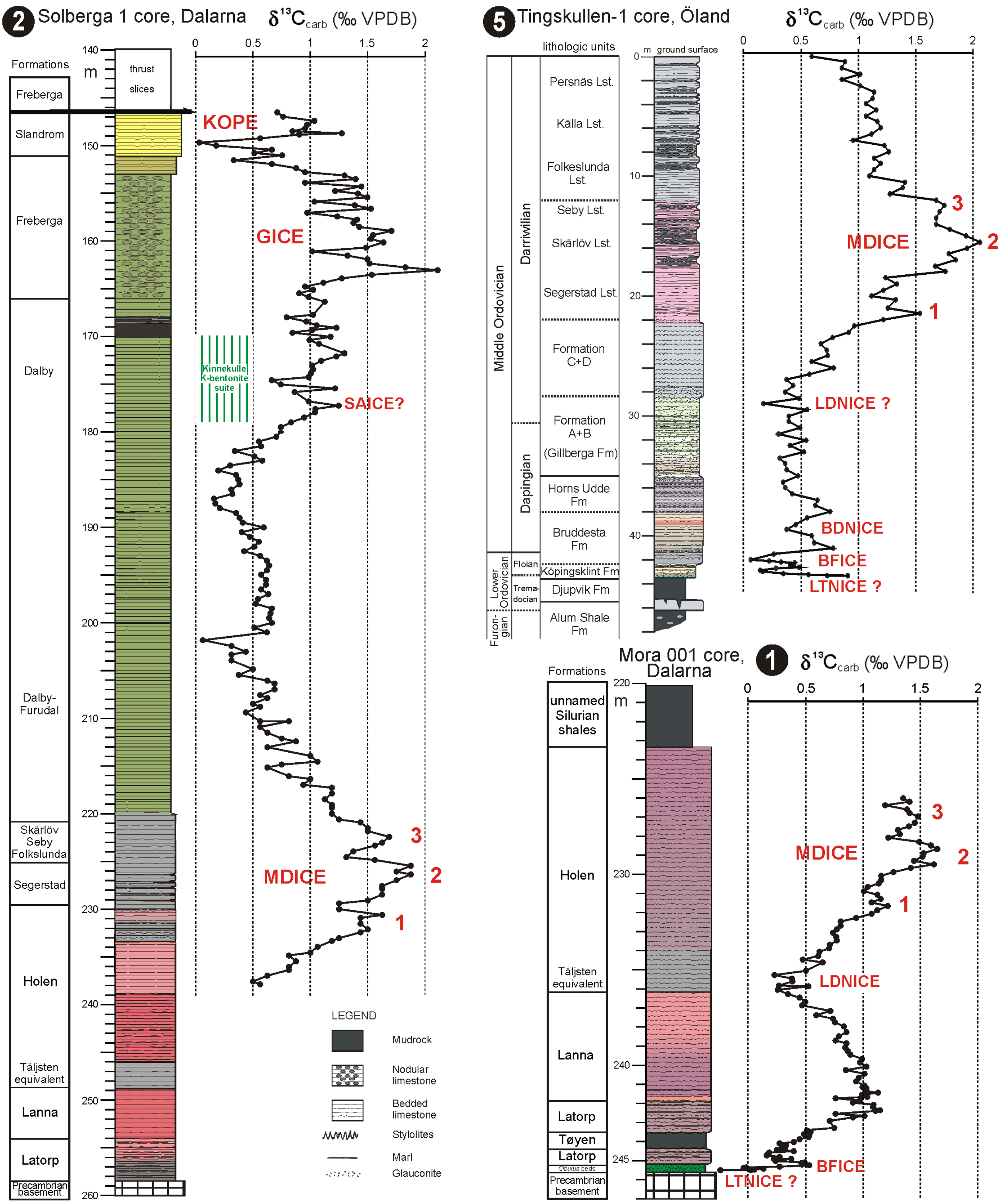

Fig. 4. Stratigraphy, $\delta^{13}C$ chemostratigraphy and sedimentary profiles of the upper Tremadocian through lower Katian succession in the Siljan core sections (Mora 001 and Solberga 1) and of the upper Tremadocian through Darriwilian strata in the Tingskullen-1 core from northeastern Öland (Calner et al. 2014). The encircled numbers beside the names of the cores refer to the corresponding location numbers shown in Fig. 2.

METHOD AND DATA

More than 300 whole-rock samples have been analysed – 125 samples from the Mora 001 core and 199 samples from the Solberga 1 core – to compile the Lower to lowermost Upper Ordovician $\delta^{13}C$ record presented in this paper. Tables with respective data are available in the online catalogue at http://dx.doi.org/10.15152/GEO.4 Carbonate powders recovered by a dental drill were reacted with 103% phosphoric acid at 70 °C using a Gasbench II connected to a ThermoFinnigan Five Plus mass spectrometer. All values are reported in per mil relative to V-PDB (Vienna Pee Dee Belemnite) by assigning a $\delta^{13}C$ +1.95‰ to NBS19. The accuracy and precision of the carbon isotope measurements were checked by replicate analysis of standards NBS19 and laboratory standards. Reproducibility was better than ±0.05‰.

Figure 4 shows the two Siljan core sections and their $\delta^{13}C$ curves in comparison with the $\delta^{13}C$ record in the Tingskullen-1 core from northeastern Öland (southern Sweden).

RESULTS AND DISCUSSION

Following the lowest $\delta^{13}C$ data in the glauconitic beds immediately resting on the Precambrian basement (minimum at –0.24‰ and probably indicating the most negative values of the LTNICE), a short-term and small basal Floian (?) positive $\delta^{13}C$ excursion (BFICE?, peak value at 0.53‰) is observed. This peak needs to be dated by conodonts but it could correlate with a comparable excursion in the *P. proteus* Zone of the Argentine Precordillera, which is followed by the well-established long-term increase in $\delta^{13}C$ ('Floian–Darriwilian rise', Fig. 1). It could as well be coeval to a small excursion in the *O. evae* Zone in the Tingskullen-1 core. In the latter section there is also a significant negative shift in $\delta^{13}C$ in its lowermost part that may correspond to the LTNICE (Fig. 3). This event may be compared to the negative shift in $\delta^{13}C$ in the *Hunnegraptus copiosus* graptolite Zone in the lower Hunghuayuan Formation in the Yangtze Region of South China. The positive excursion in the *T. approximatus* graptolite Zone in the upper part of this formation corresponds to the BFICE.

The conodont *O. evae* occurs above the glauconitic beds in the lowermost Köpingsklint Formation of the Tingskullen-1 core, indicating that the small excursion there is Floian in age (BFICE). In the Mora 001 core section a general increase in $\delta^{13}C$ is recorded during the Floian and Dapingian, culminating in the uppermost part of the Latorp and basal part of the Lanna formations. The continuous rise in $\delta^{13}C$ observed in the expanded Precordilleran carbonate succession (lower part of the 'Floian–Darriwilian rise', Fig. 1; increase in values between the BFICE and the BDNICE, Fig. 2) is not well developed in the Siljan district and values are slowly decreasing in the upper Lanna Formation in the Mora 001 core section (Fig. 4). Values clearly decrease in the Lower Darriwilian during the deposition of equivalents to the lower Täljsten interval. This negative $\delta^{13}C$ excursion is observed in various sections on Baltica and is herein termed the Lower Darriwilian Negative Isotope Carbon Excursion (LDNICE, minimum $\delta^{13}C$ value 0.23‰). It represents a characteristic intrabasinal chemostratigraphic marker and includes the most negative shift in $\delta^{13}C$ values measured in the Darriwilian $\delta^{13}C$ curves of Baltoscandia. It is not so obvious in the uppermost part of the San Juan Formation in the Argentine Precordillera (Buggisch et al. 2003), but may be observed in the published records of pre-MDICE strata from western Laurentia (Edwards & Saltzman 2014) and South China (Munnecke at al. 2011). It could be represented by the low values in the basal Darriwilian of the southern Great Basin in the Shingle Pass (Nevada) and Ibex (Utah) sections (Edwards & Saltzman 2014, figs 5, 6, 9). The LDNICE most probably is indicated by low $\delta^{13}C$ values in the lower Darriwilian in the Honghuayuan section in the Yangtze area (uppermost Meitan Formation), followed by a distinct positive excursion of about 2‰ in the middle part of the Shihtzupu Formation presumably representing the MDICE (Munnecke et al. 2011, fig. 7).

In the upper transgressive part of the Täljsten interval, $\delta^{13}C$ values start to rise and shift into the expanded middle Darriwilian isotopic carbon excursion (MDICE, maximum $\delta^{13}C$ value 1.84‰ in central Sweden). The MDICE is well developed and displays a tripartite subdivision in its peak interval, which has been observed also in the Tingskullen-1 core from northeastern Öland (Fig. 3). The deposition of the upper Holen Formation through the top of the interval including the Skärlöv, Seby and Folkslunda limestones spans the peak interval of the MDICE comprising three smaller 'positive excursions' separated by two small 'negative excursions'. The MDICE is not only of special importance for global correlation as suggested by several studies (e.g. Schmitz et al. 2010; Calner et al. 2014), but its tripartite subdivision (indicated in Figs 1 and 3) may also be of special significance for detailed intrabasinal correlations in Baltoscandia. The published record of the MDICE from different palaeocontinents (Baltica, Laurentia and South China) and terranes (Argentine Precordillera) and its range in terms of conodont biostratigraphy were recently discussed and compiled by Calner et al. (2014).

In Sweden, only an incomplete MDICE was known from quarries in Västergötland due to the erosion of strata deposited during time of its 'falling limb' (Meidla et al. 2004; Schmitz et al. 2010) until a complete MDICE was documented from the 'orthoceratite limestone' succession on northeastern Öland (Calner et al. 2014) (Fig. 3).

Between the pronounced positive excursions of the MDICE and the GICE, the latter located in the Freberga Formation, there are two smaller positive excursions which have to be investigated for their potential to correlate on an intrabasinal scale. For example, also some less pronounced excursions occur in this interval in some Sandbian sections in the East Baltic area.

Leslie et al. (2011, fig. 3) introduced the SAICE (Sandbian Isotope Carbon Excursion) for a conspicuous excursion present in the Clear Spring Maryland Section along Interstate-70 in the Sandbian (Turinian, lower Mohawkian) close to the contact between the Pinesburg Station and St. Paul groups of eastern North America, ranging from the uppermost *Cahabagnathus friendsvillensis* Zone through at least the upper *Amorphognathus tvaerensis* Zone. The Laurentian uppermost *C. friendsvillensis* Zone corresponds to the uppermost *Pygodus serra* Zone (*Eoplacognathus lindstroemi* Subzone), a level that corresponds to the upper Furudal Formation of southern Sweden. Leslie et al. (2011) show the peak of this event above the *Baltoniodus alobatus* Subzone, which in the Borenshult core corresponds to the uppermost Dalby Formation and a level at about the Kinnekulle K-bentonite or slightly above (Bergström et al. 2012). Based on this information, the SAICE in the Solberga 1 core may start roughly at about 184 m and range up to about 175 m within the middle part of the Kinnekulle K-bentonite suite. In the Sandbian of South China (Huangnitang section, Hulo Formation), the increase in $\delta^{13}C$ values may correspond to this level below the GICE, which is observed in the overlying Lower Katian Yenwashan Formation (Munnecke et al. 2011, fig. 9).

In the Borenshult core in Östergötland, Bergström et al. (2012) documented the GICE a few metres above the Kinnekulle K-bentonite, within the middle Freberga Formation (upper *A. tvaerensis* Zone) with a peak value of 1.88‰. In the less condensed Solberga core, the GICE appears to start in the uppermost Dalby Limestone in the upper part of a suite of K-bentonites, including the Kinnekulle K-bentonite, suggesting numerous eruptions (Huff et al. 2013). The baseline values of the GICE may be a point of discussion and whether the SAICE is just a separate peak within the overall peak morphology on the 'rising limb of the GICE'. The $\delta^{13}C$ peak value of the GICE in the Solberga 1 core is 2.10‰. Bergström et al. (2012) have recently compiled the stratigraphic and geographic record of this event and its global significance.

The Kope $\delta^{13}C$ excursion in the Solberga 1 core is observed at the transition from the Freberga Formation to the Slandrom Formation and has a $\delta^{13}C$ peak value of 1.07‰ within the latter unit. Its 'falling limb' is partly cut off by the basal fault of a major fault zone in this core section. In the Amtjärn quarry in the southeastern part of the Siljan district (Fig. 3B: Aq), the Kope $\delta^{13}C$ excursion is observed in the Skålberget Limestone, resting on the truncated top of the Kullsberg Limestone (Calner et al. 2010). There, the upper part of this unit was deposited during the GICE and the Kullsberg mound development terminated during the late GICE interval when sedimentation continued in the deeper setting at Solberga.

CONCLUSIONS

A detailed $\delta^{13}C$ record spanning the upper Tremadocian through lower Katian strata of the Mora 001 and Solberga 1 drill cores is herein provided. It represents the first continuous $\delta^{13}C$ record from the Lower–Middle Ordovician carbonates of the Siljan district.

The Ordovician succession of the Siljan district has the following charateristics:

1. The Tremadocian and Floian succession on Öland and in the Siljan district is extremely condensed and stratigraphically incomplete.
2. A strong negative shift in $\delta^{13}C$ in the glauconitic beds in the lowermost part of the Ordovician sections in the Siljan district and on Öland presumably can be correlated with the LTNICE. It is obviously succeeded by the BFICE in both sections. The negative $\delta^{13}C$ excursion in the Bruddesta Formation most probably represents the BDNICE on Öland.
3. The complete MDICE record, preceeded by the LDNICE, shows a tripartite subdivision that, if calibrated by detailed conodont biostratigraphy, may provide good estimates of missing biozones in incomplete successions affected by erosion and/or non-deposition.
4. When compared to previously published data from Öland, the internal peak morphology of the MDICE provides a good tool for detailed intrabasinal and intercontinental chemostratigraphic correlations as demonstrated by the Siljan district $\delta^{13}C$ record.
5. The SAICE, GICE and Kope excursions can be recognized in the Solberga 1 core section, although separation of the SAICE from the 'rising limb' of the protracted GICE interval may be a matter of debate.

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