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Upper Ordovician $\delta^{13}C_{org}$ chemostratigraphy, K-bentonite stratigraphy, and biostratigraphy in southern Scandinavia: A reappraisal

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Abstract

A pioneer $\delta^{13}C_{org}$ study through the upper Sandbian and Katian (Upper Ordovician) succession in the Röstånga 1 drill in the classical geological outcrop area at Röstånga in southernmost Sweden produced a wealth of new carbon isotope data which are useful for local and regional correlations. Among the Upper Ordovician positive $\delta^{13}C$ excursions, the Guttenberg (GICE,) Waynesville (Saunja), Whitewater (Moe), Paroveja, and Hirnantian (HICE) isotopic carbon excursions are recognized but the Kope (Rakvere) $\delta^{13}C$ excursion is missing, suggesting a stratigraphic gap. All these isotopic excursions are tied closely to biostratigraphy, especially graptolite biostratigraphy, and in the case of the Waynesville (Saunja) and Whitewater (Moe) excursions, for the first time anywhere in the world. The Röstånga GICE $\delta^{13}C_{org}$ curve from the upper Sularp Shale shows a striking similarity to that of the Katian GSSP in Oklahoma, suggesting the potential of trans-Atlantic correlation. Based on a projection from the Katian GSSP, the previously poorly constrained position of the base of the Katian in southern Sweden appears to be in the uppermost Sularp Shale in strata of the upper *Diplograptus foliaceus* Zone. Previous interpretations of the relations between K-bentonite successions in southern Scandinavia are somewhat revised and the Kinnekulle K-bentonite is recognized for the first time in Scania. Based on new radiometric dates, this very prominent and widespread ash bed appears to be slightly older than the Deicke and Millbrig K-bentonites in eastern North America.

1. Introduction

There are many outcrops of Upper Ordovician strata in the Provinces of Västergötland and Dalarna, and a few in the Province of Östergötland, in south-central Sweden. However, in the Province of Skåne (Scania) in southernmost Sweden, and on the Island of Bornholm in Denmark, exposures of rocks of that age are restricted to a few localities , which in Scania are mainly located in the Fågelsång, Röstånga and Tommarp-Järrestad areas (Fig. 1). Also in the latter areas, the Upper Ordovician outcrops do not expose long stratigraphic intervals but rather consist of limited exposures of short successions that are separated by significant covered intervals. Attempts to describe in detail the stratigraphic succession through this part of the Ordovician therefore have to be based on drill cores. The most significant drill cores currently available are the Röstånga 1 in the Röstånga area (e.g. Bergström et al., 1997, 2014; Pålsson 1996, 2002), and the Koängen (Nilsson, 1977) and Lindegård (Glimberg, 1961) drill cores from the Fågelsång area. The Upper Ordovician succession on the Danish island of Bornholm in the Baltic is known from a few stratigraphically limited outcrops (e.g. Hadding, 1915a, 1915b) and the Billegrav 2 and two other drill cores. Whereas the Fågelsång Upper Ordovician succession has become relatively well known through the work by Nilsson (1977) and Glimberg (1961), that of the Röstånga area was quite incompletely described prior to the drilling of the Röstånga 1 well in the summer of 1997. This well provided the first continuous succession from the upper Sandbian through the top of the Hirnantian stages (Upper Ordovician) as well as through much of the lower and middle Llandovery (Lower Silurian) in this area (Bergström et al.. 1999). Subsequent work on this drill core has resulted in several publications (Pålsson, 2002; Koren' et al., 2003; Grahn and Nõlvak, 2007; Badawy et al., 2014; Bergström et al., 2014; Maletz et al., 2014, Kiipli et al., 2015) but some aspects of this drill core, such as the pre-Hirnantian $\delta^{13}C_{org}$ chemostratigraphy, have not been studied previously. The latter research topic is the primary focus of the present study. As will be shown below, this chemostratigraphic study produced some unexpected results that initially were confusing but later, combined with other types of evidence, proved useful for a regional reappraisal of the stratigraphy of the upper Sandbian and Katian successions in southern Scandinavia.

2. Geologic setting and stratigraphy

Ordovician strata in the Röstånga area have a long exploration history, the earliest publications dating back to the 1870s (for a useful summary of the early work, see Moberg (1910)}. The previous papers on the Röstånga drill core and the adjacent outcrop along Kyrkbäcken (Church Brook) published by Bergström et al. (1997, 1999, 2014) and by Pålsson (1996, 2002) provide general reviews of past stratigraphic and paleontological work on the Upper Ordovician in the Röstånga area and reference to these publications is made for such information. As is also the case with the succession in the Fågelsång area, which is located approximately 32 km south of Röstånga (Fig. 1A), the Ordovician succession at Röstånga was deposited in an outer shelf or upper slope environment near the margin of the Baltic platform. This part of Scania is located within the structurally complex Tornquist

Zone that separates the Baltic Shield from the European continent (Fig. 1B). In the terminology of Jaanusson (1976, 1995), the Ordovician rocks in Scania represent the Scanian confacies (or lithofacies) belt that is characterized by dominantly clastic sediments deposited in relatively deep water. The Scanian successions, which contain diverse graptolite faunas, differ conspicuously from the carbonate-dominated successions in the more central parts of the Baltic Shield, especially in the East Baltic region, which yield abundant shelly faunas but few graptolites.

With a single exception, we use the same formation classification of the Upper Ordovician pre-Hirnantian succession in the Röstånga 1 drill core and the adjacent exposures along Kyrkbäcken as in Bergström et al. (1997). The only difference is that the term Skagen Formation, which has been employed previously for the calcareous interval between the Sularp Shale and the Mossen Formation, is replaced by the term Freberga Formation. As will be shown below (p. x), the principal reason for this change is the fact that the present chemostratigraphic study indicates that much of this unit is substantially younger than the Skagen Formation in south-central Sweden. Because the present study deals not only with the Röstånga succession but also with some other Scandinavian successions, the Upper Ordovician stratigraphic terminology used herein is summarized in Fig. 2. In the case of global Ordovician stages and stage slices, we follow the terminology of Bergström et al. (2009a).

The biostratigraphic work carried out on Upper Ordovician strata in the Röstånga area has been reviewed by Bergström et al. (1997) and Pålsson (1996, 2002) and we summarize only some pertinent data. The Sularp Shale in its outcrop along Kyrkbäcken has yielded about a dozen conodont species but the fauna is dominated by coniform taxa of little biostratigraphic significance and diagnostic index species have not been found. The absence of *Baltoniodus* species*,* which are very common, and used as subzonal index fossils, in the Dalby Limestone in south-central Sweden (Bergström, 1971) suggests that the upper Sularp Shale is younger than the Dalby Limestone, which is in agreement with the aspect of the fauna, which is similar to that of the Freberga Formation, which overlies the Dalby Limestone in south-central Sweden. In general, the conodont fauna appears to represent an interval around the *Amorphognathus tvaerensis/A. superbus* zonal boundary but in the absence of the index taxa, the position of this horizon cannot be located. Bergström et al. (1997) recorded more than a dozen chitinozoan species from the Sularp Shale of the Kyrkbäcken section and essentially the same species association was listed by Grahn and Nõlvak (2007) based on samples from the same locality. Although composed of mainly long-ranging taxa, this chitinozoan fauna was interpreted as representing the *Spinachitina cervicornis* Zone that ranges from the upper Sandbian *Baltoniodus alobatus* conodont Subzone into the lower Katian. We conclude that the available microfossil data from the upper Sularp Shale are not very diagnostic biostratigraphically. A few graptolites have been recorded from the Sularp Shale in the Kyrkbäcken outcrop (Moberg, 1910) but these are in need of taxonomic revision. Comparison with the similar succession in the Koängen drill core (Nilsson, 1977) clearly suggests that the top part of the Sularp Shale corresponds to part of *Diplograptus foliaceus* Zone. Although the thin Mossen Formation at Röstånga has not yet yielded diagnostic graptolites, comparison with the Koängen drill core succession indicates that in all likelihood this unit is also referable to the *Dicranograptus clingani* Zone. This is supported by the fact that it has yielded a trilobite fauna (Pålsson, 1996) that includes the stratigraphically important species *Tretaspis ceriodes* (Angelin) that in Västergötland is characteristic of, and restricted to, the Mossen Formation (e.g. Skoglund, 1963). The Mossen Formation at Röstånga has also yielded the characteristic conodont *Hamarodus brevirameus (*formerly *H. europaeus*) that elsewhere first appears in the *A. superbus* Zone (Fan et al., 2015) in strata equivalent to the *D. clingani* Zone. The biostratigraphically diagnostic graptolite succession in the Fjäcka Shale and Lindegård Formation described by Pålsson (2002) will be further discussed below. Whereas the Fjäcka Shale has yielded graptolites of the *Pleurograptus linearis* Zone, this unit contains relatively few shelly fossils. The lower portion of the overlying Lindegård Formation in the Kyrkbäcken outcrop contains a rather diverse shelly fauna (Olin, 1906; Pålsson, 1996) that includes the stratigraphically important trilobite *Nankinolithus granulatus* (Wahlenberg), This species provides a correlation link to the lower Jonstorp Formation in south-central Sweden. This portion of the Lindegård Formation also contains graptolites of the *Dicellograptus complanatus* Zone, including the geographically widespread and biostratigraphically important zone index species. The known vertical ranges of selected trilobites and graptolites in the Röstånga study successions are illustrated in Fig. 3.

Because the uppermost Sandbian and lower-middle Katian succession on Bornholm plays an important role in the present study, it is appropriate to briefly review its stratigraphy (cf. Fig. 2). This part of the Bornholm succession is dominated by shales and mudstones containing diverse graptolite faunas that allow correlation with coeval units in the Koängen and Röstånga successions (Hadding, 1915a, 1915b; Bruvo and Nielsen, 2005; Vandenbroucke et al., 2013). Because the same lithic units can be recognized in these three sequences, we prefer to use the Scanian terminology (Mossen Formation and Fjäcka Shale) rather than the outdated term *Dicellograptus* Shale for the lower and middle part of the Katian succession on Bornholm.

At the classical Vasagård section (Hadding, 1915a), the principal K-bentonite complex is overlain by <1 m of Sularp Shale with fossils indicating the *Diplograptus foliaceus* Zone (Bergström and Nilsson, 1974; Bravo and Nielsen, 2005; Vandenbroucke et al., 2013). On the top of this formation is a 4.5 m thick dark shale containing graptolites of the *Dicranograptus clingani* Zone (Bruvo and Nielsen, 2005) that can be classified as the Mossen Formation. The contact between the Sularp Shale and the Mossen Formation is marked by a thin phosphoritic conglomerate (Vandenbroucke et al., 2013). The Mosssen Formation is overlain by approximately 3.5 m of dark shales, which are similar lithologically to those of the Mossen Formation but yield graptolites of the *Pleurograptus linearis* Zone. Because this unit agrees both lithologically and biostratigraphically with the Fjäcka Shale in Sweden, we apply this formation designation also to the Bornholm unit. At the contact between the Mossen Formation and the Fjäcka Shale there is a thin pyritic-phosphoritic bed that was described already by Hadding (1915b). It has been interpreted as indicating a regional stratigraphic gap (Poulsen, 1966; Stouge and Rasmussen, 1996). This disconformity appears to have a wide distribution in

Baltoscandia (e.g. Poulsen, 1966) and is also present in the outcrop along Kyrkbäcken at Röstånga, where a thin pyritic and phosphoritic limestone bed separates the Mossen formation from the overlying Fjäcka shale (Bergström et al., 1997).

3. Previous Sandbian-Katian chemostratigraphic work in southern Scandinavia

Although a large amount of Ordovician chemostratigraphic work has been carried out in the East Baltic region (e.g. Kaljo et al., 2004; Ainsaar et al., 2010), all these investigations have been based on $\delta^{13}C_{carb}$ using samples from carbonate-dominated successions. This has also been the case in studies in Sweden and Norway (e.g. Bergström et al., 2004, 2010a, 2010b, 2010c, 2011a, 2012, 2014, 2015; Meidla et al., 2004; Schmitz and Bergström, 2007; Lehnert et al., 2014; Ebbestad et al. , 2015; Calner et al., 2015). As far as we are aware, $\delta^{13}C_{org}$ has previously been used in the Ordovician of Baltoscandia only by Bergström et al. (2014) in their investigation of the Hirnantian of the Röstånga 1 drill core, and in the study of the latest Katian and Hirnantian succession in the Billegrav drill cores on Bornholm (Hammarlund et al., 2012; also cf. Bergström et al., 2014). Importantly, the previous studies and the present one show that the values obtained from $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ investigations are closely comparable chemostratigraphically and useful for correlations between clastic and carbonate successions in Baltoscandia .

4. Materials and methods

The present study is based on 137 samples collected at approximately 0.5 m intervals through the drill core section between 52.5 m and 132.5 m depth in the Röstånga drill core (Fig. 3). This study interval has a stratigraphic thickness of approximately 55 m based on an average dip of 35 degrees of the strata penetrated, and it ranges from the upper Sularp Shale through the upper Lindegård Formation. In terms of global stages (Bergström et al., 2009a), the base of the sample interval is in the upper Sandbian and the top at the base of the Hirnantian. In order to illustrate the chemostratigraphy through the entire uppermost Ordovician, the Hirnantian drill core data published by Bergström et al. (2014) were added to the $\delta^{13}C_{org}$ curve.

All the samples were crushed and subjected to the following treatment to obtain the $\delta^{13}C_{org}$ values. Sample powders were accurately weighted (~ 1 g) and then acidified with 6 N HCL to remove carbonate minerals. Insoluble residues were then repeatedly rinsed in ultrapure water, centrifuged, and dried overnight at 80°C. The dried residues were homogenized, weighted and loaded into tin cups for $\delta^{13}C_{org}$ analysis. Samples were dropped under helium into an oxidation furnace packed with chromium (VI) oxide and silvered cobaltic/cobaltous oxide (to remove any halogens) at 1000°C. The gas was then passed through a reduction furnace packed with elemental copper at 680°C to reduce all nitrogen bearing compounds to gaseous nitrogen. The resulting gases were then passed through a water trap to eliminate moisture. Stable $\delta^{13}C_{org}$ values were obtained using a Costech Elemental Analyzer coupled to a ThermoFinnigan Delta Plus XP through an open split - Conflo III. Carbon isotope rations were corrected for ^{17}O contribution and reported in per mil notation relative to the Vienna Pedee Belemnite standard (‰ VPDB). Precision and calibration of data were monitored through routine analyses of in-house standards that are rigorously calibrated against IAEA standards. Standard deviations for $\delta^{13}C$ are ±0.0(one sigma) and ±0.07% for %C (one sigma). Weight percent of total organic carbon (TOC)) in samples were determined by comparison of voltages for the ion beam intensities of masses 41, 45, and 46 CO_2^+ between our samples and known wt % carbon of the gravimetric standard Acetanilide. The curve based on plotting the $\delta^{13}C_{org}$ values is shown in Fig. 3.

5. $\delta^{13}C_{org}$ chemostratigraphy of the Upper Ordovician of the Röstånga 1 drill core

5.1. Primary nature of the $\delta^{13}C_{org}$ trends

Sedimentary organic matter undergoes many biological (cell growth rates, cell shape, local $CO_{2\ (aq)}$ levels, microbial remineralization) and geological (burial or tectonically induced thermal alteration) processes that impart effects upon $\delta^{13}C_{org}$ values (e.g. Pomp et al., 1998; Hayes et al., 1999). Another potential concern is mixing of terrestrial and marine sources of organic matter (e.g. Shluijs and Dickens, 2012). However, the sedimentary TOC analyzed from our section is expected to be largely from marine sources as these Upper Ordovician strata were deposited in a distal shelf to slope setting with little, if any, input from terrestrial environments. Additionally, a well-established terrestrial biosphere is unlikely to have been present during Katian times (e.g. Steemans and Wellman, 2004). Although alteration of primary $\delta^{13}C_{org}$ values may have occurred in our stratigraphic succession (e.g. thermal alteration or oxidation loss of certain biomolecules), we do not see evidence that such processes are responsible for the large-scale trends in our $\delta^{13}C_{org}$ values. Furthermore, we observe no covariance between $\delta^{13}C_{org}$ and wt % TOC (see Table 1) that may be expected if differential alteration of organic matter occurred in horizons that are poor versus relatively rich in organic carbon. Despite the greater scatter of our $\delta^{13}C_{org}$ values compared to previously published $\delta^{13}C_{carb}$ values, the larger trends in our isotope curve are similar to those present in some published $\delta^{13}C_{carb}$ curves through coeval stratigraphic intervals. This supports the idea that generally, the primary values have been preserved.

5. 2. Significant $\delta^{13}C_{org}$ trends through the Upper Ordovician of the Röstånga 1 drill core

Despite the fact that that there is conspicuous scatter in the $\delta^{13}C_{org}$ values (Fig. 3) in some stratigraphic intervals in the drill core (e.g. in the upper part of the Fjäcka Shale and lower part of the Lindegård Formation), there are a series of positive excursions (+2‰ to +3‰ in magnitude) that clearly deviate from baseline values that range between -31‰ and -30‰. By far most prominent of these excursions is that in the Hirnantian with peak values of about -26.5‰. Bergström et al. (2014) described this excursion in some detail, and identified it as the Hirnantian isotope carbon excursion (HICE). It will not be further discussed herein. However, the isotope curve segment of the previously unstudied Sandbian-Katian interval in the drill core exhibits several other excursions that we discuss individually below, starting with the stratigraphically oldest excursion.

There is one problem when discussing Upper Ordovician isotope excursions, namely that several of these coeval intervals with elevated values initially received different names in Baltoscandia and in North America .(cf. Bergström et al., 2009a, 2010b, 2010c, 2015). Some excursion designations, such as the GICE and the HICE, have now been employed virtually globally and are well established. Recently, Ebbestad et al. (2014) used a third type of excursion designations, employing as excursion names units (consisting of letters and numbers) in the Baltic chemostratigraphic zonation introduced by Ainsaar et al. (2010). Because we feel that names are much easier to associate with a particular excursion than the letter and number combinations used in this zonation, and the fact that the isotope zone boundaries are not always easy to recognize precisely, especially outside Baltoscandia, we prefer to use the name designations in the present study.

5.3. The Guttenberg $\delta^{13}C$ *excursion (GICE)*

The beginning of the oldest major excursion in the study interval is at approximately 115 m drill core depth (Fig 3) and the elevated geochemical values end approximately at the 104 m level in the drill core . At the 115 m core depth the $\delta^{13}C_{org}$ values increase from baseline values of ~29.5‰ to nearly 27‰ although most of the excursion values are between -28‰ and 28.5‰ prior to a relatively gradual decline to 30.8‰ at the l04 m core depth. This positive shift in $\delta^{13}C_{org}$ values is broadly consistent with $\delta^{13}C_{org}$ trends in correlative strata in North American and Chinese sections (Patzkowsky et al., 1997; Young et al., 2008). We identify this excursion as the Guttenberg excursion (GICE). A little below the GICE curve segment there are slightly elevated $\delta^{13}C_{org}$ values that may possibly represent the Sandbian isotopic carbon excursion (SAICE), which was first recognized and named in eastern USA (Leslie et al., 2011). However, we do not consider the Röstånga $\delta^{13}C_{org}$ values high enough to be diagnostic for the SAICE.

A recent detailed GICE record is from the Freberga Formation in the Solberga 1 drill core from the Siljan region in south-central Sweden (Lehnert et al., 2014) was based on $\delta^{13}C_{carb}$. As shown in Fig. 4, there is a striking similarity between the Solberga and Röstånga isotope curves even if the latter is based on $\delta^{13}C_{org}$. This strongly indicates that they represent the same paleoceanographic event.

The biostratigraphy of the interval around the GICE has not yet been investigated in the Solberga 1 drill core but comparison with the lithologically very similar succession at the well-known Fjäcka locality, which is situated only approximately 16 km from Solberga, suggests the approximate conodont biostratigraphy illustrated in Fig. 4. Although the conodont faunas in the GICE interval in the Röstånga drill core are poor in diagnostic species, there is a great deal of similarity between the faunas of this interval in these two successions. It is of special interest to note the presence of *Rhodesognathus elegans* (Rhodes) in the Freberga Formation at Fjäcka (Bergström, 2007) and in the upper Sularp Shale because this species is in Baltoscandia only known from the GICE interval.

The GICE has now been identified virtually worldwide, being described from many localities in North America (e.g. Ludvigson et al., 1996; Bergström et al., 2010b, 2010c; Barta et al., 2007; Young et al., 2005, 2008), Baltoscandia (e.g. Kaljo et al., 2004; Bergström et al., 2010a, 2010b, 2012), China (e.g. Young et al., 2008; Bergström et al., 2009b; Munnecke et al., 2011; Fan et al., 2015) and even Malaysia (Bergström et al., 2010d). In Sweden, the GICE has previously not been recognized in Scania but is known from several localities in Dalarna (e.g. Bergström et al., 2004, 2010a, 2011a), Östergötland (Bergström et al., 2012) and Västergötland (Meidla et al., 2004; Bergström et al., 2010b).

The fact that the GICE starts well below the top of the Sularp Shale in the Röstånga 1 succession was initially surprising and even confusing in view of the fact that at other localities in Baltoscandia, as well as in North America, the beginning of this excursion is typically a little above the principal K-bentonite complex. This apparent anomaly could be explained as being due to at least two reasons: (1) the beginning of the GICE is not of the same age everywhere, and/or (2) the previous correlation of the Scanian K-bentonite complex (Bergström and Nilsson, 1974; Bergström et al., 1995) is in need of some modification. Of particular significance in the Sandbian portion of the ash bed complex in Baltoscandia is the prominent and widespread Kinnekulle K-bentonite that can be traced from southeastern Norway across Sweden and the East Baltic region to the St. Petersburg area in Russia (Bergström et al., 1995). At most localities there is only a relatively thin interval between the top of the Kinnekulle bed and the raising limb of the GICE. Applying this fact to the Röstånga succession suggested that the Kinnekulle bed, if present, probably was identical with one of the several ash beds below the 115 m drill core level although the identification of the Kinnekulle bed remained a matter of speculation. The matter was further complicated by the fact that earlier attempts to identify the Kinnekulle K-bentonite, which is generally the thickest of the Sandbian ash beds, by geochemical fingerprinting of the beds in the Kyrkbäcken section were unsuccessful, as the several investigated ash beds had a closely similar chemistry and mineralogy (Bergström et al., 1997).

A breakthrough in our efforts to identify the Kinnekulle K-bentonite in the Röstånga succession, and the regional relations of its K-bentonite complex, was provided by the recent publication of a geochemical investigation of the Sandbian-Katian interval in the Billegrav-2 drill core succession on the Danish Island of Bornholm (Kiipli et al., 2014). Their analysis of the relations of trace elements amounts (Nb, Ti, Th, Zr) in 34 K-bentonite beds resulted in the identification of an 80 cm thick K-bentonite between the Billegrav-2 drill core levels 88.30 m and 89.10 m as the Kinnekulle K-bentonite. Because this drill core turned out to have a sequence of prominent K-bentonite beds that shows a great deal of similarity to those of the Scanian Koängen and Röstånga 1 drill cores, we found it possible to construct a detailed correlation diagram between these successions. This correlation could also be extended to the important Kinnekulle and Sinsen successions (Fig. 5). Although in the absence of specific rare element data, the precise correlation between the Swedish and Norwegian sections will necessarily involve some uncertainty, the relations presented in this diagram are in agreement with the biostratigraphic data. Importantly, in the case of the Röstånga succession, the ash bed approximately 6-7 m below the base of the Mossen Formation and between 117-118 m in the drill core (Bergström et al., 1999, fig. 3) and Bed T in the Kyrkbäcken outcrop (Bergström et al., 1997, fig. 2) are herein identified as the Kinnekulle K-bentonite. As shown in Fig. 5, we trace this bed to its type section on

Kinnekulle and further to the much thicker Sinsen section in the Oslo region in southeastern Norway. In the latter section, which is the best outcrop of the Sandbian K-bentonite complex in Norway, the Kinnekulle bed occurs in the upper part of the Arnestad Formation, which is overlain, with gradational contact, by the Frognerkilen Formation that has an excellent development of the GICE (Bergström et al., 2011a). Hence, the relations between the GICE and the K-bentonite succession are the same in these sequences.

Of special biostratigraphic interest is Olin's (1906) record of the distinctive species *Toxochasmops macrourus* (Angelin) from the outcrop of the upper Sularp Shale along Kyrkbäcken. This species is the index of what used to be called the Macrourus Limestone, which was later renamed the Moldå Formation, and now forms the upper part of the Freberga Formation. The presence of this species is in excellent agreement with the stratigraphic age interpretation presented herein.

In previous studies of the Röstånga succession, the rather prominent limestone bed between 106 m and 110 m in the drill core and the bed in the same position relative the K-bentonite complex in the Kyrkbäcken section, have in recent papers been referred to as the Skagen Limestone. This bed, which was formerly known as the Ampyx Limestone (Funkquist, 1919), has a wide distribution in Scania, being known also from the Koängen drill core (Nilsson, 1977), the Tommarp well in southeastern Scania (Bergström et al., 1997), and, as newly excavated boulders, at Rävatofta in northwestern Scania (Bergström et al., 1968). The recognition of the Skagen Limestone in southernmost Scandinavia was based on similarity in lithology and stratigraphic position to the type Skagen Limestone in Västergötland as well as on its development in Dalarna. However, a previous recent investigation shows that most of the type Skagen Limestone is of pre-GICE age (Bergström et al., 2011a) and hence, it is coeval with a portion of the upper part of the Sularp Shale. The limestone bed in the Röstånga area corresponds to the middle-upper portion of the GICE and hence, is partly younger than the type Skagen Limestone. Accordingly, the designation Skagen Limestone is inappropriate and because it correlates with the middle-upper part of the calcareous Freberga Formation, we now use the latter formation designation in the Scanian successions.

The proposed chemostratigraphic correlation of the GICE interval between the Röstånga drill core, the stratigraphically substantially more complete succession in the Borenshult drill core (Bergström et al., 2012), and the type Skagen Formation at Mossen, Kinnekulle (Bergström et al., 2011a) is illustrated in Fig. 6.

5.4. Other Katian $\delta^{13}C_{org}$ excursions

In the drill core interval between 52.5 m and 106 m, we recognize in ascending order, the Mossen Formation, the Fjäcka Shale, the Lindegård Formation, and the lowermost 2.5 m of the Kallholn Formation. In this succession, which corresponds to most of the Katian Stage and the lowermost part of the Hirnantian Stage, we recognize, in ascending order, four $\delta^{13}C_{org}$ excursions, namely the Waynesville (Saunja), Whitewater (Moe), Paroveja, and HICE excursions (Fig. 3). Another, but very poorly developed, excursion between the Whitewater (Moe) and Paroveja excursions in the lower Lindegård Formation may possibly represent the incompletely known Elkhorn excursion in North America. Because we have already described in some detail the HICE in the drill core (Bergström et al., 2014) and no new data are available, the following discussion is concentrated on the other excursions. The correlation of these excursions to the corresponding ones in the East Baltic succession and the classification in Baltic isotope zones are shown in Fig. 7.

A distinctive $\delta^{13}C_{org}$ excursion in the lower half of the Fjäcka Shale is identified as the Waynesville (Saunja) excursion. This excursion, which occurs between approximately 95 m and 103 m in the drill core, starts at the base of the Fjäcka Shale with $\delta^{13}C_{org}$ values of ~-31‰ and there is a gradual value increase through the lower Fjäcka Shale to ~-29‰. This interval of elevated values is followed by a relatively rapid decrease to nearly -31‰ that marks the end of the excursion near the middle of the Fjäcka Shale. Although no stratigraphically diagnostic conodonts are known from the excursion interval at Röstånga, diverse conodont faunas in other successions, especially in North America, show that the base of the global *Amorphognathus ordovicicus* Conodont Zone corresponds to a level just below the base of this excursion (e.g. Bergström et al., 2009a). The Fjäcka Shale contains graptolites of *Pleurograptus linearis* Zone (e.g. Pålsson, 1996, 2002) and this excursion typically occurs in an interval corresponding to the lower-middle part of this graptolite zone (Fig. 3). The Fjäcka Shale has previously not yielded $\delta^{13}C$ data and the investigated equivalent units in the East Baltic region have not produced biostratigraphically diagnostic graptolites. Hence, the presence of the Waynesville (Saunja) excursion in the Röstånga region is of special interest for the correlation with the graptolite zone succession.

There is no excursion in the Röstånga 1 drill core corresponding to the slightly older Kope (Rakvere) excursion. This excursion typically is present in the Slandrom Limestone, which is missing in the drill core as is also the case in many other sections in southern Sweden, the only exceptions being a weak development at a few localities in Östergötland (Bergström et al., 2011b) and Västergötland (Holmer, 1986). Both the lithostratigraphy and the shape of the $\delta^{13}C_{org}$ curve suggest that there is a stratigraphic gap in the Röstånga succession at this level but if this gap is at the top of the Freberga Formation or at the top of the Mossen Formation, or at both these levels, requires further study. It should be noted that according to Badawy et al. (2014), the top surface of the Freberga Formation in the Röstånga 1 drill core shows solution features that may indicate the presence of a disconformity. The magnitude of this apparent stratigraphic gap is uncertain but it is obviously of post-GICE age and hence younger than the lower portion of the Oandu Stage (cf. Bergström et al., 2011a).

The next younger $\delta^{13}C_{org}$ excursion in the drill core is the Whitewater (Moe) excursion, which occurs in the upper *P. linearis* and lower *Dicellograptus complanatus* graptolite zones (Fig. 3). This excursion starts about 7 m below the top of the Fjäcka Shale, ranges through the top 1/3 of the unit and continues into the lower 3 m to 4 m of the Lindegård Formation. Most of the $\delta^{13}C_{org}$ values are between ~-29‰ and ~-30‰ but there is some value variation and peak values are as high as ~-27‰. According to Pålsson (2002), the graptolite zone index fossil *Dicellograptus complanatus* appears at the 88.56 m drill core level, which is taken as the base of the *D. complanatus* Zone. This level is slightly above the middle of the excursion. The Whitewater (Moe) excursion ends in the Lindegård Formation at ~ 82 m core depth, which according to Pålsson (2002) is still within the *D. complanatus* Zone. In a recent study, Ebbestad et al. (2015) identified a brief and very minor increase in $\delta^{13}C_{carb}$ values in two sections of the Boda Limestone in the Siljan area as this excursion, which was by these authors referred to as BC12. However, in the absence of any biostratigraphic control, this excursion identification remains tentative. The Röstånga succession is currently the only one in the world in which the range of the Whitewater (Moe) excursion can be directly tied to the graptolite zone succession.

A minor increase in $\delta^{13}C_{org}$ values around the 81 m drill core level may possibly correspond to a small unnamed excursion in the middle of the Estonian BC13 zone but in the absence of useful biostratigraphic evidence, this identification is problematic. This possible excursion may correspond to the poorly known North American Elkhorn excursion (Bergström et al., 2009a). This excursion interval appears to correspond approximately to the top of the *Tanuchitina bergstroemi* Chitinozoan Zone (Grahn and Nõlvak, 2007) but because the chitinozoan zone index species is not known from the Röstånga drill core, the precise level of the top of this chitinozoan zone remains uncertain.

In the drill core interval between approximately 66 m and 77 m there is a distinctive $\delta^{13}C_{org}$ shift of ~2‰ magnitude that we identify as the Paroveja excursion. Most of the isotopic values of this excursion are between -29‰ and -30‰ but there is also a peak value of -27.8‰ at the 75.5 m drill core level. This excursion is best known from the upper half of the Pirgu Stage in Estonia (e.g. Ainsaar et al., 2010) but it has recently been identified also in the Boda Limestone in three sections in the Siljan region in Dalarna (Ebbestad et al., 2014). The latter identification appears to be correct although supporting biostratigraphic evidence is lacking. The global distribution of this isotope excursion is still poorly known but Husinec and Bergström (2014) tentatively identified it in late Katian successions in South Dakota and on Anticosti Island, Quebec.

As noted above, the Hirnantian excursion (HICE) in the Röstånga drill core has recently been dealt with by Bergström et al. (2014) and reference to that study is made for pertinent information. In Fig. 7 we illustrate our interpretation of the relations between the excursions in the Röstånga drill core and those in the Jurmala R-1 drill core from Estonia (after Ainsaar et al., 2010). In order to remove some curve noise to facilitate comparison of the two curves, we use for the Röstånga 1 succession a 3-point average curve in this figure.

6. Comparison with the GSSP of the Katian Stage

Although the present study is centered on South Scandinavia and it is outside its scope to deal with the chemostratigraphy of Upper Ordovician sections globally, it is appropriate to make a comparison with the Katian GSSP at Black Knob Ridge in southeastern Oklahoma. This section was described in detail by Goldman et al. (2007), who also provided a $\delta^{13}C_{org}$ curve through the interval around the base of the type Katian Stage. Such a comparison is of special interest because this is the only section of this age in North America in which $\delta^{13}C_{org}$ has been investigated, and the GSSP section has useful conodont and graptolite biostratigraphy. Furthermore, such a comparison may assist in clarifying the position of the base of the Katian Stage in Baltoscandia, which has been unclear in the absence of a continuous graptolite succession having the basal Katian index species *Diplacanthograptus caudatus*. As shown in Fig. 8, there is a remarkable similarity between the $\delta^{13}C_{org}$ curves from Röstånga 1 and the Black Knob Ridge in especially the GICE interval, which supports the interpretation that the interval of the upper Sularp Shale and the Freberga Formation are equivalent to the uppermost Womble Shale and the lower part of the overlying Bigfort Chert. Importantly, the $\delta^{13}C_{org}$ chemostratigraphy also suggests that the base of the global Katian Stage corresponds to a level just below the prominent K-bentonite above the Kinnekulle K-bentonite in the Röstånga 1 succession (Fig. 8).

Although the key index graptolite *D. caudatus*, whose appearance level defines the base of the Katian Stage, has been recorded from several localities in Sweden, there is considerable doubt about both its appearance level at some localities and the specific identity of some of the reported Swedish specimens. The species was first recorded from the the upper Darriwilian in the Fågelsång succession by Hadding (1913), who recognized some differences to the typical form, especially in size, and this stratigraphically very early occurrence is now considered to represent a different species. Possibly more reliable records are from from the uppermost Örå Shale at its type locality in the Province of Jämtland (Thorslund, 1940; specimens determined by O. M. B. Bulman), where the species occurs in a *D. clingani* Zone fauna similar to that from the lower Mossen Formation of the Koängen drill core (Nilsson, 1977). The species has also been recorded, but not figured, in a similar fauna in the Mossen Formation of the Lindegård drill core in the Fågelsång area (Glimberg, 1962). Both these records appear to be biostratigraphically younger than the level of the base of the Katian Stage suggested by the present chemostratigraphic work in the Röstånga succession. This level appears to correspond to ~115 m level in the Röstånga drill core, which is ~2 m above the Kinnekulle bed (Fig. 8). Comparison with the graptolite-bearing Koängen drill core succession (cf. Fig. 5 and Nilsson, 1977) indicates that this level is in the upper part of the *D. foliaceus* Zone. Unfortunately, the graptolite fauna in this interval in the Koängen drill core has too little in common with that of the Katian GSSP to permit a graptolite-based correlation. However, the inferred position of the base of the Katian below the base of the *D. clingani* Zone in Scania is consistent with the appearance of *D. caudatus* below the appearance of *D. clingani* in the classical Hartfell Score in South Scotland (Zalasiewicz et al., 1995).

7. Age of the Kinnekulle K-bentonite

Few, if any, Ordovician ash beds have been subjected to so many radiometric datings as the Kinnekulle K-bentonite. As summarized by Huff (2008) there are at least 14 dating attempts using a variety of isotope techniques, and several more have followed in recent years. Still, its precise age has remained a matter of discussion. Many of these dating attempts reflect efforts to clarify the age relations between the Kinnekulle K-bentonite bed and the two most prominent Sandbian ash beds in eastern North America, which are known as the Deicke and the Millbrig K-bentonites (Huff et al., 1992, 1996). These thick and widespread ash beds, which represent some of the largest known volcanic ash falls in the Earth's Phanerozoic history, occupy a biostratigraphically similar position as the Kinnekulle K-bentonite (e.g. Huff et al., 1992). Although it is outside the scope of the present study to discuss the exact relations between these major ash beds, it should be noted that the U-Pb ages (453.6±6.6 Ma and 454.9±4.9 Ma) of the Kinnekulle bed recently reported by Bauert et al. (2014) using samples from is type section at Mossen on Kinnekulle, and from northern Estonia, respectively, clearly are based on samples from the Kinnekulle bed. On the other hand, the ages recorded by Sell et al. (2013) from the Kinnekulle bed on Bornholm and northern Estonia are most likely from beds above the Kinnekulle bed, probably from the Grimstorp bed complex. Their Bornholm sample was collected from the base of the classical Vasagård section but according to Kiipli et al. (2014), this bed is not the Kinnekulle bed. It probably corresponds to the ash bed between 87.25 m and 88.00 m in the Billegrav-2 drill core succession, that is, the topmost thick bed above the Kinnekulle bed. Their Estonian sample is stated to come from 3.5 m above what has been taken as the Kinnekulle bed in this rather condensed Estonian drill core succession. Hence, their ages, 454.41±0.17 Ma and 454.65±0.56 Ma, respectively should not be used without reservation as the precise isotopic age of the Kinnekulle K-bentonite.

Of special interest in the discussion of the precise isotopic age of the Kinnekulle K-bentonite is a recent dating (Svensen et al., 2015) based on samples from this bed in the well-known road cut outcrop along Slemmestadveien (Highway 165) at Vollen in the Oslo region, Norway (cf. Bergström et al., 1995, fig. 7). Eleven zircon grains gave a high-precision mean $^{206}Pb/^{238}U$ age of 454.52±0.50 Ma. Because the thick K-bentonite in the Arnestad Formation at Vollen can be correlated with confidence with the Kinnekulle K-bentonite bed at its reference locality at Mossen on Mt. Kinnekulle in Västergötland (Bergström et al., 1995), we consider this to be the most precise age of this prominent ash bed published thus far. It should be noted that this age is closely similar to that reported from the thick bed on Bornholm by Sell et al. (2013). It is also of interest that the radiometric age of 453.91± 0.37 Ma recorded by Svensen et al. (2015) for the post-Kinnekulle Grimstorp bed at Vollen is closely similar to that of the North American Deicke K-bentonite, which according to Sell et al. (2013) is 453.74 ±0.20 Ma.

In this connection it is also worth noting that two rather conspicuous K-bentonites are present in the Katian GSSP section at Black Knob Ridge in Oklahoma. They are located about 5 m below the top of the Womble Shale and 8.5-9 m below the base of the global Katian Stage. According to Sell et al. (2013), the two Black Knob Ridge K-bentonites have yielded U-Pb ages of 453.16.±0.24 and 453.98 ±0.33 Ma, respectively, that is, essentially the same age as the Deicke and Grimstorp K-bentonites. The radiometric ages now available suggest that the Kinnekulle K-bentonite is slightly older (approximately 454.50 Ma) than these ash beds, which is consistent with its different chemical composition.

8. Summary of conclusions

Although the present project started out as a more or less straightforward description of the $\delta^{13}C_{org}$ chemostratigraphy of the Upper Ordovician portion of the

Röstånga 1 drill core, the data assembled resulted in a number of partly unexpected results of more than local interest. These may be summarized as follows.

1. This is the first $\delta^{13}C_{org}$ investigation in the upper Sandbian through Katian successions of Sweden and one of the very few dealing with this interval in the entire world. Interestingly, the $\delta^{13}C_{org}$ trend through the study interval is closely similar to those based on $\delta^{13}C_{carb}$ from coeval successions elsewhere.
2. A characteristic development of the GICE is present in the upper portion of the Sularp Shale in an interval that by correlation with the Fågelsång succession is within the upper part of the *D. foliaceus* Zone.
3. Using K-bentonite bed correlation with the successions on Bornholm and in the Fågelsång area, the key Kinnekulle K-bentonite bed is identified in the Röstånga drill core succession where it occupies an interval 6-7m stratigraphically below the top of the Sularp Shale. This ash bed is overlain by several thick K-bentonite beds, the lower two of which appear to represent the Grimstorp K-bentonite bed complex of Bergström et al. (1995).
4. The GICE ranges from about two meters above the Kinnekulle bed up into the Mossen Formaton with a total stratigraphic thickness of approximately 11 m. This $\delta^{13}C_{org}$ curve has a striking similarity to the GICE $\delta^{13}C_{carb}$ curve recorded from the Solberga 1 drill core in Dalarna.
5. Apart from the GICE and the HICE, three isotope excursions are positively identified in the drill core, namely the Waynesville (Saunja), Whitewater (Moe) and Paroveja excursions. An additional excursion, possibly corresponding to the poorly known Elkhorn excursion in North America, may be present in the BC13 isotope zone between the Whitewater (Moe) and Paroveja excursions. The absence of the Kope (Rakvere) excursion above the GICE is interpreted as indicating a stratigraphic gap, or gaps, in the succession. The presence of such a gap is also suggested by the unusually small thickness of the Mossen Formation at Röstånga compared with that in the otherwise similar Fågelsång succession.
6. The new $\delta^{13}C_{org}$ chemostratigraphy integrated with available biostratigraphic data provide for the first time the ranges of the Waynesville (Saunja) and Whitewater (Moe) excursions in terms of graptolite biostratigraphy. This study also shows that the Whitewater excursion is located in the topmost part of the KA3 Stage Slice and lowermost part of the Ka4 Stage Slice of Bergström et al. (2009a).
7. The GICE $\delta^{13}C_{org}$ trend from the Röstånga 1 drill core shows a striking similarity to the $\delta^{13}C_{org}$ trend across the base of the Katian Stage at the Katian GSSP at Black Knob Ridge in Oklahoma, suggesting the possibility of detailed trans-Atlantic correlations between these successions, which have implications for both the graptolite and conodont zonal schemes. Using this chemostratigraphic correlation, and assuming the lack of a prominent stratigraphic gap at the base of the Katian in these sections, the base of the global Katian Stage would correspond to a level in the upper portion of the Sularp Shale and in the upper part of the *D. foliaceus* Zone in the Röstånga 1 drill core.

8. Some recently published precise radiometric ages of the Kinnekulle K-bentonite are based on samples from ash beds that are likely to be located stratigraphically slightly above the Kinnekulle bed. Recently, samples from the basal part of the Kinnekulle bed in the Oslo region, Norway gave a radiometric age of 454.52±0.50 Ma, which is slightly older than that of the Deicke K-bentonite in eastern North America (453.74 Ma).
9. Our new Röstånga 1 drill core data have clarified several previously very poorly known aspects of the classical succession in the Röstånga area. Although the many local manual excavations carried out by Hadding (1913) and Ekström (1937) provide useful information about the graptolite succession through the upper Darriwilian Almelund Shale (cf. Bergström et al., 2002), there are still several essentially unknown intervals, including much of the Sularp Shale. Because there are no outcrops of these intervals, a core drilling through the lower Sandbian and the Darriwilian sequence in all likelihood would yield many valuable new data and is clearly desirable.

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Figures

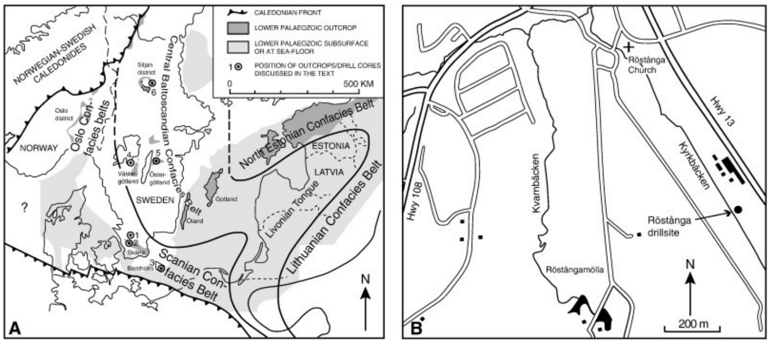

Fig. 1. A, sketch-map of Baltoscandia showing the distribution of confacies belts and the location of localities discussed in the text. 1. Röstånga; 2. Fågelsång; 3. Billegrav; 4. Mossen, Kinnekulle; 5. Borenshult; 6. Solberga.. B, Detailed map of part of the Röstånga area west of Highway 13 showing the location of the Röstånga 1 drill site and the Kyrkbäcken outcrop, which is situated a couple of hundred m from the drill site along the western side of the brook opposite the name Kyrkbäcken.

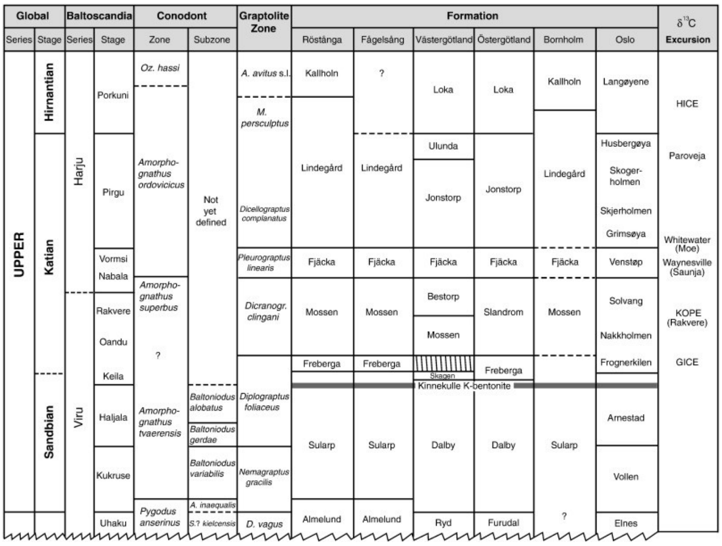

Fig. 2. Stratigraphic diagram showing lithostratigraphic, biostratigraphic, and chemostratigraphic terminology used in the present paper. Note the position of the Kinnekulle K-bentonite below the GICE.

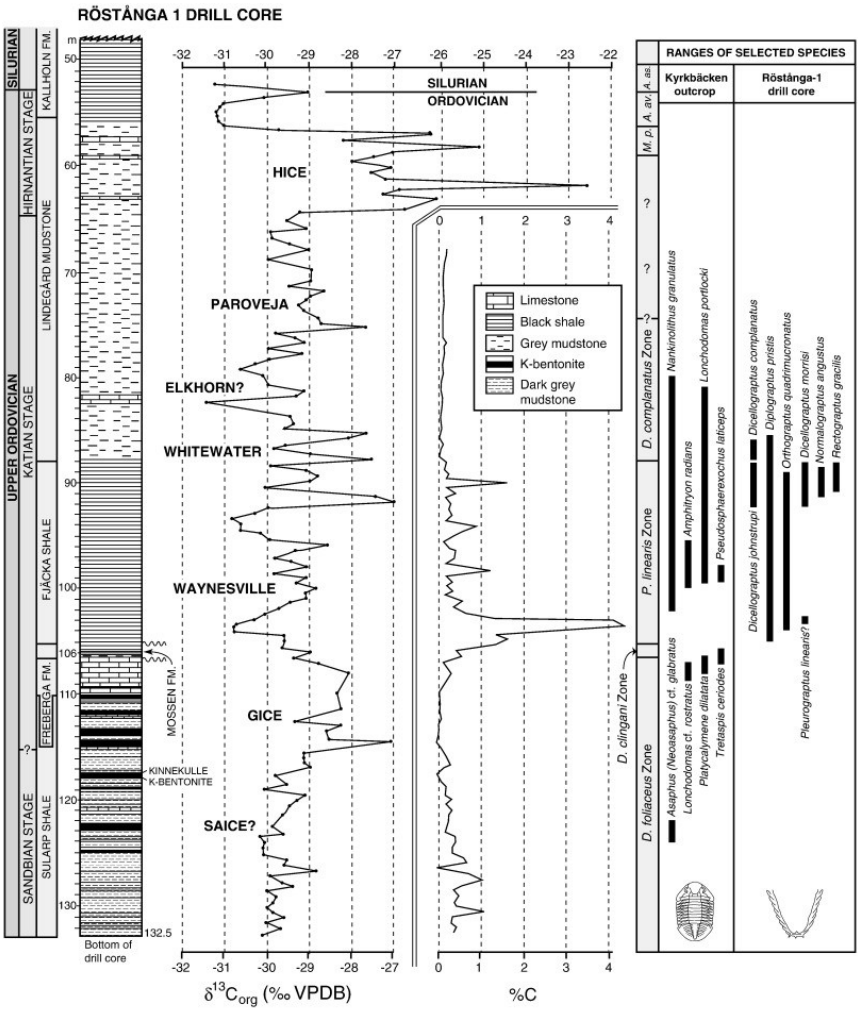

Fig. 3. Plot of $\delta^{13}C_{org}$ values and total C through the upper Sandbian, Katian, and Hirnantian portions of the Röstånga 1 drill core. Only the major K-bentonites in the upper part of the Sularp Shale are shown. Note the location of the Kinnekulle K-bentonite between the drill core levels 117 m and 118 m. The recognition of the Kinnekulle bed in the Scanian sections is based on the identification of this ash bed in the Billegrav-2 succession using trace elements (Kiipli et al., 2014). Also note the positions of the various $\delta^{13}C_{org}$ excursions recognized in the present study. In the right box of the figure, we illustrate the vertical ranges of some biostratigraphically significant trilobite and graptolite species, and the ranges of graptolite zones in the dill core. Note that this is the first time the Whitewater excursion has been documented from a biostratigraphically tightly controlled graptolite zone succession. Abbreviations of graptolite zone designations around the

Ordovician/Silurian boundary (cf. Bergström et al., 2014): *M. p,. Metabolograptus persculptus; A. av., Avitograptus avitus; A. as., Akidograptus ascensus.*

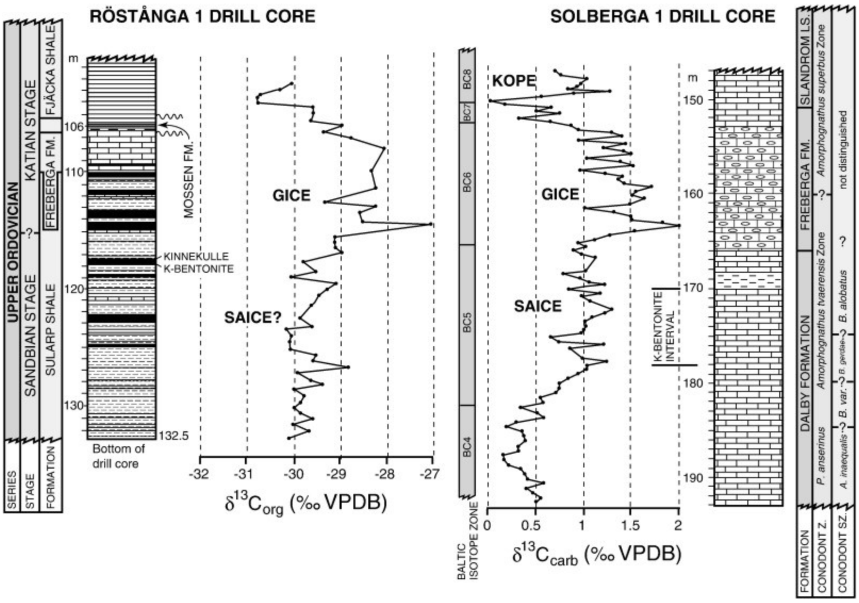

Fig. 4. Comparison between the early Katian $\delta^{13}C_{org}$ based GICE curve from the Röstånga 1 drill core and the $\delta^{13}C_{carb}$ based GICE curve of the Solberga 1 drill core from the Siljan region (from Lehnert et al., 2014). Note the close similarity between these curves, which indicates their great potential for close correlation between these successions.

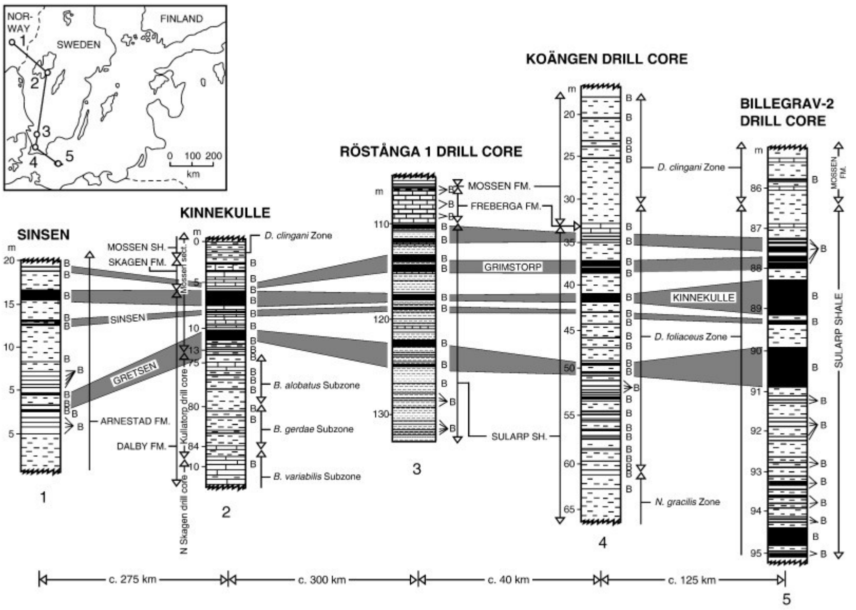

Fig. 5. Correlation of major upper Sandbian and lower Katian K-bentonites along an approximately 740 km long transect between the Billegrav-2 drill core (after Kiipli

et al., 2014), the Koängen drill core (Nilsson, 1977), the Röstånga 1 drill core, and the Kinnekulle and Sinsen successions (after Bergström et al., 1995).

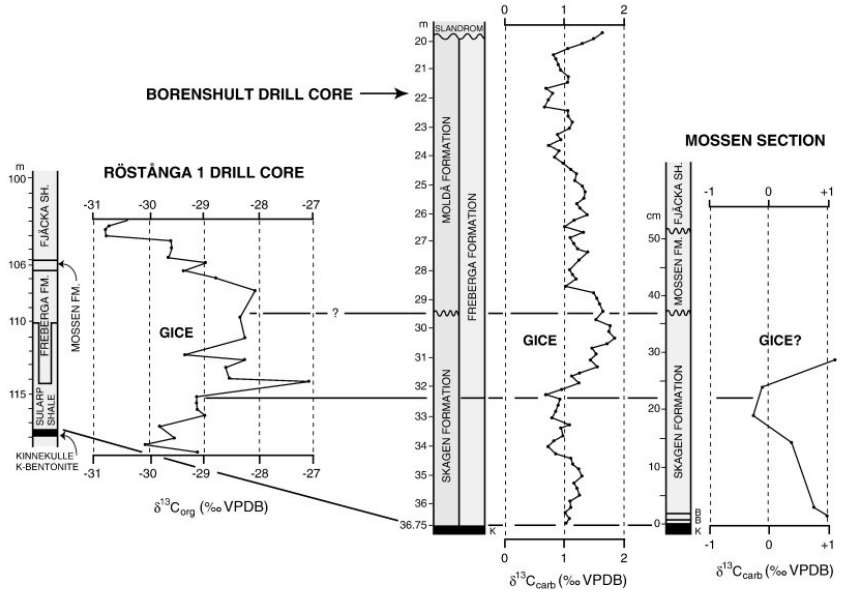

Fig. 6. Comparison of the $\delta^{13}C_{org}$ data through the GICE interval in the Röstånga 1 and Borenshult (after Bergström et al., 2012) drill cores and the Mossen outcrop (after Bergström et al., 2011a). For the location of these sies, see Fig. 1A. Note that the Röstånga 1 thickness values represent stratigraphic thickness. As shown in this figure, the thickness of the GICE interval in the Röstång 1 succession >8 m) is more than two times as large as in the Borenshult drill core (~3 m). Also note that based on chemostratigraphy, the base of the Moldå Formation in the Borenshult drill core corresponds to a level near the base of the Freberga Formation in the Röstånga succession.

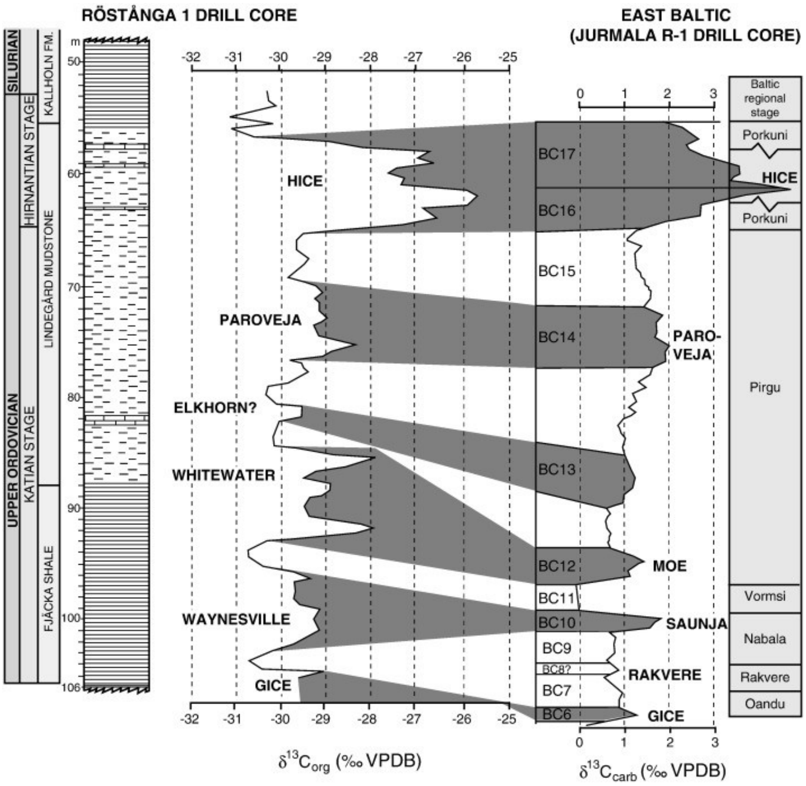

Fig. 7. Classification of the Katian and Hirnantian δ^{13}C excursions at Röstånga in terms of the North American (Bergström et al., 2009) and Baltic excursion terminology and isotope zones of Ainsaar et al. (2010). Note that the Rakvere (Kope) excursion is not recognized in the Röstånga succession indicating that the Estonian BC7 isotope zone is cut out by a gap in the succession. Such gaps, of locally and regionally variable magnitude, are common in the interval between the Freberga Formation and Fjäcka Shale in south-central Sweden (cf. Skoglund, 1963; Calner et al., 2010b). Also note that the unnamed excursion corresponding to the BC13 isotope zone is poorly developed in the Röstånga 1 drill core and its identification is questionable. As noted above, parts of the Katian $\delta^{13}C_{org}$ curve from the Röstånga 1 drill core are somewhat noisy, and for more easy comparison with the Estonian $\delta^{13}C_{carb}$ curve, we use in this figure 3-point average values in the Röstånga 1 isotopic curve.

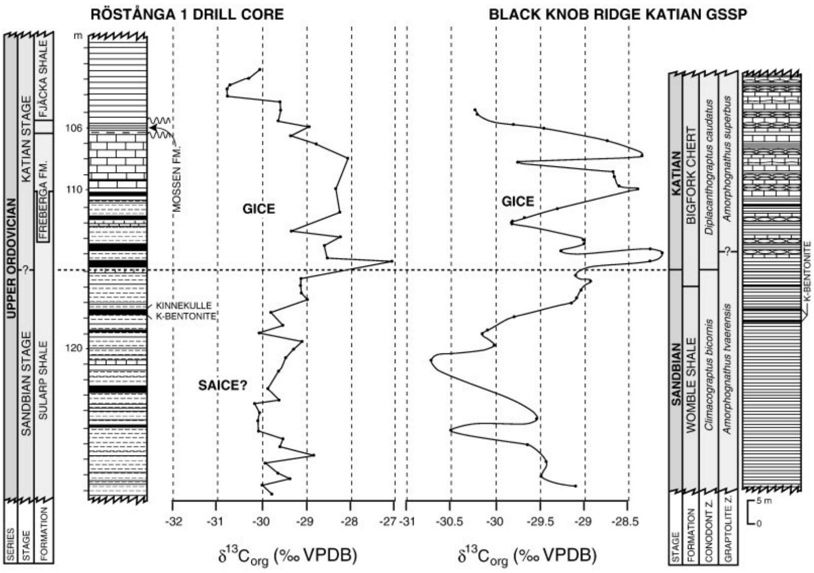

Fig. 8. Comparison between the upper Sandbian to lower Katian $\delta^{13}C_{org}$ curves from the Röstånga 1 drill core and the Katian GSSP at the Black Knob Ridge in Oklahoma (the latter after Goldman et al., 2007). Note the remarkable similarity between these isotope curves, especially in the GICE interval. Using $\delta^{13}C_{org}$ chemostratigraphy, the previously very poorly constrained location of the base of the Katian Stage in Baltoscandia is interpreted to be at a Röstånga 1 drill core level of approximately 115 m, which is slightly more than 2 m above the Kinnekulle K-bentonite. Based on this correlation, the upper, but not uppermost, Sularp Shale, which by comparison with the Koängen succession belongs to the *D. foliaceus* Zone, correlates with the upper Womble Shale (*C. bicornis* Zone). Also, the lower Bigfort Chert (*D. caudatus* Zone) appears to be equivalent to the uppermost Sularp Shale, the Freberga Formation, and the Mossen Formation.

Table 1. List of study samples showing total organic C (wt. %) and $\delta^{13}C_{org}$ (‰) data.

Sample	Sample (mg)	% C	$\delta^{13}C_{VPDB}$ (‰)
RÖST 68.5	49,756	0.12	− 29.9
RÖST 69	49,059	0.10	− 29.9
RÖST 69.5	48,981	0.09	− 29.5
RÖST 70	49,749	0.07	− 29.0
RÖST 70.5	48,647	0.06	− 29.0
RÖST 71	49,048	0.05	− 29.0
RÖST 71.5	48,924	0.09	− 29.5
RÖST 72	48,186	0.05	− 28.7
RÖST 72,5	49,188	0.07	− 29.0
RÖST 73	49,167	0.07	− 29.1

Sample	**Sample (mg)**	**% C**	**$\delta^{13}C_{VPDB}$ (‰)**
RÖST 73.5	49,100	0.07	− 29.3
RÖST 74	48,994	0.05	− 29.2
RÖST 74.5	48,578	0.05	− 28.8
RÖST 75	49,602	0.07	− 28.7
RÖST 75.5	49,334	0.05	− 27.8
RÖST 76	48,517	0.06	− 29.8
RÖST 76.5	49,476	0.05	− 29.4
RÖST 77	48,965	0.05	− 29.1
RÖST 77.5	48,930	0.10	− 30.0
RÖST 78	48,131	0.08	− 29.2
RÖST 78.5	48,799	0.08	− 29.9
RÖST 79	49,186	0.08	− 30.3
RÖST 79.5	48,918	0.07	− 30.7
RÖST 80	48,823	0.06	− 30.1
RÖST 81	48,974	0.07	− 30.0
RÖST 81.5	48,561	0.03	− 29.1
RÖST 82	49,096	0.06	− 29.3
RÖST 82.5	48,714	0.07	− 31.5
RÖST 84	48,978	0.07	− 29.5
RÖST 84.5	48,726	0.06	− 29.4
RÖST 85	48,509	0.07	− 29.6
RÖST 85.5	49,794	0.05	− 27.7
RÖST 86	48,711	0.04	− 28.1
RÖST 86.5	49,420	0.17	− 29.6
RÖST 87	48,478	0.18	− 29.8
RÖST 87.5	49,558	0.06	− 29.0
RÖST 88	49,055	0.06	− 27.8
RÖST 88.5	48,971	0.46	− 29.9
RÖST 89	48,633	0.15	− 29.2
RÖST 89.5	49,000	0.11	− 28.9
RÖST 90	48,556	0.13	− 29.0
RÖST 90.5	48,374	1.56	− 30.1
RÖST 91	49,300	0.16	− 29.1
RÖST 91.5	49,510	0.46	− 27.5
RÖST 92	49,777	0.10	− 27.1
RÖST 92.5	48,814	0.21	− 30.0
RÖST 93	48,897	0.22	− 30.4

Sample	**Sample (mg)**	**% C**	**$\delta^{13}C_{VPDB}$ (‰)**
RÖST 93.5	48,679	0.26	− 30.9
RÖST 94	49,776	0.17	− 30.7
RÖST 94.5	49,282	0.47	− 30.7
RÖST 95	49,842	0.61	− 30.2
RÖST 95.5	48,553	0.37	− 30.0
RÖST 96	49,132	0.10	− 28.6
RÖST 96.5	49,811	0.23	− 29.4
RÖST 97	49,759	0.43	− 29.9
RÖST 97.5	48,743	0.27	− 29.5
RÖST 98	48,368	0.22	− 29.3
RÖST 98.5	48,927	1.18	− 29.9
RÖST 99	48,627	0.21	− 29.2
RÖST 99.5	48,456	0.31	− 29.4
RÖST 100	48,720	0.15	− 28.9
RÖST 100.5	48,441	0.21	− 29.2
RÖST 101	48,639	0.18	− 29.2
RÖST 101.5	48,401	0.31	− 29.5
RÖST 102	48,560	0.40	− 29.8
RÖST 102.5	48,367	0.61	− 30.1
RÖST 103	49,023	1.22	− 30.4
RÖST 103.5	9638	4.17	− 30.8
RÖST 104	9890	4.39	− 30.8
RÖST 104.5	8806	1.41	− 29.6
RÖST 105	49,171	1.26	− 29.6
RÖST 105.5	48,336	1.39	− 29.6
RÖST 106	48,993	0.45	− 29.0
RÖST 106.5	48,292	0.52	− 29.4
RÖST 107	49,893	0.17	− 27.9
RÖST 108	48,887	0.31	− 28.1
RÖST 110	48,537	0.09	− 28.4
RÖST 111.2	49,309	0.06	− 28.7
RÖST 111.8	48,292	0.08	− 29.4
RÖST 112.5	48,418	0.09	− 29.2
RÖST 113	49,354	0.07	− 28.6
RÖST 113.5	48,938	0.07	− 28.7
RÖST 114.1	48,473	0.02	− 28.6
RÖST 114.5	48,321	0.02	− 27.4

Sample	Sample (mg)	% C	$\delta^{13}C_{VPDB}$ (‰)
RÖST 115.6	48,444	0.13	− 29.1
RÖST 116	48,713	0.23	− 29.1
RÖST 116.5	48,392	0.35	− 29.1
RÖST 117	49,466	0.22	− 29.0
RÖST 117.65	48,902	0.02	− 29.8
RÖST 118.5	48,606	0.10	− 29.6
RÖST 119	49,863	0.21	− 30.1
RÖST 119.5	49,016	0.23	− 29.2
RÖST 120	48,857	0.28	− 29.4
RÖST 120.5	48,924	0.23	− 29.5
RÖST 121	48,960	0.32	− 29.6
RÖST 121.5	48,438	0.25	− 29.7
RÖST 122.3	49,387	0.26	− 29.9
RÖST 123.2	49,303	0.20	− 29.8
RÖST 123.5	49,281	0.44	− 30.2
RÖST 124	49,231	0.42	− 30.1
RÖST 124.5	48,854	0.35	− 30.1
RÖST 125	48,391	0.33	− 30.1
RÖST 125.5	48,396	0.64	− 29.5
RÖST 126	48,313	0.71	− 29.6
RÖST 126.5	48,248	0.03	− 28.8
RÖST 127	48,731	0.72	− 29.9
RÖST 127.5	49,253	1.07	− 29.7
RÖST 128	49,854	0.54	− 29.4
RÖST 128.5	48,998	0.44	− 30.0
RÖST 129	49,492	0.49	− 29.8
RÖST 129.5	49,785	0.41	− 29.9
RÖST 130	48,724	0.42	− 30.0
RÖST 130.5	48,333	1.15	− 29.9
RÖST 131	49,570	0.30	− 29.6
RÖST 131.5	48,596	0.26	− 30.0
RÖST 132	48,436	0.48	− 29.7
RÖST 132.5	49,293	0.39	− 30.1