Darriwilian (Middle Ordovician) $\delta^{13}C_{carb}$ chemostratigraphy in the Precordillera of Argentina: Documentation of the middle Darriwilian Isotope Carbon Excursion (MDICE) and its use for intercontinental correlation

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ABSTRACT

Although documented from Estonia, Latvia, Sweden, eastern North America, and China, the Middle Ordovician (Darriwilian) positive $\delta^{13}C$ excursion known as the MDICE has previously not been recognized with certainty in South America. The most promising region in South America for detailed Middle Ordovician carbon isotope research is the Precordillera of western Argentina, where there are many excellent exposures of biostratigraphically well-dated carbonate successions spaning the Tremadocian through Sandbian stratigraphic interval. For this project, we collected numerous isotope and conodont samples from the middle Darriwilian Las Chacritas and Aguaditas formations at their type localities, which yielded important biostratigraphic data as well as informative $\delta^{13}C_{carb}$ values. In the *E. pseudoplanus* Zone in the upper half of the Las Chacritas Formation, there is a relatively modest but distinct $\delta^{13}C_{carb}$ excursion. Because its stratigraphic position and magnitude closely agree with the MDICE in other parts of the world, we recognize it as the first firm record of this excursion in South America. The fact that the $\delta^{13}C_{carb}$ curve from the Las Aguaditas Formation shows no such excursion is due to the existence of a stratigraphic gap between the Lower and Middle Members of this formation that cuts out the excursion interval. The Precordilleran MDICE is used for detailed long-range correlations with successions in Baltoscandia, Newfoundland, and China illustrating the usefulness of also this $\delta^{13}C_{carb}$ excursion as a global stratigraphic tool. A recent proposal of a greatly extended chronostratigraphic range of the Table Head Group on Newfoundland is rejected based on well-established biostratigraphic evidence.

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1. Introduction

One of the least studied among the named Ordovician positive $\delta^{13}C$ excursions (Fig. 1) is the Middle Darriwilian Isotope Carbon Excursion that is commonly known as the MDICE. It was first recognized in the Middle Ordovician of Baltoscandia (Ainsaar et al., 2004, 2010; Meidla et al., 2004; Martma, 2005; Kaljo et al., 2007; Schmitz et al., 2010) and has later been recorded also in the Yangtze Platform of China (Schmitz et al., 2010) and eastern United States (Leslie et al., 2011). In Baltoscandia, this relatively small but geographically very widespread excursion has been identified in several drillcores in Estonia and Latvia (e.g. Ainsaar et al., 2010). Swedish records include surface sections in the Hällekis and Gullhögen quarries in the Province of Västergötland (Ainsaar et al., 2010; Schmitz et al., 2010) and at

Kårgärde in the Province of Dalarna (Ainsaar et al., 2010). The first records from China are from sections at Maocaopu in Hunan Province and Puxi River in Hubei Province, both localities being situated on the Yangtze Platform (Schmitz et al., 2010). The only previous record of MDICE in the United States is from the eastern thrust belts in the Appalachian Mountains near Clear Spring, Maryland (Leslie et al., 2011). Although a small $\delta^{13}C$ excursion in the uppermost San Juan Formation in the Precordillera of western Argentina (Buggisch et al., 2003) has been compared with MDICE (Ainsaar et al., 2010), Schmitz et al. (2010) noted that additional study was needed to clarify the precise biostratigraphic position of this excursion before it could be positively identified as the MDICE. New data to be presented below indicate that this excursion is not MDICE but a slightly older carbon isotope excursion. In a recent paper, Thompson et al. (2012) presented >70 $\delta^{13}C$ values from the Las Aguaditas and Las Chacritas formations in the Precordillera of Argentina and they suggested that these elevated values may represent the MDICE. Regrettably, the $\delta^{13}C$ values from these formations were not separated but combined in points plotted in their Fig. 3. Furthermore, because they lacked

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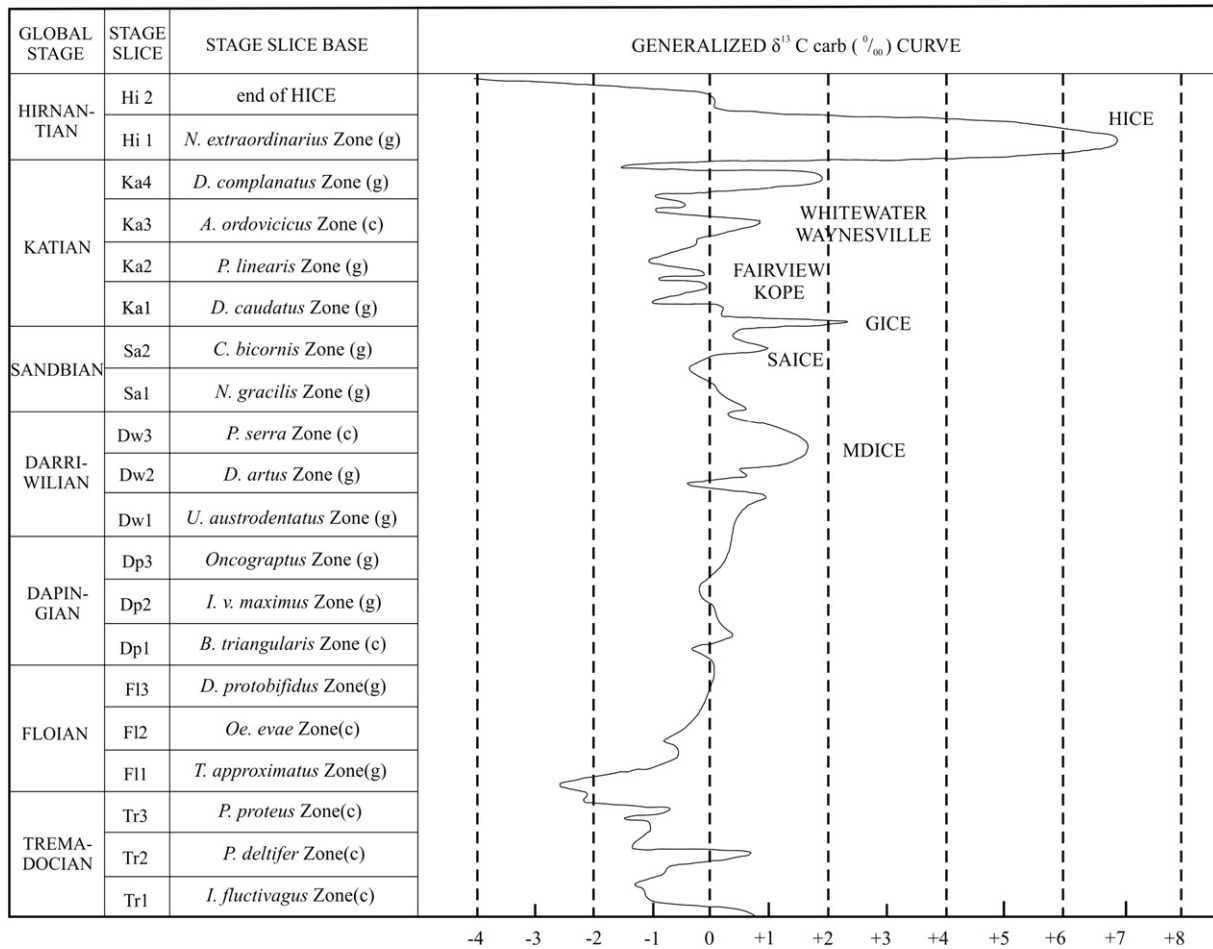
GLOBAL STAGE	STAGE SLICE	STAGE SLICE BASE	GENERALIZED δ¹³C carb (‰) CURVE
HIRNAN-TIAN	Hi 2	end of HICE	
	Hi 1	*N. extraordinarius* Zone (g)	
KATIAN	Ka4	*D. complanatus* Zone (g)	
	Ka3	*A. ordovicicus* Zone (c)	
	Ka2	*P. linearis* Zone (g)	
	Ka1	*D. caudatus* Zone (g)	
SANDBIAN	Sa2	*C. bicornis* Zone (g)	
	Sa1	*N. gracilis* Zone (g)	
DARRI-WILIAN	Dw3	*P. serra* Zone (c)	
	Dw2	*D. artus* Zone (g)	
	Dw1	*U. austrodentatus* Zone (g)	
DAPIN-GIAN	Dp3	*Oncograptus* Zone (g)	
	Dp2	*I. v. maximus* Zone (g)	
	Dp1	*B. triangularis* Zone (c)	
FLOIAN	Fl3	*D. protobifidus* Zone(g)	
	Fl2	*Oe. evae* Zone(c)	
	Fl1	*T. approximatus* Zone(g)	
TREMA-DOCIAN	Tr3	*P. proteus* Zone(c)	
	Tr2	*P. deltifer* Zone(c)	
	Tr1	*I. fluctivagus* Zone(c)	

Labels on curve: HICE, WHITEWATER, WAYNESVILLE, FAIRVIEW, KOPE, GICE, SAICE, MDICE

Axis: -4 -3 -2 -1 0 +1 +2 +3 +4 +5 +6 +7 +8

Fig. 1. Generalized δ¹³C$_{carb}$ curve and its relations to global stages and stage slices. Note the position of the MDICE in Stage Slices Dw2 and Dw3. Figure is slightly modified after Bergström et al. (2012).

access to any useful biostratigraphic data from these formations, their data were illustrated in a generalized biostratigraphic framework based on sections elsewhere with no consideration to the fact that these formations differ greatly in stratigraphic range and thickness. Hence, the chemostratigraphic data presented by Thompson et al. (2012) in their pioneer study are not very useful for detailed regional comparisons. In another recent paper, Thompson and Kah (2012) provided the first δ¹³C data from the Darriwilian Table Head Group of western Newfoundland in Canada. Because these were adequately tied to specific stratigraphic levels in biostratigraphically well-studied sections, these data are important and useful. Based on these data, Thompson et al. (2012) recognized the MDICE in the Table Head Group succession.

As described in numerous papers, there is a substantial number of excellent sections in the Argentine Precordillera exposing Lower and Middle Ordovician strata in carbonate facies. The most widely distributed and prominent stratigraphic unit is the locally more than 330 m thick San Juan Formation that ranges in age from the late Tremadocian to the early–middle Darriwilian. Based on detailed conodont biostratigraphy, the top of the San Juan Formation appeared to be slightly older than the base of the MDICE interval. The San Juan Formation is in most outcrops overlain by successions of mudstones and shales, which are classified as the Gualcamayo, Los Azules and other formations. These formations are dominantly clastic and hence unsuitable for obtaining detailed δ¹³C$_{carb}$ records through substantial stratigraphic intervals. However, in two long and well-exposed sections, the San Juan Forma-tion is overlain by middle–upper Darriwilian, dominantly calcareous,

strata suitable for carbon isotope work. At one of these outcrops, which is known as the Las Chacritas River section, there is an approxi-mately 55 m thick succession of marly limestone and dark shale and mudstone, which was classified as the Las Chacritas Formation by Peralta et al. (1999). In our study section along the river just east of the Las Chacritas stall and to the south of the type section, across the hill that separates both profiles, the exposed thickness of the unit is about 50 m. In this study area, the Las Chacritas Formation is uncon-formably overlain by the Sandbian Las Aguaditas Formation (Peralta et al., 1999; Heredia et al., 2005) although this unit is covered or missing by a stratigraphic gap in our study section. Heredia (2012) redefined the whole Ordovician succession between the San Juan Formation and the mostly Silurian La Chilca Formation as the Las Aguaditas Formation despite the significant stratigraphic differences between these two units recognized by Peralta et al. (1999). Herein, we follow the classifica-tion by the latter authors and maintain the designation Las Chacritas for our study unit.

The other locality, referred to as Las Aguaditas (Baldis et al., 1982), is in a more western outcrop belt than that of Las Chacritas and sep-arated from the latter locality by a distance of approximately 25 km. At Las Aguaditas there is a ca. 330 m thick succession of dominantly calcareous strata, classified as the Las Aguaditas Formation, which in age ranges from the middle Darriwilian to the late Sandbian (Lehnert, 1995; Ortega and Albanesi, 1998). Recent detailed conodont biostratigraphic studies, which are largely presented herein, suggest that these two formations were likely to cover at least a portion of the MDICE interval. The taxonomic and biostratigraphic studies for

the sections of Las Chacritas and Las Aguaditas were carried out as original works by F. Serra and N. A. Feltes, respectively, in their undergraduate theses (Universidad Nacional de Córdoba, Argentina), which are unpublished. Although the results of these studies were referred to in Serra et al. (2011) and Albanesi et al. (2012), the details of the stratigraphic sampling, taxonomic descriptions, as well as the analyses of biozones and biofacies will be published elsewhere.

The purpose of the present research was to investigate the Darriwilian δ¹³C chemostratigraphy in the Precordillera with special focus on the possible occurrence of MDICE in the Las Chacritas and Las Aguaditas formations. Provided that the MDICE could be firmly identified, a second study goal was to use this excursion as a precise chemostratigraphic tool for long-range correlations with MDICE successions on other continents. In view of the marked global biogeographic differentiation of Ordovician marine faunas, such correlations are commonly difficult to establish by fossils. However, investigations during the past few years (e.g. Bergström et al., 2006, 2010, 2011, 2012; Ainsaar et al., 2010; Munnecke et al., 2011) have clearly shown that several of the named Ordovician δ¹³C excursions have a global distribution and can be used very successfully as chronostratigraphic tools.

2. Geological setting

The geological province of Precordillera is located in the northwestern region of Argentina (Fig. 2). It is bordered by the Sierras Pampeanas to the east and the Cordillera Frontal to the west, and has an extension of 450 km north-south and 110 km east-west (Furque and Cuerda, 1979). The stratigraphy is characterized by an up to 2300 m thick succession of Cambro-Ordovician limestones, which to the east were deposited in platform environments. To the west these sediments interdigitate with clastic slope deposits (Keller et al., 1993; Astini et al., 1996).

The Precordillera Central represents the only Lower Paleozoic basin in South America with a platform sedimentary sequence of diverse carbonate rocks deposited in a range of environments ranging from shallow intertidal to marginal shelf or deep distal ramp settings (Cañas, 1999; Bordonaro, 2002).

3. Stratigraphy

For a general review of the stratigraphic classification of Darriwilian and Sandbian strata in the Precordillera, see Fig. 3.

3.1. The Las Aguaditas Formation

The Las Aguaditas Formation crops out along the eastern flank of Los Blanquitos Range, 15 km southwest of the Town of Jáchal (Fig. 2) in the Precordillera Central of the San Juan Province (Keller et al., 1993). This formation consists of marls, limestones, and reef limestones. They are characterized by their yellowish weathering color and are clearly distinguishable from the rocks of the underlying San Juan Formation (Baldis et al., 1982), the upper part of which consists of nodular limestone. The thickness of the Las Aguaditas Formation is approximately 330 m, and the unit ranges in age from the middle Darriwilian to the early Sandbian (Keller et al., 1993).

In their original description of the Las Aguaditas Formation, Baldis and Blasco (1974) differentiated four members. In the Blaquintos Range, the Las Aguaditas Formation rests paraconformably on the San Juan Formation (Fig. 4), the formational contact being marked by a regional hardground surface (Astini, 1995). The biostratigraphic age of the top of the San Juan Formation at Las Aguaditas Creek, which was proposed as Floian by Sarmiento et al. (1986), was revised by Albanesi et al. (1998) to middle Darriwilian. The lower member of Las Aguaditas Formation correlates with the Las Chacritas and Gualcamayo formations (Astini, 1994). In the type section, the upper part of the Las Aguaditas Formation is referable to the lower Sandbian Amorphognathus tvaerensis Zone based on conodonts (Albanesi and Ortega, 1998). Baldis and Blasco (1974) recognized a stratigraphic gap between the upper member of Las Aguaditas Formation and the overlying uppermost Ordovician–Silurian La Chilca Formation.

The Las Aguaditas Formation is an important unit because, along with the Las Chacritas and Sassito formations, it is the only representation of carbonate deposits younger than the carbonate depositional cycle represented by the San Juan Formation in the entire Precordillera (Astini, 1995, 1999). Sedimentological analyses show that Las Aguaditas Formation is the only carbonate succession in the Precordillera showing a transition from a platform depositional environment to a slope environment (Keller et al., 1993). Carrera and Astini (1998) characterized the top part of the San Juan Formation as representing a distal ramp environment, with a low degree of storm influence. It is overlain by a calcareous–pelitic unit that forms a transition to the Las Aguaditas Formation. As there is no evidence of a hiatus at the formational contact, the sudden occurrence of a mixed calcareous–pelitic unit is interpreted as caused by a flooding
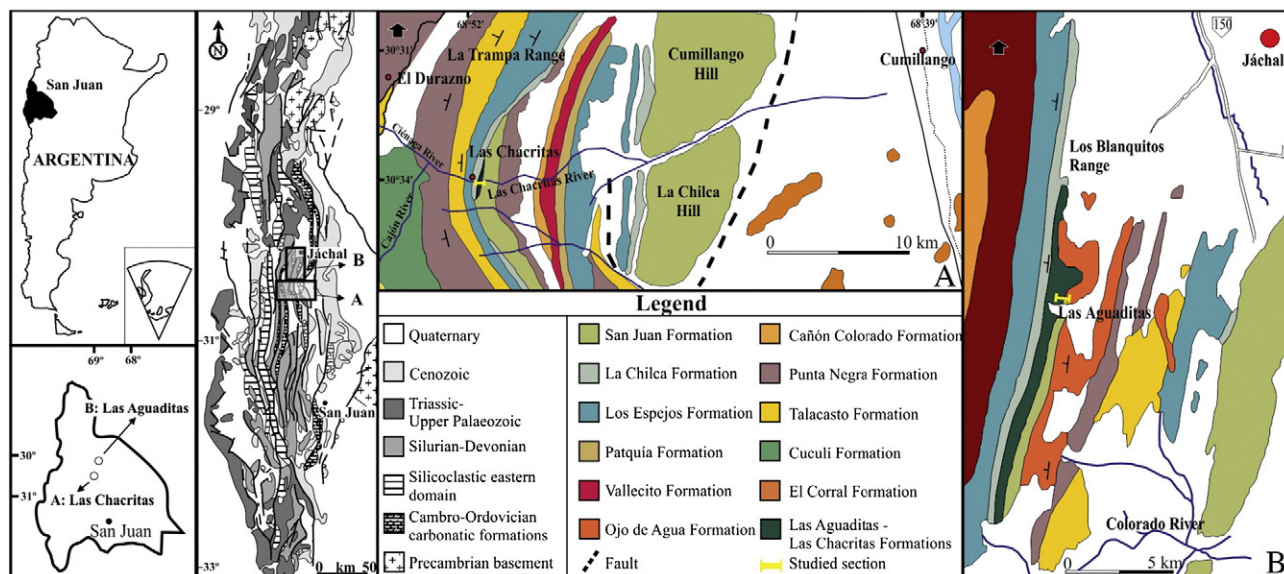

Fig. 2. Geologic map of part of the Argentine Precordillera showing location of study localities.

Fig. 3. Stratigraphic diagram showing relations between conodont zone and subzone classifications in Argentina and other study regions. Baltoscandic column after Zhang (1998a), Rasmussen (2001) and Löfgren and Tolmacheva (2008); Newfoundland column after Stouge (1984); China column after Zhang (1998a); and Precordillera column after Albanesi and Ortega (2002), Albanesi (in Benedetto et al., 2007) and Serra et al. (2011). Abbreviations: *Eopl.*, *Eoplacognathus*; *Yangtz.*, *Yangtzeplacognathus*; *S. ki.*, *Sagittodontina? kielcensis*; *E. li.*, *Eoplacognathus lindstroemi*; *E. ro.*, *Eoplacognathus robustus*; *E. re.*, *Eoplacognathus reclinatus*; *Y. fo.*, *Yangtzeplacognathus foliaceus*; *P.*, *Pygodus*; *Py. lunn.*, *Pygodus lunnensis*; *M. oz.*, *Microzarkodina ozarkodella*; *Mi. hag.*, *Microzarkodina hagetiana*; *Ph. polonicus*, *Phragmodus polonicus*; *C. sweeti*, *Cahabagnathus sweeti*; *C. friendsvillensis*, *Cahabagnathus friendsvillensis*; *Y.*, *Yangtzeplacognathus*; *Dzik. tablepointensis*, *Dzikodus tablepointensis*; *Py. anitae*, *Pygodus anitae*; *Yangtz. crassus*, *Yangtzeplacognathus crassus*.

event on the platform and the beginning of a new depositional cycle (Keller et al., 1993). The combined effects of tectonics and eustatic events may have been the cause of the basin drowning (Astini et al., 1995; Astini, 1999).

In the global cycle of warming and cooling in the Ordovician, the first cooling peak was reached during the middle Darriwilian (Webby, 1984). This was followed by a rapid warming and a rapid sea level rise and the deposition of black shales and mudstones (Fortey, 1984). This led to a facies change and a platform expansion formed by hemipelagic limestone at the transition to the lower member of the Las Aguaditas Formation (Keller et al., 1993). The latter authors suggested a deep water depositional environment with typical slope rocks for the Las Aguaditas Formation.

In the type section there is a marked faunal change between the San Juan Formation and Las Aguaditas Formation, which is associated with an environmental change observable in the lithology. The top part of the San Juan Formation is dominated by sponges while Las Aguaditas Formation is dominated by bryozoans (Carrera, 1997; Carrera and Ernst, 2010). The dominance of the latter group indicates an adverse paleoenvironmental change for the sponge fauna. This could be caused by global and local changes, such as decrease in temperature, sea level rise, Precordillera migration to higher latitudes (Astini, 1995), an increase in nutrients and turbidity, all limiting the platform carbonate development, and favoring the development of bryozoans (Wood, 1993). In 1995, Huff and colleagues discovered K-bentonites in the transition between the San Juan and Los Azules Formations (Huff et al., 1997). These may have led to an increase locally in nutrients. This faunal turnover coincides with a change in global sea level (Webby et al., 2004).

Albanesi et al. (1998) recorded the *Lenodus variabilis* conodont Zone in the upper part of the San Juan Formation at Las Aguaditas Creek. The conodont biostratigraphy through the contact interval between these two units is revised herein (cf. Hünicken and Ortega, 1987; Sarmiento et al., 1988; Lehnert, 1995; Albanesi et al., 1998; Albanesi and Astini, 2000; Ortega et al., 2007; Mestre, 2012). In the Precordillera, the maximum diversification of conodonts occurred in the *H. sinuosa–E. suecicus* interval (Albanesi and Bergström, 2004, 2010). The *Eoplacognathus pseudoplanus* Zone, located between the *L. variabilis* and *E. suecicus* zones, was identified in the Sierra de la

Invernada Formation at the eponymous locality (Albanesi et al., 2009; Ortega et al., 2010). This biostratigraphic unit occupies the upper part of the *L. variabilis* Zone in the previous conodont scheme of the Precordillera published by Albanesi and Ortega (2002), and overlies the *Yangtzeplacognathus crassus* Zone in the recently proposed biozonal succession (Serra et al., 2011).

Eberlein (1990) and Lehnert (1995) recognized the *Pygodus serra* and *Pygodus anserinus* zones in the middle and upper parts of Las Aguaditas Formation. Our revision of the conodont taxonomy and biostratigraphic sampling suggests that the *P serra* Zone is missing and that the first record of *P. anserinus* is directly above strata having a conodont species association of the *E. pseudoplanus* Zone. A hiatus in between these biozones is verified by the record of a graptolite association from the Sandbian Stage, which consists of *Leptograptus*, *Dicellograptus*, *Dicranograptus*, *Pseudoclimacograptus*, *Archiclimacograptus*, and *Acrograptus*, at 10 m from the base of the Middle Member of the Las Aguaditas Formation. In the top strata of the formation, the presence of the graptolite *Nemagraptus gracilis* indicates the basal part of the Upper Ordovician. Also present in this interval is *A. tvaerensis* (Albanesi and Ortega, 1998), associated with typical open sea conodonts such as *Baltoniodus variabilis*, *B. gerdae* and *Cahabagnathus sweeti* (Albanesi and Ortega, 1998; Lehnert et al., 1999).

The outer-shelf environments represented by the San Juan and Las Chacritas formations, as well as much of the Lower Member of Las Aguaditas Formation, show the highest conodont species diversity. This is probably due to a shallow-deep water exchange through the thermocline, as well as nutrient enrichment as a product of upwelling currents (Albanesi et al., 2006).

3.2. The Las Chacritas Formation

The outcrop of this formation at the Las Chacritas River (Baldis and Chebli, 1969) is located in the northern section of the La Trampa Range, southwest of Jáchal (Fig. 2) in the Central Precordillera of the San Juan Province. This formation was first formally studied by Espisúa (1968), and has later been investigated by Peralta and Baldis (1995), Astini (1994), and Carrera and Astini (1998). It was finally properly defined by Peralta et al. (1999).
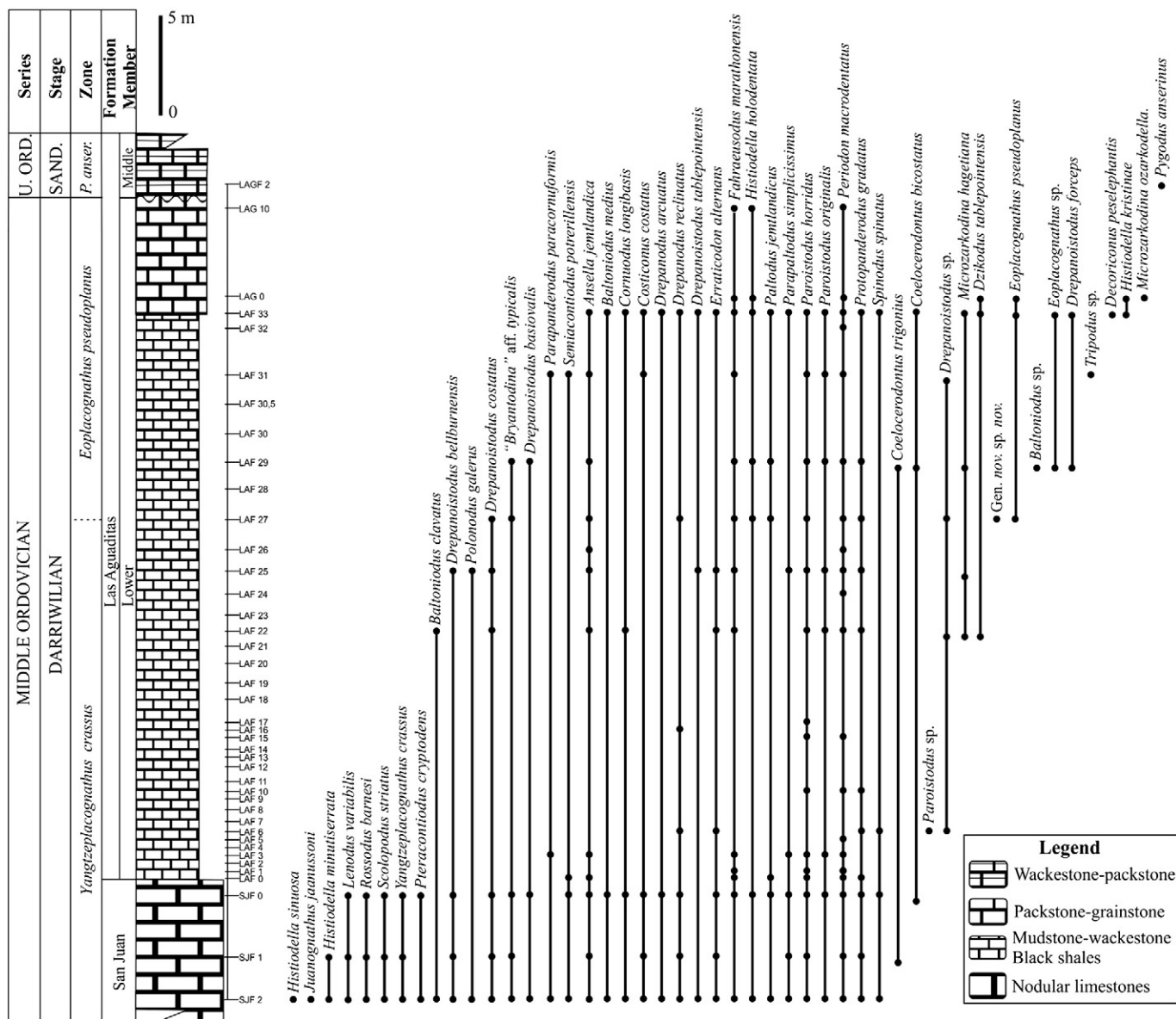
Fig. 4. Ranges of conodont taxa and conodont biostratigraphy of the Las Aguaditas Formation (Lower and basal Middle members) at the Las Aguaditas section. Abbreviations: U. Ord., Upper Ordovician; Sand., Sandbian; *P. anser.*, *Pygodus anserinus*.

In the Las Chacritas River valley the base and top of the Las Chacritas Formation are well exposed. Our study succession (Fig. 5) begins in the upper Lower to lower Middle Ordovician San Juan Formation, which is composed of fossiliferous limestone and dolomite with conspicuous chert nodules. The San Juan Formation is conformably overlain by the Las Chacritas Formation of early Darriwilian age. The Las Chacritas Formation is paraconformably overlain by lower Sandbian deposits referred to the Las Aguaditas Formation, with a stratigraphic gap corresponding to the middle and upper Darriwilian. The Las Aguaditas Formation is in turn overlain by the La Chilca Formation (Fig. 5), an uppermost Ordovician to lower Silurian fine-grained siliciclastic unit (Peralta et al., 1999; Heredia et al., 2005).

The Ordovician stratigraphic succession exposed along the Las Chacritas River area is composed of dark gray carbonates, marls and mixed carbonate/siliciclastic sediments, which were deposited in an open sea shelf setting (Carrera, 1997). The Las Chacritas Formation is a relatively thick succession of fine-grained siliciclastic/carbonate strata, in which two members have been recognized by Peralta et al. (1999), who estimated a total formation thickness of 55 m in their

study section. According to these authors, the Lower Member is 38 m thick with a bed of K-bentonite present at the contact with the San Juan Formation. The Las Chacritas Formation is made up of tabular, thin to medium bedded, fossiliferous, dark mudstone, and nodular wackestone to packstone. Synsedimentarily deformed beds occur in the middle and upper part of the unit, indicating a transport toward north on a deepening slope. The Upper Member is 17 m thick and it is composed of thin-bedded wackestone, bioclastic grainstone, mudstone, and spiculitic mudstone. It is very fossiliferous with increased fossil content towards the top (Carrera and Astini, 1998; Peralta et al., 1999).

At the Las Chacritas section, Albanesi and Astini (1994) reported conodonts from the *Eoplacognathus suecicus* Zone at the top of the San Juan Formation (*sensu* the original designation by Espisúa, 1968; i.e., the upper part of the Las Chacritas Formation of recent authors). Lehnert (1995) recorded the *E. suecicus* and *P serra* conodont zones from the uppermost part of the same formation. The *L. variabilis* Zone in the lower Las Chacritas Formation was first mentioned by Peralta et al. (1999) and was later verified by Albanesi and Ortega

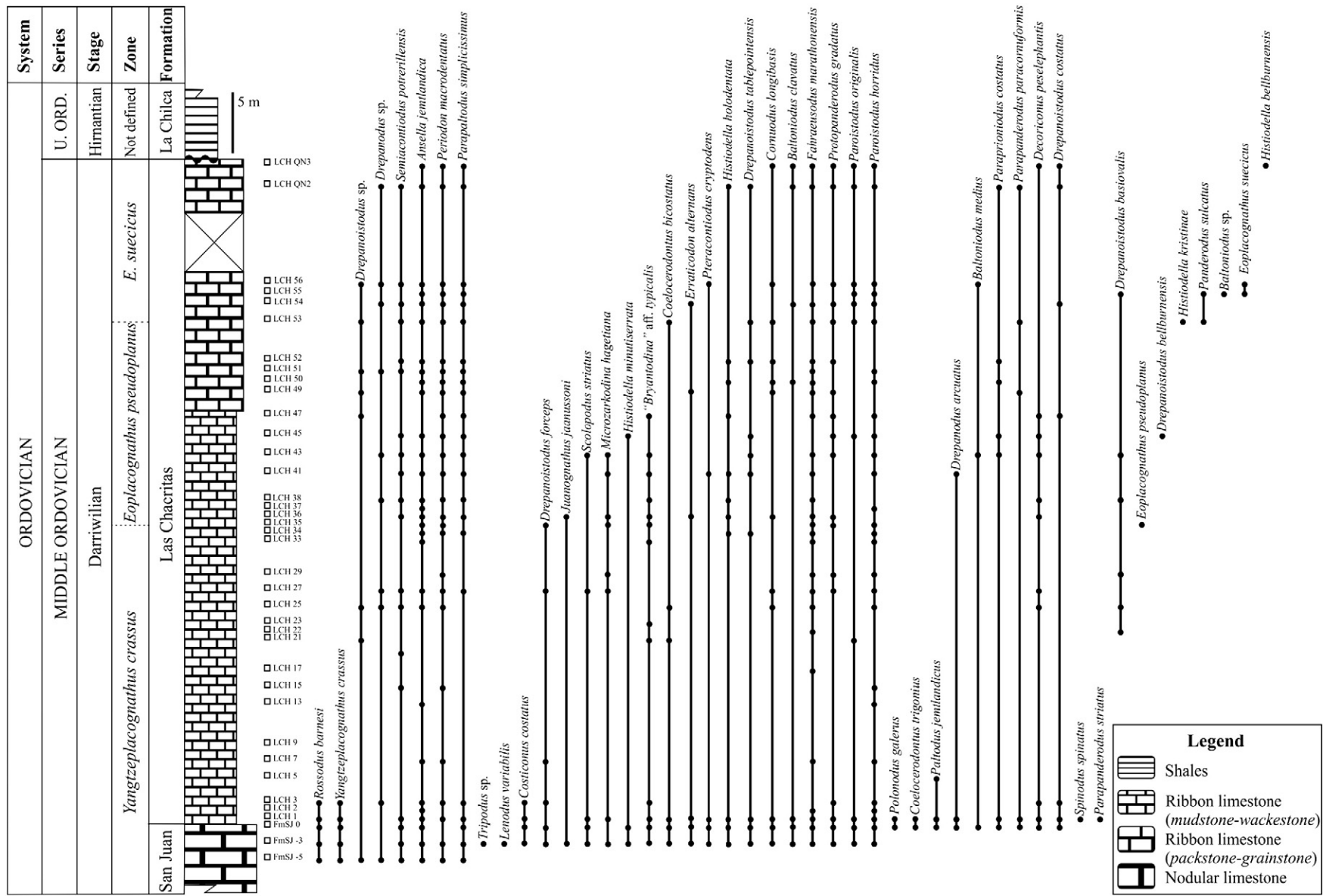**Fig. 5.** Ranges of conodont taxa and conodont biostratigraphy of the Las Chacritas Formation at the Chacritas River section.

(2002). Albanesi and Astini (2000) reported the *E. pseudoplanus* Zone with the appearance of the homonymous species in the middle part of the unit. The presence of species of *Microzarkodina* enabled these authors to divide the biozone into lower and upper subzones as had been established in the Baltic and Chinese conodont zone schemes.

In our study section along the Las Chacritas River, the topmost part of the Las Chacritas Formation is partly covered (Fig. 5). The total thickness of the exposed part of the formation is approximately 50 m. The thickness of the Lower Member is 38 m and that of the Upper Member 12 m.

4. Conodont biostratigraphy

Detailed studies of the Darriwilian conodont biostratigraphy in different regions of the world have led to the establishment of several regional zonal schemes (Fig. 3). Because the regional biogeographic differentiation of the Darriwilian conodont faunas, it does not appear very likely that a precise zone classification can be worked out that is applicable globally. According to the formal biostratigraphic scheme by Albanesi et al (1998), the Central Precordillera conodont zone scheme for the middle Darriwilian includes the *L. variabilis* Zone, with the *Periodon gladysae* and *Paroistodus horridus* subzones, and the *E. suecicus* Zone, with the *Histiodella kristinae* and *Pygodus anitae* subzones.

In Laurentia, this interval has recently been subdivided into the *Periodon macrodentatus* Zone with two subzones (*Histiodella holodentata* and *Histiodella* cf. *holodentata* subzones), and the *Periodon zgierzensis* Zone with two subzones (*H. kristinae* and *Histiodella bellburnensis* subzones) (Stouge, 2012). Several studies of Darriwilian conodonts in the Baltoscandic region, Laurentia, and China reveal great similarity to the conodont associations from the Precordillera. This enables a precise conodont-based correlation between the studied interval and coeval strata elsewhere.

In the Baltoscandic region the corresponding interval includes the *Yangtzeplacognathus crassus*, *E. pseudoplanus* and *E. suecicus* zones (Löfgren, 2004). In South China, Zhang (1998a) recognized a *Dzikodus tablepointensis* Zone, most of which is a correlative of the Baltoscandic *E. pseudoplanus* Zone (Löfgren, 2004), and of the upper part of the *L. variabilis* Zone and the lower part of the *E. suecicus* Zone in the Precordilleran zonation (Heredia et al., 2005). In the present study, we use the Baltoscandic zonation based on the record of all the index taxa. Some important taxa, such as species of *Histiodella*, *Dzikodus*, *Microzarkodina*, and *Periodon*, are employed for intercontinental correlation, particularly with successions in Laurentia and Australia.

4.1. Las Aguaditas section

According to Albanesi and Ortega (2002), the Lower Member of the Las Aguaditas Formation correlates with the upper *L. variabilis* Zone. New collections from the strata spanning the contact between the San Juan and Las Aguaditas formations yielded conodonts of the *Y. crassus* Zone, following more recent schemes (e.g., Löfgren and Zhang, 2003). This interval is also characterized by the presence of several species found in association with the zonal index species, such as *Ansella jemtlandica*, *Drepanoistodus basiovalis*, *Drepanoistodus bellburnensis*, *Fahraeusodus marathonensis*, *H. holodentata*, *Parapaltodus simplicissimus*, *P. horridus*, *P. macrodentatus*, and *Protopanderodus gradatus*.

The K-bentonite beds in the top portion of the San Juan Formation and the lower part of the Los Azules Formation allowed isotopic dating of this interval as 461 + 7/-10 Ma (Huff et al., 1997), which corresponds to the *Y. crassus* Zone described in the present study (see also Ortega et al., 2007). Heredia et al. (2011) also mentioned the presence of K-bentonites at the contact between the San Juan and Las Chacritas formations in the La Trampa Range. That the transition between the San Juan Formation and overlying units, *i.e.* the Las

Aguaditas, Las Chacritas, Gualcamayo, and Los Azules formations, is coeval in the central area of the Precordillera, is confirmed by the record of conodonts from the *Y. crassus* Zone in this interval (Serra et al., 2011). The similarity between the fauna of this zone with the conodont association described from the Baltoscandic Region, along with the occurrence of the index species *Y. crassus*, reinforces that global correlation of this interval is possible.

The base of the *E. pseudoplanus* Zone is identified by the appearance of the zone index species at 14.6 m above the base of the Las Aguaditas Formation (Fig. 4). Significant in that interval is also the presence of *D. tablepointensis*. This unit correlates with the upper part of the Lower Member of the Los Azules Formation (Ortega et al., 2007), the *E. pseudoplanus* Zone in the Las Chacritas Formation (Albanesi and Astini, 2000) and in the Sierra de la Invernada Formation (Albanesi et al., 2009; Ortega et al., 2010).

Moreover, the appearance of the index species *H. kristinae* and *Microzarkodina ozarkodella* at 23 m above the base of the Las Aguaditas Formation, close to the top of the Lower Member, indicates the upper subzone of the *E. pseudoplanus* Zone. The occurrence of a stratigraphic gap is indicated by the presence of the stratigraphical key species *P. anserinus* in the lowermost strata of the Middle Member. The *H. kristinae* Zone has been recorded from several areas of the Precordillera, for instance, it was reported by Sarmiento (1991) from the Gualcamayo Formation in Sierra de Villicum. This interval correlates with the upper part of the *D. tablepointensis* Zone and the lower part of the *E. suecicus* Zone in South China (Zhang, 1998a, 1998b), and with the transition interval of the *E. pseudoplanus* to *E. suecicus* zones in the Baltoscandic scheme (Zhang, 1998b). Furthermore, this unit correlates with the *H. kristinae* Subzone of the *P. zgierzensis* Zone the Table Point Formation on western Newfoundland, which was defined recently by Stouge (2012).

4.2. Las Chacritas section

Based on the ranges of conodont species recovered from the Las Chacritas Formation (Fig. 5), it can be correlated with the the *P. horridus* Subzone of the upper part of the *L. variabilis* Zone and the lower part of the *E. suecicus* Zone (Albanesi et al., 1998). In addition, the record in this study of the first appearance of *Y. crassus* in the upper part of the San Juan Formation and its presence in the lower part of the Las Chacritas Formation indicate correlation of this interval with the *Y. crassus* Zone in the Baltoscandic and Chinese schemes. Supporting this evidence is the fact that the conodont species association that includes the index taxon is very similar at the species level to that of the coeval Baltoscandic association. For this reason, we recognize the *Y. crassus* Zone in the Darriwilian Central Precordillera conodont zonation.

The *E. pseudoplanus* Zone was also recognized based on the first appearance of the homonymous species. The conodont species association of this zone is similar to that from the Baltoscandic *E. pseudoplanus* Zone as described by Löfgren (2004, also see recent contributions by Viira, 2011, and Männik and Viira, 2012), including *Baltoniodus medius*, *Cornuodus longibasis*, *Drepanoistodus basiovalis*, *H. holodentata*, *Microzarkodina hagetiana*, *Parapaltodus simplicissimus*, and *Paroistodus originalis*. The *E. pseudoplanus* Zone as identified herein corresponds to the top part of the *L. variabilis* and lower part of the *E. suecicus* zones in the Baltoscandic scheme according to Löfgren (1978), and to the *E. pseudoplanus* Zone from the Island of Öland in Sweden (Stouge and Bagnoli, 1990). It is also equivalent to the *D. tablepointensis* Zone as defined by Zhang (1998a) in South China.

The appearance of the index species *H. kristinae* in the upper Las Chacritas Formation marks the base of the eponymous subzone and the *E. suecicus* Zone (Fig. 5). This is supported by the appearance of *E. suecicus* and *Histiodella bellburnesis* in the uppermost strata of the study section.

In Newfoundland, the *P. macrodentatus* and *P. zgierzensis* zones are recognized in the Darriwilian by Stouge (2012). The former includes the *Histiodella sinuosa*, *H. holodentata* and *H.* cf. *holodentata* subzones and the latter the *H. kristinae* and *H. bellburnensis* subzones. In the Cow Head and Table Head groups, *P. macrodentatus* appears together with *Y. crassus* and *P. horridus* (Stouge, 2012). The *Y. crassus* Zone established here is older than the *H. holodentata* Subzone and the interval referred to as *E. pseudoplanus* Zone probably represents *Histiodella* cf. *holodentata* Subzone of the *P. macrodentatus* Zone. The Newfoundland *H. kristinae* Subzone of the *P. zgierzensis* Zone may correspond to the Precordilleran *H. kristinae* Subzone of the *E. suecicus* Zone. Hence the Precordilleran zones correlate with the major part of those from the Table Point Formation in western Newfoundland.

Based on conodont biostratigraphy, the Las Chacritas Formation correlates with the lower and middle members of the Gualcamayo Formation (Albanesi et al., 1998, 1999), lower member of the Las Aguaditas Formation at the Los Blanquitos section, as well as with the upper part of the San Juan Formation at Don Braulio Creek in the Villicum Range (Sarmiento, 1985), the Rinconada section at the Chica de Zonda Range (Lehnert, 1995), and the Lower Member of the Los Azules Formation at Cerro Viejo de Huaco (Ottone et al., 1999; Ortega et al., 2007).

5. Laboratory treatment of isotope samples

In order to obtain $\delta^{13}C_{carb}$ values, we subjected our carbonate samples from the San Juan, Las Chacritas and Las Aguaditas formations to the standard laboratory treatment described in Bergström et al. (2006) and Schmitz and Bergström (2007). All isotopic work was carried out in the Stable Isotope Laboratory, Department of Geology, University of Copenhagen, Denmark. The reproducibility was found to be better than ± 0.03‰ for $\delta^{13}C_{carb}$ expressed as standard deviation for 10 identical samples. All our results are reported in per mil (‰) deviations from the V-PDB (Vienna Pee Dee belemnite) standard.

6. $\delta^{13}C_{carb}$ chemostratigraphy

6.1. The Las Chacritas River section

The $\delta^{13}C_{carb}$ values obtained from 28 samples from the uppermost 5 m of the San Juan Formation and the entire thickness (approximately 50 m at the measured section) of the Las Chacritas Formation in the Las Chacritas River section are illustrated in Fig. 6. As seen in that figure, the lower half of the Las Chacritas Formation is characterized by somewhat variable $\delta^{13}C$ baseline values of ~ − 1‰. However, a few m thick interval in the uppermost San Juan Formation and very lowermost Las Chacritas Formation, which corresponds to the upper part of the *Y. crassus* Zone, shows elevated $\delta^{13}C$ values of up to ~0‰. This slight increase may appear insignificant but Buggisch et al. (2003) documented a similar minor $\delta^{13}C$ excursion from the top part of the San Juan Formation at their Cerro La Chilca section. Furthermore, Schmitz et al. (2010) reported similar elevated $\delta^{13}C$ values within the same biostratigraphic interval in the Maocaopu and Puxi River sections in China and also documented this positive excursion in the succession at the Hällekis Quarry in southern Sweden. Hence, this still unnamed excursion does not seem to be a local feature but to have a very wide geographical distribution, but its safe recognition requires a firmly established precise conodont biostratigraphy. Typically, this excursion occurs in the uppermost *L. variabilis* and lowermost *Y. crassus* zones, an interval coeval with the lower portion of the range of the geographically widespread and stratigraphically important conodont *H. holodentata*. The suggestion by some authors that this excursion may be the MDICE is unlikely to be correct because the latter excursion is typically present within a stratigraphically younger interval, namely the *M. ozarkodella* Subzone of the *E. pseudoplanus* Zone and slightly younger strata (cf. Schmitz et al., 2010, Fig. 8).

In the Las Chacritas River section there is a distinct increase from baseline values of ~ − 1‰ to ~0.5‰ in the upper 25 m of the Las Chacritas Formation. The beginning of this excursion is near the base of the *E. pseudoplanus* Zone and in the upper part of the range of *H. holodentata* (Fig. 6). This is in close agreement with the position of the base of MDICE in Baltoscandia and China. Because the magnitude and stratigraphic range of the Las Chacritas excursion are also similar to that of the MDICE elsewhere, we conclude that this Precordilleran excursion is indeed the MDICE. However, this excursion, which in Baltoscandia extends into somewhat younger strata than the *E. suecicus* Zone (Ainsaar et al., 2010), is apparently incomplete in the Las Chacritas succession. This is indicated by the fact that the *E. suecicus* Zone in the topmost portion of the Las Chacritas Formation is quite thin, and the overlying uppermost Ordovician to lower Silurian La Chilca Formation (Peralta and Baldis, 1995), is separated by a significant stratigraphic gap from the middle Darriwilian Las Chacritas Formation.

6.2. The Las Aguaditas section

Whereas the Darriwilian chemostratigraphy of the Las Chacritas succession is closely similar to that known from Baltoscandia and China, this is not the case with that of the Las Aguaditas Formation despite the fact that the conodont biostratigraphy indicates that these units have a considerable stratigraphic overlap.

The $\delta^{13}C$ curve from the Las Aguaditas Formation (Fig. 7), which is based on more than 150 samples, may be subdivided into two parts with different $\delta^{13}C$ values. The lower part, which represents the Lower Member, is characterized by $\delta^{13}C$ values showing some scattering but suggesting baseline values of ~ − 1‰. In general, these values are not markedly different from those of the lower half of the Las Chacritas Formation but it is difficult to recognize an excursion around the top of the San Juan Formation similar to that present in the Las Chacritas succession. Importantly, the elevation of $\delta^{13}C$ values typical of the MDICE is not obvious in the Las Aguaditas succession in the *E. pseudoplanus* (*D. tablepointensis*) Zone above the *Y. crassus* Zone.

The upper part of the $\delta^{13}C$ curve, which represents most of the Middle Member of the Las Aguaditas Formation, shows remarkably uniform $\delta^{13}C$ values of ~ + 1‰. This segment of the $\delta^{13}C$ curve is reminiscent of that in the coeval interval in some sections in Sweden (Bergström et al., 2012) and Estonia (Ainsaar et al., 2010) but none of these successions show anything like the increase in $\delta^{13}C$ value from ~ − 1‰ to ~ + 1‰ in the lower part of the *P. anserinus* Zone of the Las Aguaditas succession.

The absence of the MDICE in the Las Aguaditas succession is due to the presence of a stratigraphic gap between the Lower and the Middle Members of the Las Aguaditas Formation corresponding to at least a large part of the MDICE interval. Support for this interpretation is the fact that *H. holodentata* and and *Oz. hagetiana*, as well as four other conodont species, disappear at the very top of the Lower Member, making this the most conspicuous conodont faunal change in the entire study interval. In the Chinese and Newfoundland successions, *H. kristinae* replaces its evolutionary ancestor *H. holodentata* below the middle of the MDICE interval. This level is slightly higher stratigraphically than the level of replacement of *M. hagetiana* by its evolutionary successor *M. ozarkodella* (Zhang, 1998b; Löfgren and Tolmacheva, 2008), which is used as the base of the *M. ozarkodella* Subzone. In Baltscandia the *M. ozarkodella* Subzone occupies an interval just below the *E. suecicus* Zone (Fig. 3) and contains the lower part of the MDICE interval (cf. Schmitz et al., 2010). The presence of *M. hagetiana* associated with *M. ozarkodella*, *H. holodentata* and *H. kristinae* in the topmost part of the Lower Member indicates that this level represents the lower *M. ozarkodella* Subzone. Because the lower strata of the Middle Member has yielded *P. anserinus*, the index of the *P. anserinus* Zone, the gap in the Las Aguaditas Formation includes the uppermost part of the *E. pseudoplanus*, the *E. suecicus* and the
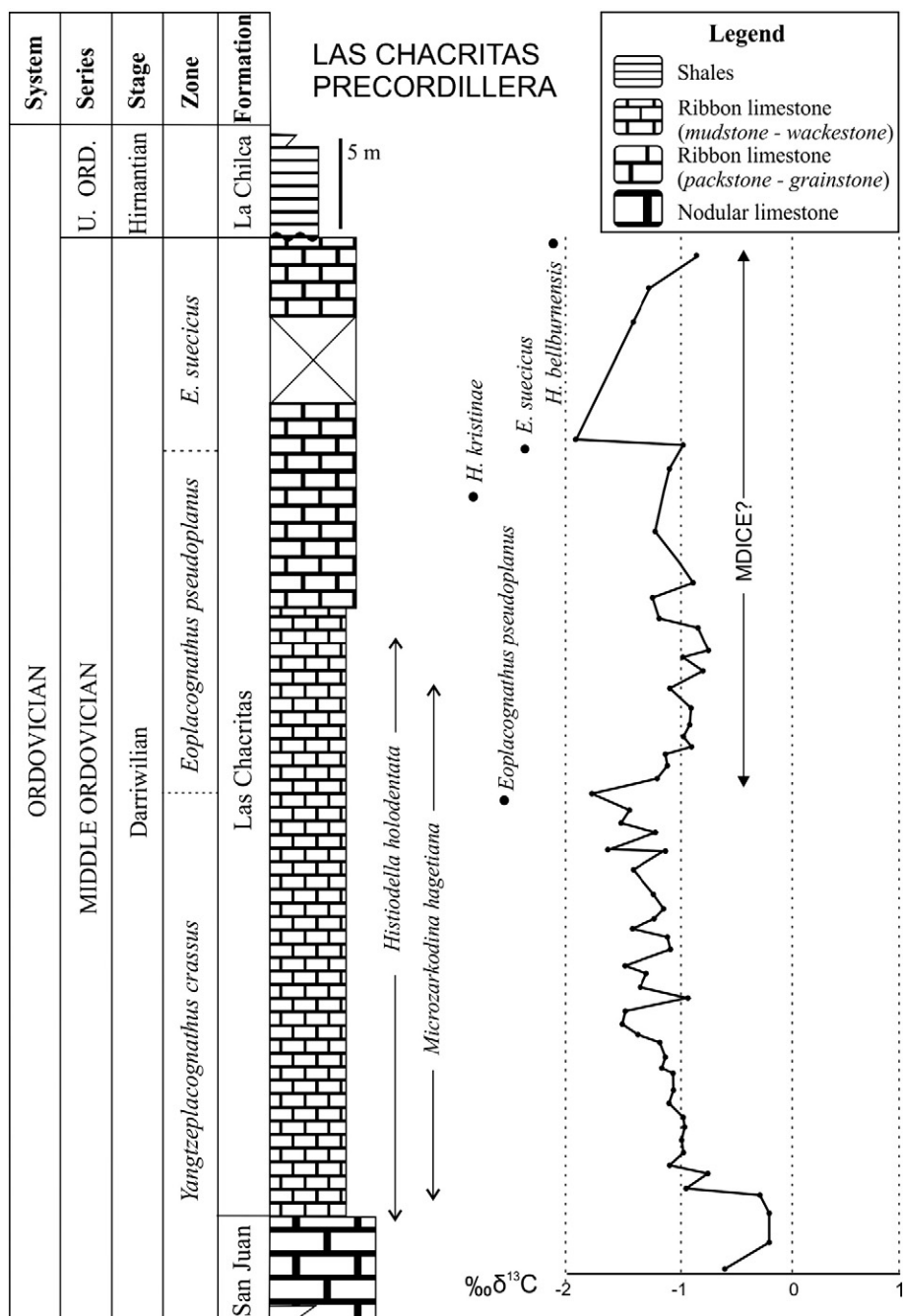
Fig. 6. The $\delta^{13}C_{carb}$ isotope curve through the Las Chacritas Formation. Note the presence of a small excursion near the top of the San Juan Formation, and the Middle Darriwilian Isotope Carbon Excursion (MDICE) in the upper half of the Las Chacritas Formation.

P. serra zones, and an undetermined part of the *P. anserinus* Zone up to the level with Sandbian graptolites at 10 m from the base of the Middle Member. However, even if there is a stratigraphic gap of this size, it does not explain the absence of the elevated $\delta^{13}C$ values expected to occur in the upper part of the *E. pseudoplanus* Zone in the uppermost part of the Lower Member. In this connection it is also of interest to note the existence of a stratigraphic gap in a comparable stratigraphic interval that cuts out a part of the MDICE in several platform successions in Sweden and China (Schmitz et al., 2010).

7. Regional comparison

To illustrate the utility of MDICE as a stratigraphic tool, we will briefly discuss the relations between $\delta^{13}C_{carb}$ isotope stratigraphy

and conodont biostratigraphy in selected MDICE successions in Baltoscandia, eastern North America, and China and compare aspects of those successions with those in the Precordillera, especially that at Las Chacritas. This is the first attempt to produce such a regional comparison between these MDICE successions and it is to be expected that further investigations will clarify some currently unclear details.

7.1. Baltoscandia

As noted above, the MDICE was first recognized in Baltoscandia (e.g. Ainsaar et al., 2004, 2007, 2010; Meidla et al., 2004; Schmitz et al., 2010) and this excursion has now been documented from more than 10 sections in Estonia, Latvia, and Sweden. For a general review of Darriwilian geology and the $\delta^{13}C$ isotope stratigraphy of the
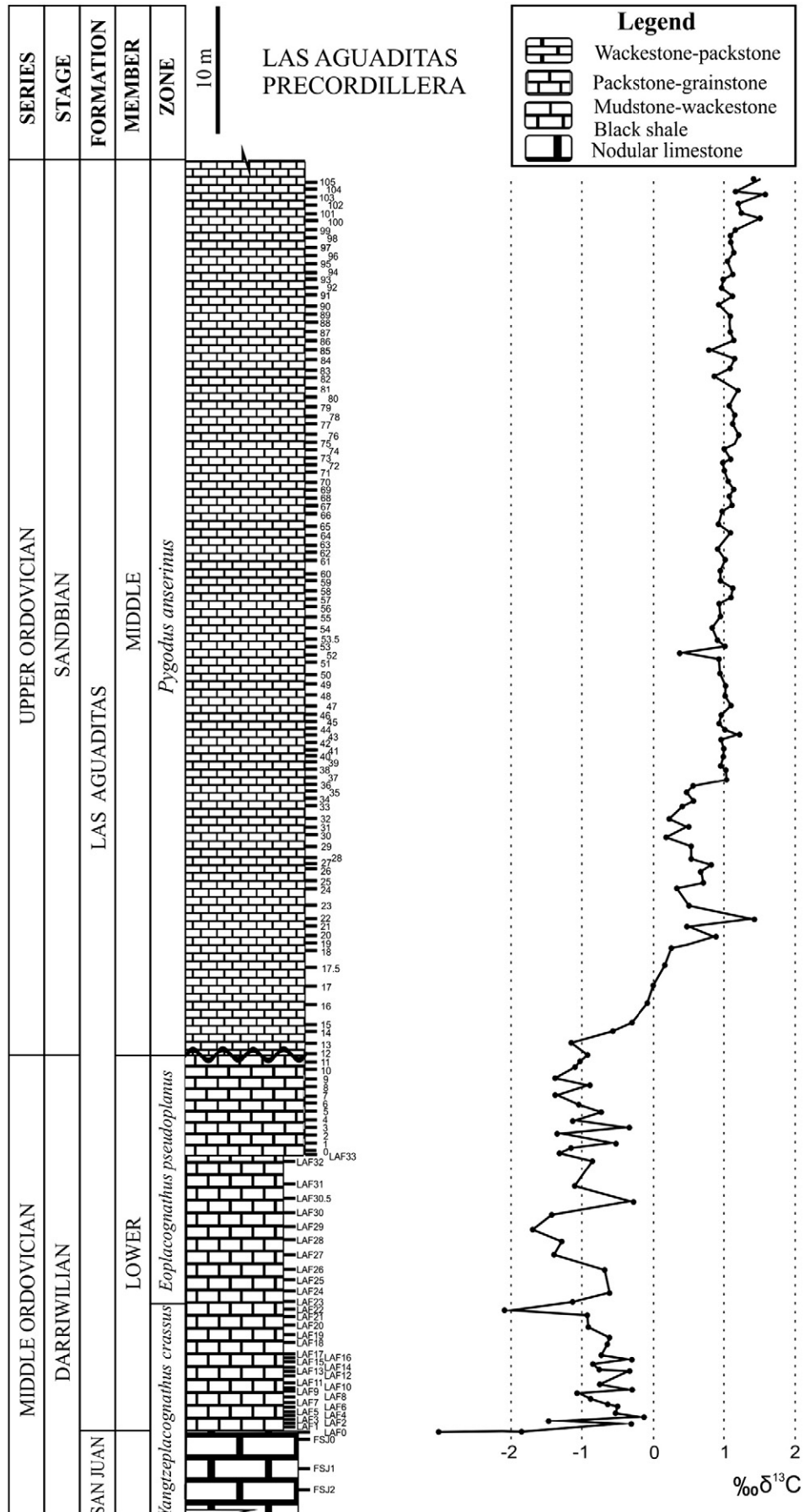
Fig. 7. The $\delta^{13}C_{carb}$ isotope curve through the Las Aguaditas Formation. Note the absence of the MDICE.

Baltoscandic platform, see e.g. Ainsaar et al. (2004) and Schmitz et al. (2010). In terms of the Baltoscandic regional stages, the MDICE is typically developed in an interval ranging from the upper Kunda Stage through the Aseri Stage and into the Lasnamägi Stage. Because the upper part of the MDICE shows a very gradual transition into baseline values in several successions, picking the precise level of the top of the excursion is in such cases difficult and arbitrary. As shown by Schmitz et al. (2010), at several localities parts of the MDICE have been cut out by a significant unconformity, herein referred to as the Darriwilian unconformity.

Extensive work during many years has led to the establishment of a detailed conodont biostratigraphy through the Baltoscandic Ordovician (e.g. Löfgren, 2004; Bergström, 2007) that is useful for correlations across the Baltic Sea as the same zones and subzones can be recognized in the East Baltic as in Scandinavia. This well-established conodont biostratigraphy greatly facilitates the recognition of the vertical ranges of the Ordovician $\delta^{13}C$ excursions.

Because of its excellent conodont biostratigraphy (Männik and Viira, 2005) and apparent stratigraphical completeness (Põldvere, 2005), Schmitz et al. (2010) proposed that the carbon isotope chemostratigraphy in the Estonian Mehikoorma (421) drillcore (Fig. 9) is useful as a reference standard of the MDICE. The $\delta^{13}C_{carb}$ chemostratigraphy of that drillcore has been dealt with by, among others, Ainsaar et al. (2004, 2010), Martma (2005), Kaljo et al. (2007), and Schmitz et al. (2010). As noted by Schmitz et al. (2010), the thickness of the MDICE is ~8 m but if its rising and falling curve limbs are added, the total thickness of the excursion interval would be >14 m. The peak values of the MDICE are +1.7‰ in the upper M. ozarkodella Subzone and lower to middle E. suecicus Zone. Assuming a baseline value of ~+1.0‰, the magnitude of the excursion would be of the order of 0.7‰. As shown by Ainsaar et al. (2010), this figure is closely similar to that of the MDICE in other Estonian and Swedish successions.

The $\delta^{13}C$ chemostratigraphy of the Las Chacritas and Mehikoorma (421) successions is compared in Fig. 8. As seen in this figure, the excursion identified as the MDICE in the Las Chacritas Formation starts at a closely similar conodont biostratigraphic level as in the Estonian drillcore, namely in the E. pseudoplanus Zone. Due to the hiatus that separates the Las Chacritas with the clastic La Chilca Formation, the end of the Precordilleran MDICE cannot be established but it probably exceeds 25 m in thickness, in the studied section. With baseline $\delta^{13}C$ values a little less than −1‰ and peak excursion values of ~−0.5‰, the magnitude of the Las Chacritas MDICE is approximately the same as that in the Estonian drillcore. In view of the relatively small magnitude of this $\delta^{13}C$ excursion and the very long distance that presumably separated Baltoscandia and the Precordillera in Ordovician time, the similarity in the development of the MDICE between these two regions is remarkable.

7.2. North America

The only published United States record of a previously firmly identified MDICE is from the Darriwilian succession in the eastern Appalachians in Maryland (Leslie et al., 2011). Although occupying a closely similar biostratigraphic position as the MDICE, this excursion has a significantly larger magnitude (~2.5‰) than the MDICE elsewhere. This MDICE occurrence and its associated biostratigraphy is currently the subject of detailed study and will not be discussed further herein.

In a recent sulfur isotope study, Thompson and Kah (2012) provided also some useful $\delta^{13}C_{carb}$ data from the Darriwilian succession on western Newfoundland. Because the focus of their investigation was sulfur isotope geochemistry rather than $\delta^{13}C_{carb}$ isotope chemostratigraphy, they only briefly reviewed that aspect of their data. Their $\delta^{13}C$ values were based on 34 samples collected through a more than 300 m thick interval of the Table Point and Table Cove

formations of the Table Head Group at the classical exposures of this unit at Table Point along the western coast of Newfoundland. These $\delta^{13}C_{carb}$ values were also briefly discussed by Thompson et al. (2012).

These $\delta^{13}C$ values are of special interest for several reasons. They come from an expanded middle Darriwilian carbonate succession, in which no significant stratigraphic gaps or faults have been recognized. Thanks to the monographic work by Stouge (1984), the conodont biostratigraphy of these two formations is well known. The conodont faunas are quite diverse as shown by the fact that Stouge (1984) recorded more than 50 multielement species, including biostratigraphically important and geographically widespread species of Histiodella, Dzikodus, Polonodus, and Baltoniodus. Based on the ranges of two species of Histiodella, Stouge (1984) recognized a H. holodentata Zone (=H. tableheadensis Zone of Stouge, 1984), which ranges through most of the Table Point Formation, and a H. kristinae Zone, which occupies the topmost part of the Table Point Formation and most of the Table Cove Formation (Fig. 9). As noted above, both these zone index species are present in our Precordilleran study successions and provide useful long-distance biostratigraphic correlation.

Very unfortunately, there are major errors in the stratigraphic range of the Table Head Group as reported by Thompson and Kah (2012, Fig. 4). They placed the base of the Table Point Formation (=base of the Table Head Group) at the base of the Baltoniodus triangularis Conodont Zone, which is the lowest conodont zone in the Dapingian Stage. This is several conodont and graptolite zones, and more than one global stage, too low chronostratigraphically. According to Stouge (1984), the lowest part of the Table Point Formation belongs to the H. holodentata (=Stouge's H. tablepointensis) Zone, the base of which correlates with a level at, or near, the base of the Baltoscandic L. variabilis Zone (e.g. Stouge, 1984; Rasmussen, 2001; Webby et al., 2004) or its top following more recent biozonal arrangements (e.g. Löfgren and Zhang, 2003). This is in good agreement with less precise graptolite evidence from the Table Point Formation (for reviews see Williams et al., 1987; Maletz et al., 2011, Fig. 2) that suggests a middle Darriwilian age.

Also the top of the Table Head Group is incorrectly dated by Thompson and Kah (2012, Fig. 4), who showed the Table Cove Formation, the middle formation of the Table Head Group, to extend as high as the Sandbian P. anserinus Conodont Zone. There is no evidence of the presence of this conodont zone in the Table Head Group. According to Maletz et al. (2011), the Black Cove Formation, which overlies the Table Cove Formation and forms the top part of the Table Head Group, contains diverse graptolites of the Nicholsonograptus fasciculatus Graptolite Zone, which is not younger than the lower part of the P. serra conodont Zone (e.g. Webby et al., 2004). This indicates that the underlying Table Cove Formation, from which Thompson and Kah (2012) obtained their stratigraphically youngest samples, is likely to correspond to the E. suecicus conodont Zone as was originally suggested by Stouge (1984). Unfortunately, the incorrect and confusing dating of the lower and middle parts of the Table Head Group was repeated by Thompson et al. (2012, Fig. 3).

Fortunately, because the $\delta^{13}C_{carb}$ values of Thompson and Kah (2012) are from samples with stated collecting levels in the Table Point section, which was also the principal section investigated by Stouge (1984), their $\delta^{13}C$ values can be directly tied to Stouge's (1984) conodont biostratigraphy as illustrated in Fig. 9. The lower ~160 m of the Table Point Formation is characterized by baseline $\delta^{13}C$ values, most of which are between −1‰ and −2‰. The values from the topmost portion of the Table Point Formation and the Table Cove Formation are distinctly elevated with peak $\delta^{13}C$ values reaching 0‰ in the Table Cove Formation indicating the presence of the MDICE. No $\delta^{13}C$ data are available from the shaly Black Cove Formation, the uppermost unit of the Table Head Group, but it is to be expected that the upper range of the MDICE is present in that unit.
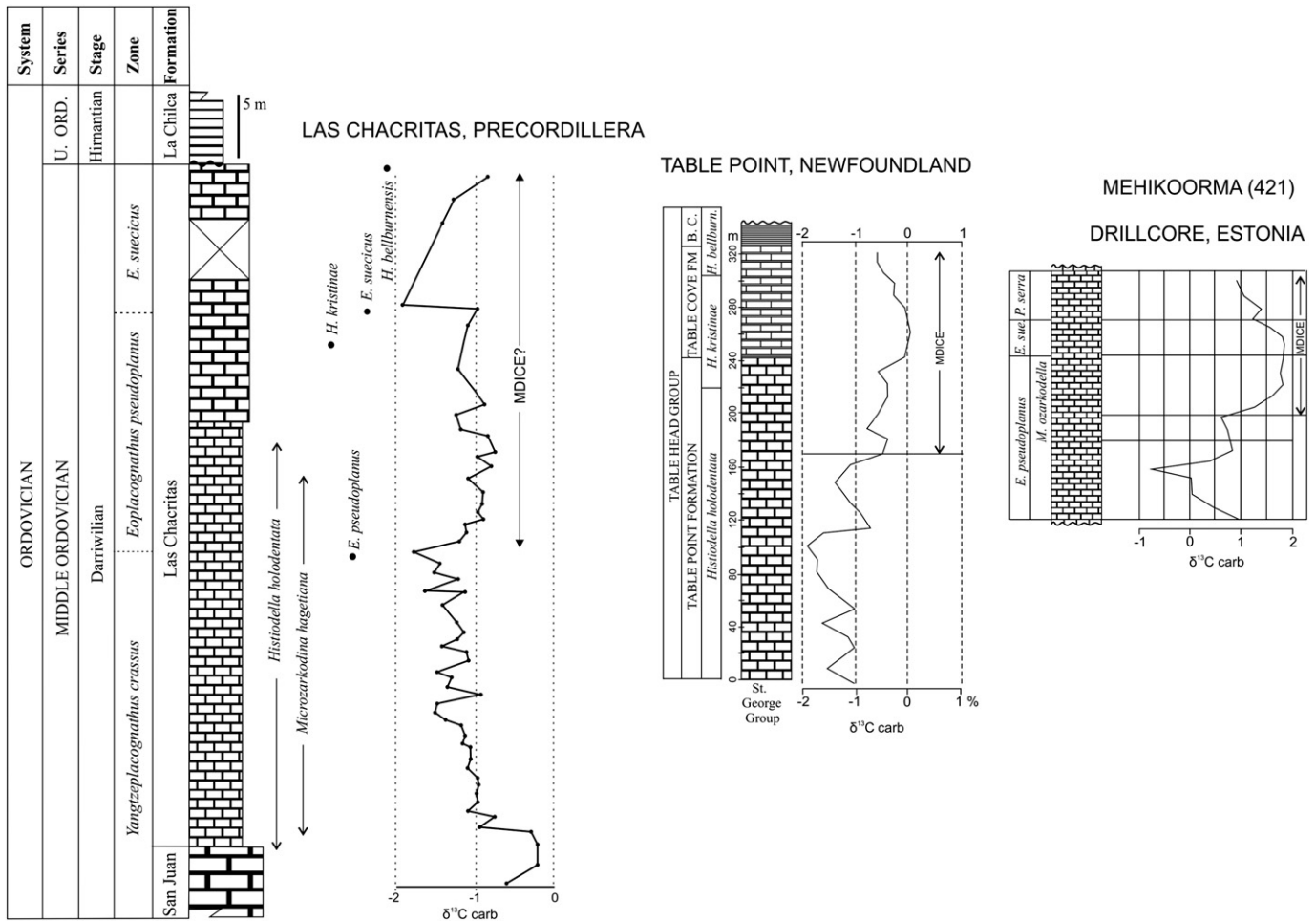
Fig. 8. Comparison of the $\delta^{13}C_{carb}$ curves from the Mehikoorma (421) drillcore, Estonia, the Table Head succession, Newfoundland, and the Las Chacritas succession. Note the similarity in the MDICE curves and its relation to biostratigraphy in the three successions. A major stratigraphic gap separates the St. George Group from the Table Head Group. Although *H. kristinae* has not been recorded from the Estonian drillcore, it appears in the middle to upper part of the *M. ozarkodella* Subzone in other successions in Baltoscandia, hence at a similar level in relation to the MDICE as in the Table Head and Las Chacritas successions. B.C. in the top Table Head succession refers the Black Cove Formation. Abbreviations: *Pyg.*, *Pygodus*; *Eo. sue.*, *Eoplacognathus suecicus*; *M.*, *Microzarkodina*; *H.*, *Histiodella*.

Compared with those from Las Chacritas section and the Mehikoorma (421) drillcore, the Table Head baseline values are of the same magnitude (~ -1‰). The excursion peak values are also similar to those of the Estonian drillcore but heavier than those of the Las Chacritas succession. However, as a whole, the $\delta^{13}C$ curves from these three successions show a great deal of similarity (Fig. 9). It is also of interest to note that the *H. holodentata*/*H. kristinae* speciation event, which marks the base of the *H. kristinae* Zone, corresponds to a level in the lower part of the MDICE curve in both the Table Point and Las Chacritas successions. Although no *Histiodella* specimens were listed from the Estonian drillcore by Männik and Viira (2005), the stratigraphically oldest specimens of *H. kristinae* recorded in Estonia, Sweden and Norway are from the middle to upper *E. pseudoplanus* Zone (Rasmussen, 2001; Viira, 2011; Männik and Viira, 2012). In relation to the MDICE, this appearance level appears comparable with those in the Las Chacritas and Table Head successions.

7.3. China

Although the Darriwilian biostratigraphy and lithostratigraphy have been extensively studied in China, until recently the $\delta^{13}C$ chemostratigraphy of that stratigraphic interval remained unknown on the Yangtze Platform. However, the investigations by Zhang et al. (2010), Schmitz et al. (2010), and Munnecke et al. (2011) have

provided important isotopic data from five Darriwilian sections on the Yangtze Platform. So far, MDICE has been documented from only two sections on the Yangtze Platform, namely Maocaopu in the Hunan Province and Puxi River in the Hubei Province (Schmitz et al., 2010). At both these places, the excursion occurs in platform carbonates with excellent biostratigraphic control provided by conodonts (Zhang, 1998a). The stratigraphically most complete study succession is at Maocaopu (Fig. 9) although at also that section, the top portion of the MDICE is cut out by an unconformity as shown by the absence of the *E. suecicus* and *P. serra* conodont zones.

The Maocaopu $\delta^{13}C$ curve (Fig. 9) starts with what appears to be the same small unnamed $\delta^{13}C$ excursion in the topmost *L. variabilis* and lowermost *Y. crassus* zones as has been documented above from the Las Chacritas successsion. This minor excursion is also known from the Hällekis Quarry succession in Sweden (Schmitz et al., 2010). As is the case at Las Chacritas, the $\delta^{13}C$ curve then flattens out but the baseline values are somewhat higher at Maocaopu ($\sim +0.5$‰ compared with -1‰). As at Las Chacritas, a few meters below the top of the range of *H. holodentata*, and below the base of the *M. ozarkodella* Subzone, the Maocaopu $\delta^{13}C$ curve shows a gradual increase to reach peak values of $\sim +1.4$‰ in the topmost part of the *M. ozarkodella* Subzone. The magnitude of the Chinese MDICE is about 1‰, hence about the double of that (~ 0.5‰) of MDICE at Las Chacritas. The upper portion of the MDICE is cut out by a significant
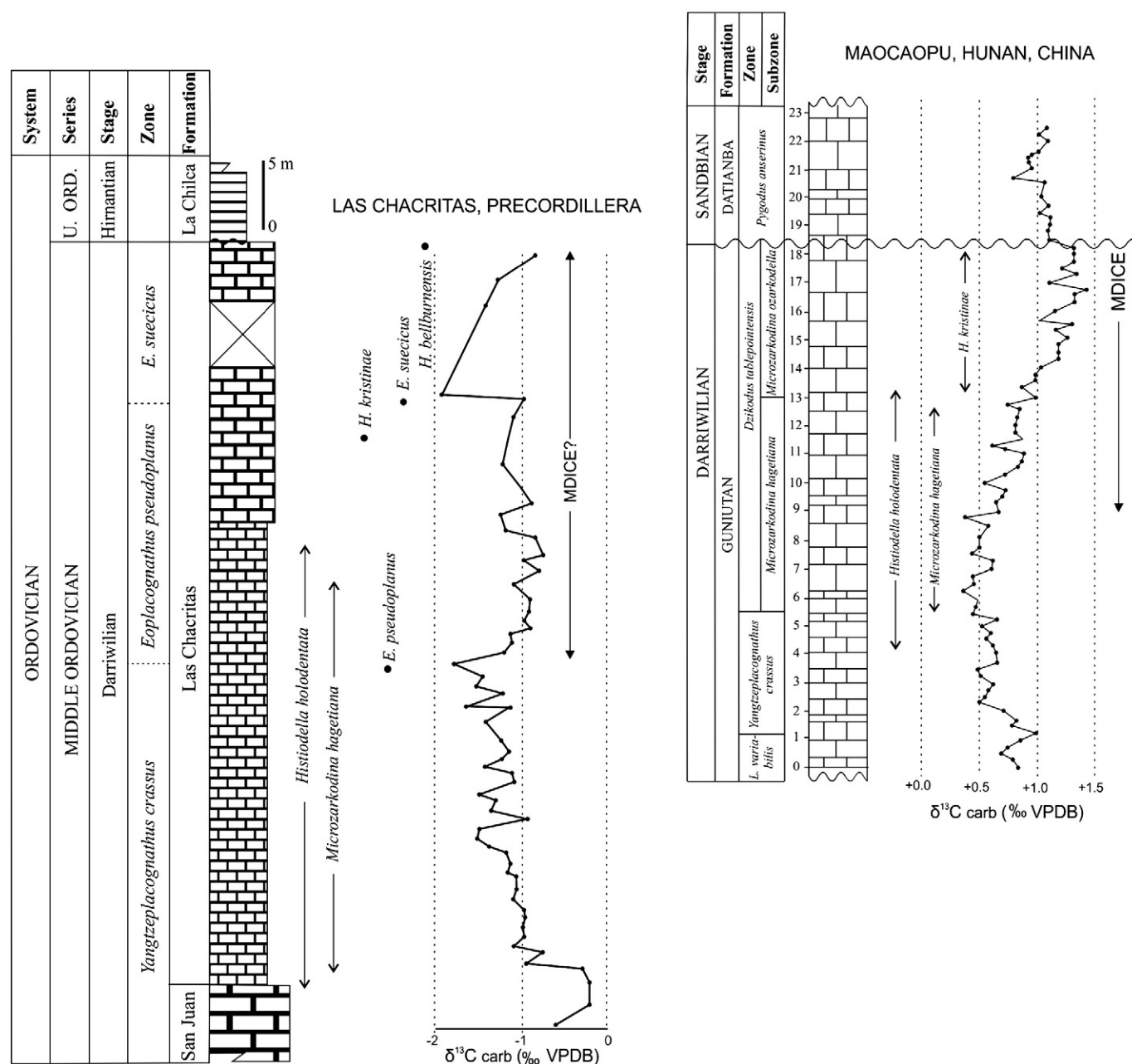
Fig. 9. Comparison of the $\delta^{13}C_{carb}$ curves from Las Chacritas and Maocaopu, Hunan, China. Note the close similarity in the relations between the excursion and the ranges of some biostratigraphically important conodonts.

unconformity at Maocaopu and the topmost MDICE is also unknown at Las Chacritas. Based on the close similarity in biostratigraphic position and appearance of the $\delta^{13}C$ curve, we conclude that these excursions reflect the same paleoceanographic event and that both represent the MDICE.

In this connection it is also of interest to comment on the two previous reports on Darriwilian $\delta^{13}C$ chemostratigraphy on the Yangtze Platform. The study by Zhang et al. (2010) dealt with the important Honghuayuan section in the Guizhou Province, and the same succession was also investigated by Munnecke et al. (2011). No MDICE was found in these investigations, and we interpret this absence as caused by the fact that the MDICE interval is cut out by a significant unconformity. In the Honghuayuan succession the lower Darriwilian *U. austrodentatus* Zone is well developed in the uppermost Meitan Formation. This unit is overlain by the Shihtzupu Formation that has yielded conodonts of the *Yangtzeplacognathus foliaceus* (formerly

E. foliaceus) Subzone (An, 1987) as well as graptolites, such as *G. linnarssoni*, which indicate the uppermost Darriwilian *Dicellograptus vagus* (formerly *H. teretiusculus*) Zone (Chen et al., 2011). Hence, an interval corresponding to at least two graptolite zones (*N. fasciculatus* and *P. elegans* zones) are missing and this absent interval corresponds to most, if not all, of the range of MDICE.

In their regional study of Ordovician $\delta^{13}C$ isotope stratigraphy in the Yangtze Platform region and adjacent areas, Munnecke et al. (2011) also examined some samples from the middle Darriwilian interval in the upper Ningkuo and lower Hulo formations in the Huangnitang section in the Zejiang Province. In this section, which is the global stratotype section (GSSP) for the base of the Darriwilian Stage, extensive studies have led to the establishment of a detailed graptolite and conodont biostratigraphy (Chen et al., 2006). Surprisingly, the $\delta^{13}C$ curve obtained by Munnecke et al. (2011) through the middle Darriwilian *A. ellesae* and *N. fasciculatus* zones shows no

distinct excursion that can be identified as the MDICE. The absence of MDICE in this deeper-water succession, which is presumed to lack significant gaps, is both unexpected and puzzling, and further, more detailed, studies of its middle Dariwilian interval are needed. At a recent visit at this locality by one of us (SMB) it was observed that this interval is not well exposed and consists mostly of shale and mudstone. This may explain why Munnecke et al. (2011) obtained only a very small number of carbonate samples from that interval for their isotope work.

8. Regional correlation

A combination of $\delta^{13}C_{carb}$ chemostratigraphy and conodont biostratigraphy is used for establishing correlations between the Darriwilian study intervals in the Precordilleran, Baltoscandian, Newfoundland, and Chinese study successions (Fig. 10). It should be stressed that in general, there is excellent agreement between evidence from biostratigraphy and $\delta^{13}C$ chemostratigraphy. This suggests that the proposed stratigraphic relationships are unlikely to be very far off. This correlation is mainly based on the ranges of *E. pseudoplanus* and *E. suecicus* zones and the *H. hagetiana* and *M. ozarkodella* subzones, the position of the *H. holodentata*/*H. kristinae* zonal boundary, and the position of the lower part of the MDICE.

As shown in Fig. 10, the Las Chacritas Formation is interpreted to be a close equivalent of the Table Point Formation of Newfoundland, the upper Holen Limestone in Sweden, the Baldone Formation in Estonia, and the Guniutan (Kuniutan) Formation of the Yangtze Platform in China. Although the top and bottom of all these units may not represent precisely the same stratigraphic level at each locality, the interval corresponding to the Las Chacritas Formation can be clearly recognized in the North American, Baltoscandic, and Chinese study successions. The correlation of the Las Aguaditas Formation is more problematic, both in terms of $\delta^{13}C$ chemostratigraphy and biostratigraphy. The lower portion of this unit appears to be coeval with the lower part of the Las Chacritas Formation, and the Middle

Member of the Las Aguaditas Formation, which includes a part of the *E. pseudoplanus* and the *P. anserinus* zones, may be at least broadly equivalent to the Table Cove formations. As discussed above, the absence of the MDICE in the Las Aguaditas succession is due to a previously unrecognized gap in the contact between the Lower and Middle members of this formation. As shown in Fig. 10 and noted above, middle Darriwilian stratigraphic gaps of significant size have previously been described from Sweden and China but if these are related to eustatic events or represent local epeirogenetic movements remains to be established.

9. Conclusions

The principal results of the present study may be summarized as follows:

* Based on numerous microfossil samples, a detailed conodont biostratigraphy has been established through the Las Chacritas and Las Aguaditas formations in the Argentine Precordillera. The conodont faunas of these units show affinities to North American faunas, such as that from the Table Head Group, but these Precordilleran faunas also include several biostratigraphically important species that are best known from Baltoscandia and China. Both Precordilleran formations are referable to the North American *H. holodentata* and *H. kristinae* zones and to the Baltoscandic–Chinese *Y. crassus* and *E. pseudoplanus*. The upper Las Chacritas Formation is referable to the *E. suecicus* zone as well.

* A rather typical representation of the MDICE occurs in the upper part of the Las Chacritas Formation but this excursion is missing in the Las Aguaditas $\delta^{13}C_{carb}$ curve. We interpret that this absence is due to a stratigraphic gap at the contact between the Lower and Middle members of the Las Aguaditas Formation that cuts out the excursion interval. In South America this is the first record of the MDICE that is controlled by high resolution conodont and graptolite biostratigraphy.

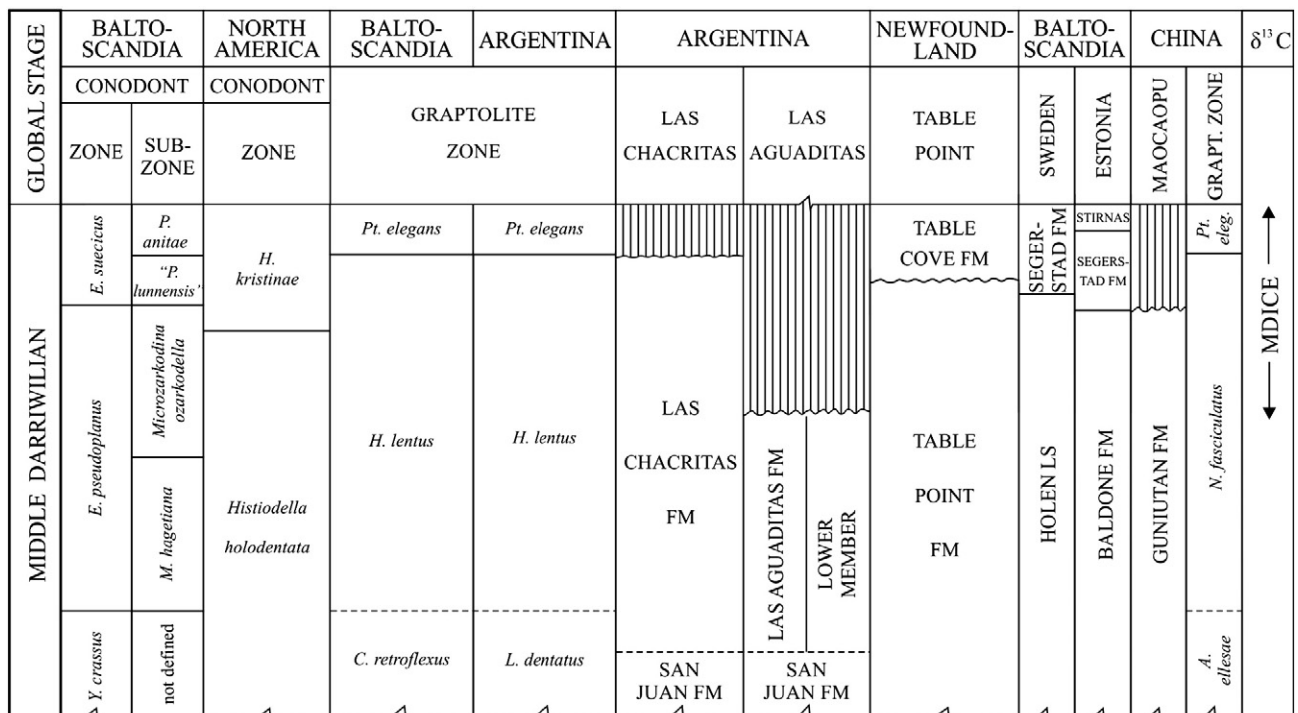**Fig. 10.** Correlation between the successions discussed in the text based on $\delta^{13}C_{carb}$ chemostratigraphy and conodont biostratigraphy. For references to figure columns, see Fig. 3. The North American column is after Bergström (1983), Sweet (1984), and Leslie et al. (2011).

* A confirmed record of the MDICE is described from the Table Head Group of western Newfoundland. This is only the second record of this $\delta^{13}C$ excursion from North America.
* Based on $\delta^{13}C_{carb}$ chemostratigraphy and conodont biostratigraphy, the Las Chacritas Formation is correlated with the Table Point Formation on Newfoundland, the upper Holen Limestone of south-central Sweden, the Baldone Formation of Estonia, and the upper Guniutan Formation of the Yangtze Platform in China. Apart from the gap between the Lower and Middle members, the Lower Member of the Las Aquaditas Formation also correlates with the Baltoscandic and Chinese units just mentioned. The Middle Member is younger than the Table Cove Formation of Newfoundland and the Segerstad and Stirnas formations of Estonia.
* The present study confirms that the MDICE has a global distribution and can be used as a stratigraphic tool for long-distance correlations.

Acknowledgments

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