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Timeline of events in the Ordovician–Silurian Transition of the Precordillera (Argentina): Paleoenvironmental, paleoclimatic and paleobiologic implications

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ABSTRACT

This paper aims at analyzing the Ordovician–Silurian (Hirnantian–early Llandoverian) Transition in the Central and Eastern Precordillera of San Juan Province based on stratigraphic relationships, diagnostic deposits and sedimentary, paleobiologic and isotope data. At the Central Precordillera, three sections have been examined and sampled: (a) Los Baños de Talacasto, (b) Poblete Norte in the Talacasto area, and (c) northward the Cerro La Chilca section. At the Eastern Precordillera, only the Don Braulio section at the Villicum Range has been considered. These four sections have been selected because they include significant brachiopod assemblages related to the three Transitional Benthic Faunas (TBF 1–3), Hirnantian and Rhuddanian graptolites zones and palynomorph assemblages, in addition to isotope data as a useful tool for dating and correlations. The analysis of these sections has allowed recognizing the timeline of four events that span early Hirnantian–early Llandoverian. Event 1 is linked to the early Hirnantian postglacial transgression, in accordance with TBF 1 and *Metabolograptus extraordinarius* Zone correlation. Event 2 developed in the middle-upper Hirnantian, is witnessed in a transgressive shallow-water succession, coeval with the Hirnantia Fauna and *Metabolograptus persculptus* Zone. Event 3 is widely represented by the basal cherty pebbly conglomerate of La Chilca Formation and its correlatives Los Bretes and lower Tambolar formations in the Central Precordillera. This conglomerate is thought to be a lag deposit, which erosively overlies Ordovician strata, as a result of the Hirnantian postglacial transgression, but it is absent in the Eastern Precordillera. Finally, Event 4, at the Villicum section, spans the late Hirnantian–early Llandoverian, standing out a shallow-water, bioturbated mudstone succession, of 12 m thick with no diagnostic fossils, indicating upwelling processes and probably including the Ordovician–Silurian Boundary. However, in the Los Baños de Talacasto and Poblete Norte sections, this succession is composed of a graptolite-rich pelite succession 12 m thick, exhibiting at the base Fe-phosphate strata, and bearing graptolite assemblages of the Hirnantian *Metabolograptus persculptus* Zone, and the Rhuddanian *Parakidograptus acuminatus* Zone, indicating the Ordovician–Silurian boundary. It should be noted that the *A. ascensus* Zone has not been registered to date in the Precordillera.

1. Introduction

The Ordovician–Silurian Boundary is still of interest for the international community due to the occurrence of several events of 3rd or lower order mainly related to glacial – deglacial processes (climatic changes) that are interpreted in terms of high resolution chronology based on multidisciplinary analyses (Ogg et al., 2016a, 2016b). Some notable examples include the pioneering studies of Williams (1983, 1988), Vandenberg et al. (1984), Cocks (1985), Cocks and Rickards (1988), Cuerda et al. (1988a, b) and, more recently, the papers by Štorch (2006), Delabroye et al. (2011), Myrow et al. (2018) and Weidong (2019). Isotopic variations of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, and N have been examined in the Ordovician–Silurian Transition (OST) in Scotia, Sweden, Baltic region, Canada and Southern China, with the purpose of

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establishing global correlations for successions lacking diagnostic fossil record. In this succession, graptolites of the Hirnantian *Metabolograptus persculptus* Zone, and the Rhuddanian *Akidograptus ascensus* and *Parakidograptus acuminatus* zones, revealed a good correlation with Hirnantian $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ curves (Bergström and Goldman, 2019), besides palynomorphs and brachiopods of the Transitional Benthic Faunas, TBFs as defined by Wang et al. (2019), among others. $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ in the Late Ordovician are a useful tool to recognizing glacial and post-glacial stages, due to significant variations in the isotope excursions, enabling global correlations (Bergström and Goldman, 2019, and references therein).

South America is a promising region for enhancing detailed researches on the Ordovician–Silurian Transition (OST), taking into account the well-preserved exposures of the Central and Eastern Precordillera (Fig. 1), as well also in the northwestern (NW) of Argentina (NOA Basin), Bolivia, Peru, Venezuela and the Paraná Basin in Paraguay and Brazil. In the Precordillera of San Juan, the Ordovician–Silurian Transition consists of fine-grained, shallow-water siliciclastic successions, biostratigraphically well-dated, spanning the Hirnantian–Rhuddanian interval. This study deals with the sequence (timeline) of events through the Ordovician–Silurian Transition in the San Juan Precordillera. With this purpose, a detailed lithostratigraphic, paleobiologic (graptolite, palynomorphs, and brachiopods) and isotopic analysis of the basal part of La Chilca Formation at three sections of the Central Precordillera (Los Baños de Talacasto, Poblete Norte and Cerro La Chilca), and the Don Braulio Formation at the Villicum Range in the Eastern Precordillera (Figs. 1 and 2) performed. In addition, the significance of diagnostic deposits (ironstones, ferro-phosphatic rocks, upwelling deposits), and stratigraphic unconformities, have also been considered in their paleoenvironmental interpretations. A correlation of the studied units is proposed combining the isotopic curves with the Hirnantian *Metabolograptus persculptus* and the Rhuddanian *Parakidograptus acuminatus* Zones, and brachiopods of the Transitional Benthic Faunas 1–3 (TBFs), and also compared with other selected successions from South America (Figs. 3 and 4) and elsewhere in Sweden and China (e.g. Luo et al., 2015; Sial et al., 2017a, 2022; Wang et al., 2019) (Fig. 5).

2. Geological setting

The Precordillera of La Rioja, San Juan and Mendoza Provinces, as defined by Furque and Cuerda (1979), is a fold-and-thrust belt divided into Eastern, Central and Western morpho-structural units. The Eastern Precordillera (Ortiz and Zambrano, 1981) is characterized as a thick skin fold and thrust belt with West vergence, composed mainly of Cambrian to Early Ordovician fossiliferous deposits of carbonate platform, then Middle–Upper Ordovician to Devonian marine siliciclastic succession, covered by marine-continental Late Paleozoic rocks. The Central Precordillera (Baldis and Chebli, 1969), characterized as a thin skin fold and thrust belt vergent to the East, composed of Cambrian–Early Ordovician marine carbonate rocks succeeded by a pile of Middle Ordovician to Devonian marine siliciclastic deposits paraconformably covered by continental and marine Late Paleozoic successions. The

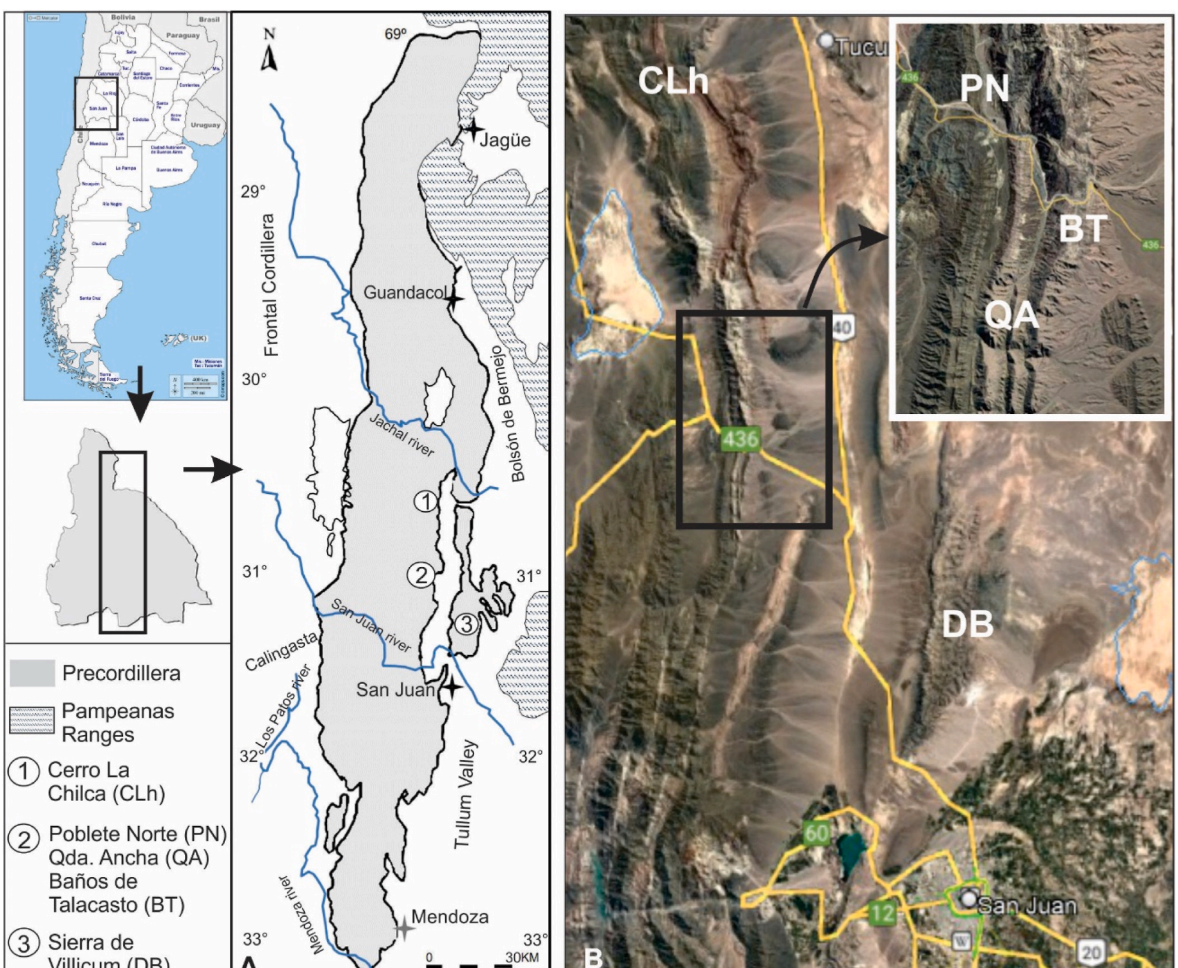

Fig. 1. (A) Map of the Precordillera showing the location of the sections analyzed in this work (modified from Baldis et al., 1982); (B) Google Earth image showing the closest access routes and location of the studied sections: Cerro La Chilca (CLh), Quebrada Ancha (QA), Poblete Norte (PN) and the Los Baños de Talacasto (BT), and Don Braulio section (DB) at Villicum Range.

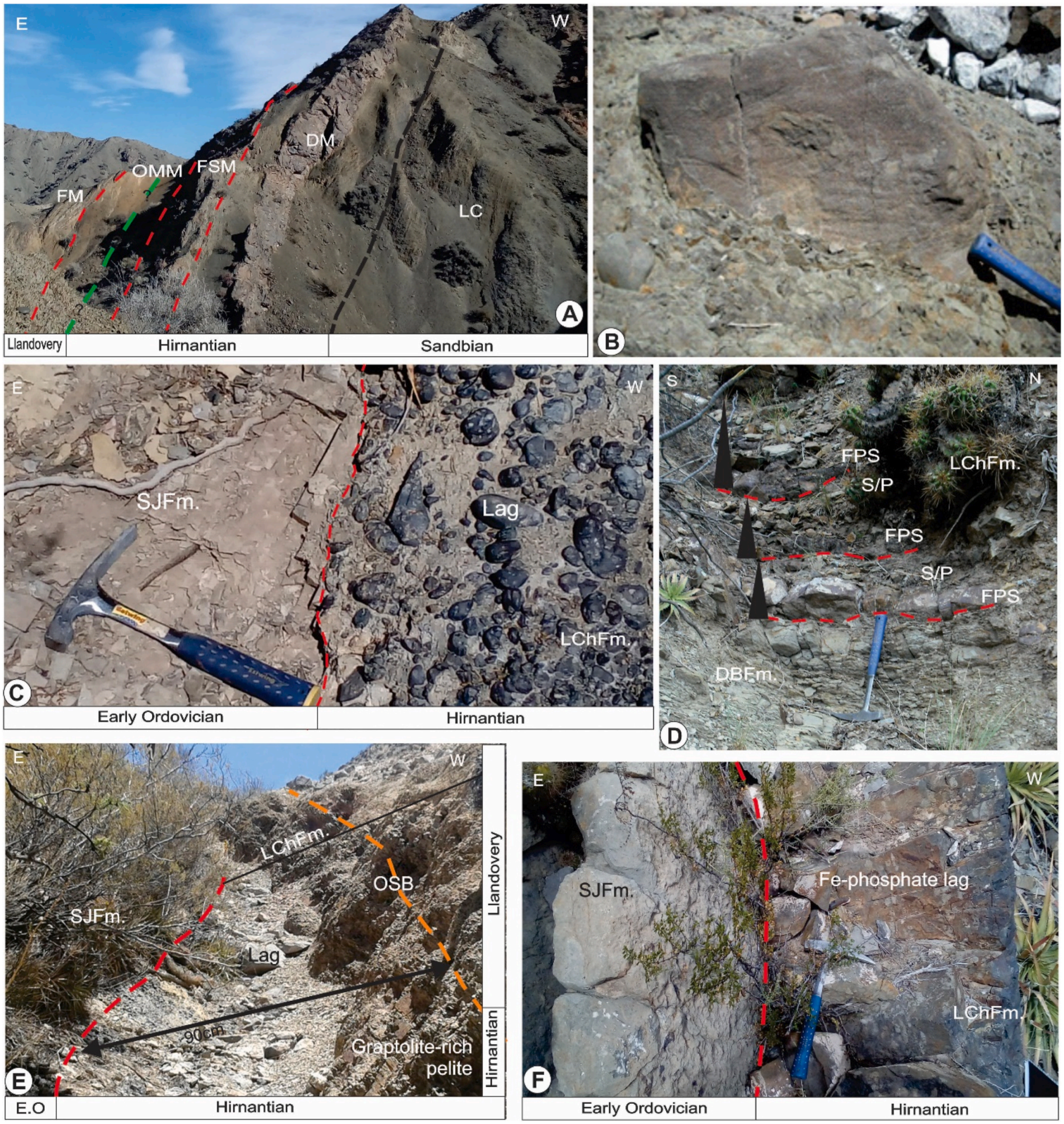

Fig. 2. (A) Stratigraphic section of the Don Braulio Formation at the Villicum Range. LC: Sandbian La Cantera Formation, DM: Diamictite Member, FSM: Fossiliferous Sandstone and Mudstone Member, OMM: Ocher Mudstone Member; FM: Upper Ferriferous Member; Ordovician–Silurian Transition (green dashed line) (B) Striated pebble from the basal diamictite of the Don Braulio Formation (Event 1) at the Villicum section. (C) Basal conglomerate (lag) (Event 3) of La Chilca Formation at Los Baños de Talacasto section, San Juan Formation (SJFm). (D) Fe-phosphatic ironstone beds at the base of La Chilca Formation at Cerro La Chilca. FPS: Fe-phosphatic sandstone, S/P: Intercalation of sandstone and pelite. LChFm: La Chilca Formation; DBFm, Don Braulio Formation. (E) Graptolite-rich pelite from the lower part of La Chilca Formation at the Baños de Talacasto section (Event 4), in which the Ordovician–Silurian Boundary (OSB) (Dashed line orange) has been defined. Red dashed line indicates the contact between La Chilca and San Juan (SJFm) formations. The black line represents 90 cm and indicates the Ordovician–Silurian Boundary (OSB) from the base of the Hirnantian basal conglomerate. (F) Calcareous sandstone and Fe-phosphate lag (Event 3) from the base of La Chilca Formation (LChFm), at Poblete Norte section. SJFm: San Juan Formation.

Western Precordillera (Baldis et al., 1982), characterized as a thick-skin folded and thrust belt with East vergence, is dominated by marine siliciclastic successions spanning Early-Late Paleozoic, but also Triassic rocks occur. Herein, the Early Paleozoic carbonate succession is absent, except as shelf-derived allochthonous Cambrian–Early Ordovician blocks, into a siliciclastic matrix containing Late Ordovician graptolite assemblages. On the other hand, in this structural setting the record of Silurian rocks remains controversial (Baldis and Peralta, 1999).

In the San Juan Precordillera, extensive exposures of Late Ordovician–Silurian sedimentary succession occur in the Central Precordillera, which can be traced from northern Jáchal area to southern San Juan River along 150 km of the Precordillera. However, in the Eastern Precordillera, the Hirnantian–Silurian siliciclastic succession is only exposed on eastern flank of the Villicum range, standing out for its fossil content. In the Central Precordillera, the Hirnantian–Silurian succession is represented by shallow-water siliciclastic deposits of the Tucunuco Group (Cuerda, 1969) including the lower of La Chilca Formation (Hirnantian–early Wenlockian), and the upper of Los Espejos Formation (middle Wenlockian–Pridolian). On the other hand, in the Eastern Precordillera, the Don Braulio Formation (Baldis et al., 1982) is made up of siliciclastic shallow-water deposits of Hirnantian–Llandoverian age in which the four members (Fig. 4) defined by Peralta (1993a) and Peralta

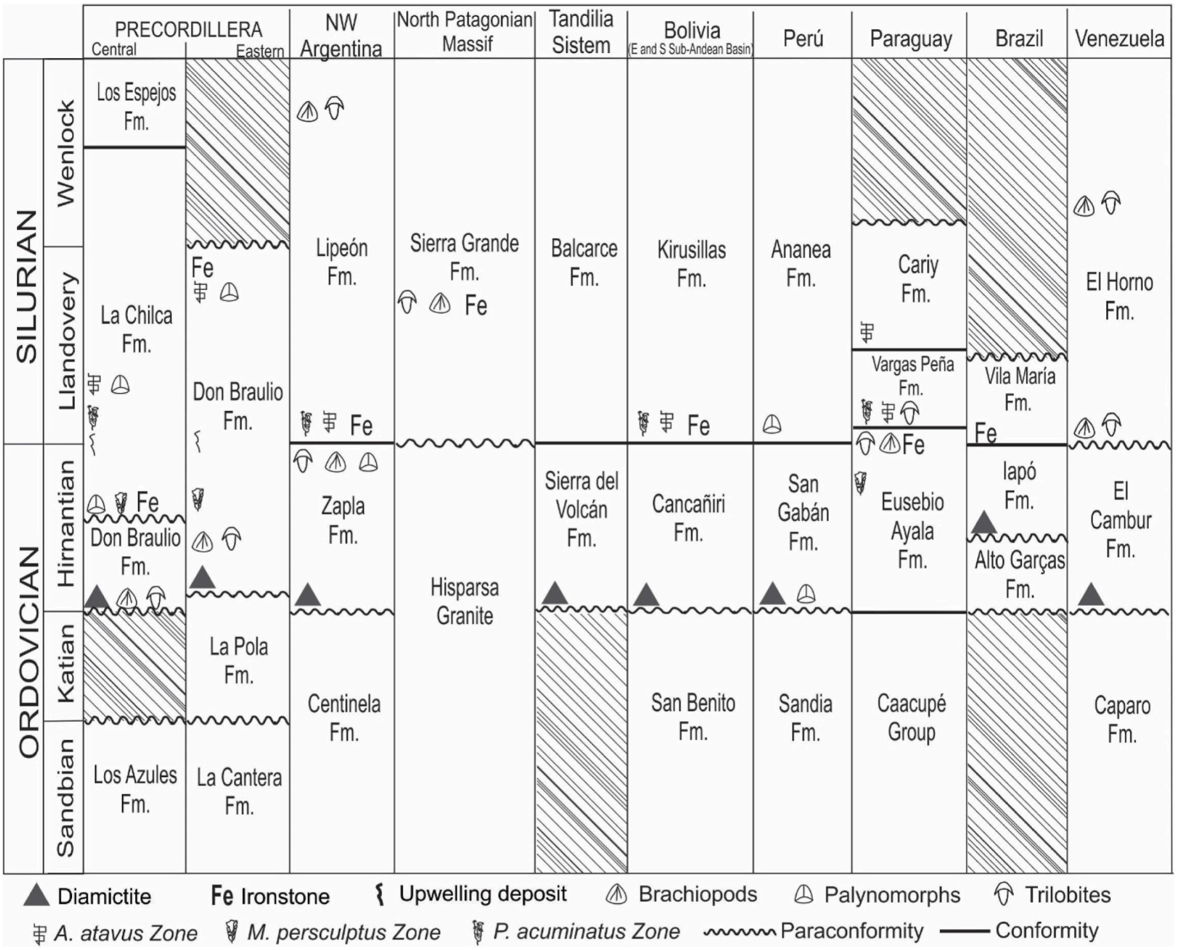

Fig. 3. Stratigraphic correlation chart for the South American OST, considering faunas of brachiopods, graptolites, trilobites, palynomorphs, and diamictitic, ironstone and upwelling deposits. The studied sections of the Central and Eastern Precordillera of western Argentina are correlated with units of NW Argentina, Bolivia, Peru, Eastern Paraguay and Paraná Basin of Brazil, and Barinas-Apure Basin in Venezuela (Gómez, 2022 and references therein). Disconformity and paraconformity are after Blackwelder (1909), Miall (2016) and Kabanov (2017).

and Carter (1999) are recognized.

At the Villicum section, Levy and Nullo (1975) provided the first record of "Asghillian" (Hirnantian) brachiopod fauna, lately referred by Benedetto (1986) to the *Hirnantia* Fauna, which was mentioned for the first time in South America. It is to be noted that in the Don Braulio Formation, a trilobite fauna reported by Baldis and Blasco (1975) occurs associated with the *Hirnantia* Fauna. In this succession, other fossiliferous records such as trilobites (Baldis and Blasco, 1975), spicules of sponge and bryozoans (Jiménez-Sánchez et al., 2014), and palynomorphs (Gómez, 2022; Gómez et al., in review), are documented (Fig. 4). In the last years, the finding of new and significant graptolite assemblages, palynomorphs and shelly faunas, besides new isotope data, had allowed to enhance the knowledge of the events in the Ordovician–Silurian Transition of the San Juan Precordillera, and compare them with similar records elsewhere in South America (Fig. 3).

3. Timeline of events

The lithological, paleobiologic and chemostratigraphic data obtained from the Hirnantian–Llandovery successions of the Central and Eastern Precordillera suggest their relationship with four transgressive pulses, correlated with the *M. extraordinarius*, *M. persculptus*, *P. acuminatus* and *A. atavus* zones, and Transitional Benthic Faunas (TBFs 1–3) (Gómez, 2022). Each transgressive pulse is not only characterized by diagnostic deposits and stratigraphic unconformities, but also by the progressive recovery of the biota after the Late Ordovician Mass Extinction Event (LOME), as defined by Brenchley and Newall (1984). A preliminary palynological analysis of a few productive samples from the Hirnantian and lower Rhuddanian intervals in the sections studied here (Figs. 4–7) allowed the recognition of chitinozoans, acritarchs, prasinophytes and scarce cryptospores (Gómez, 2022; Gómez et al., in review). The timeline or succession of events is described from the early Hirnantian up to the early Llandovery (Figs. 8–9) as follows.

3.1. Event 1- lower Hirnantian (M. extraordinarius Zone)

This event is evidenced by the post-glacial, glaciomarine diamictite of early Hirnantian age, recognized at the base of the Don Braulio Formation in its type section, in the Villicum Range, Eastern Precordillera (Fig. 1) (Peralta and Carter, 1990). According to these authors, this 12 m thick diamictite overlies paraconformably shallow-water siliciclastic deposits of La Cantera Formation bearing graptolites of the Sandbian *N. gracilis* Zone (Peralta, 1986) (Fig. 2A and 3). However, a little further south, the diamictite overlies the Sandbian–Katian sedimentary mélange of the La Pola Formation, considered an erosive relict of the Late Ordovician glaciation (Astini, 2001a, b).

The basal diamictite is characterized as a pebbly mudstone (debris flow) deposit that exhibits a massive matrix-supported fabric, which is mainly composed of scattered and unsorted clasts exhibiting glacial features. The clasts are dominated by a sedimentary population and scarce igneous rocks, most of them striated and faceted showing a pentagonal shape (Fig. 2B and 4). This diamictite is interpreted as the

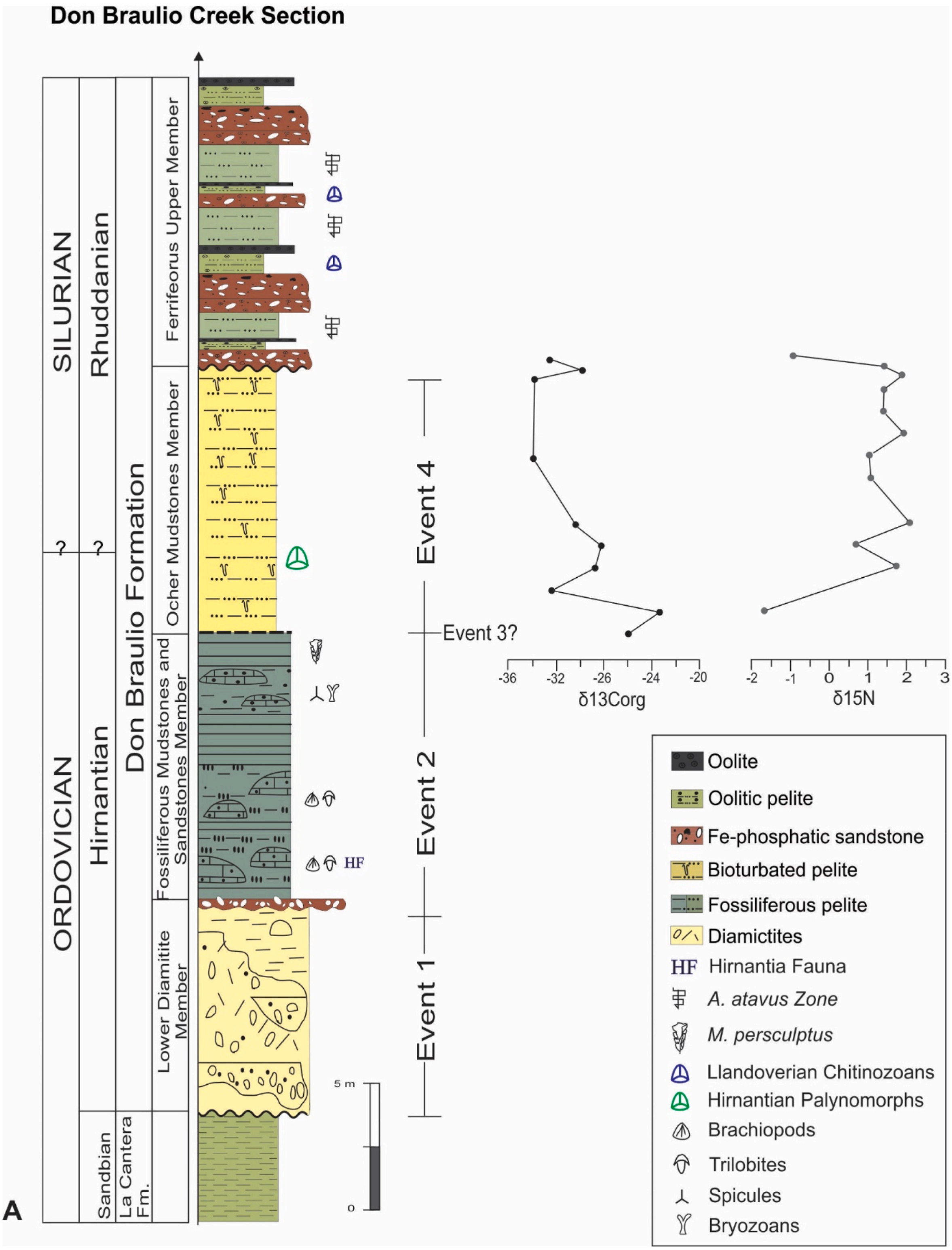

Fig. 4. Stratigraphic section of the Don Braulio Formation in the type section, showing the *Hirnantia* Fauna (Benedetto, 1986), trilobites (Baldis and Blasco, 1975), spicules and bryozoans (Jiménez-Sánchez et al., 2014), *M. persculptus* (Peralta and Baldis, 1990) and *A. atavus* zones (Peralta, 1986), Lladoverian palynomorphs (Volkheimer and Pöthe de Baldis, 1980), and the isotopic curves of δ^{13}Corg, δ^{15}N (Sial et al., 2017a). The Event 3 is not evidenced as described in the Central Precordillera sections (basal cherty pebbly conglomerate), but it is inferred below the Hirnantian *M. persculptus* level considering biostratigraphic correlation (modified from Peralta, 1993a).

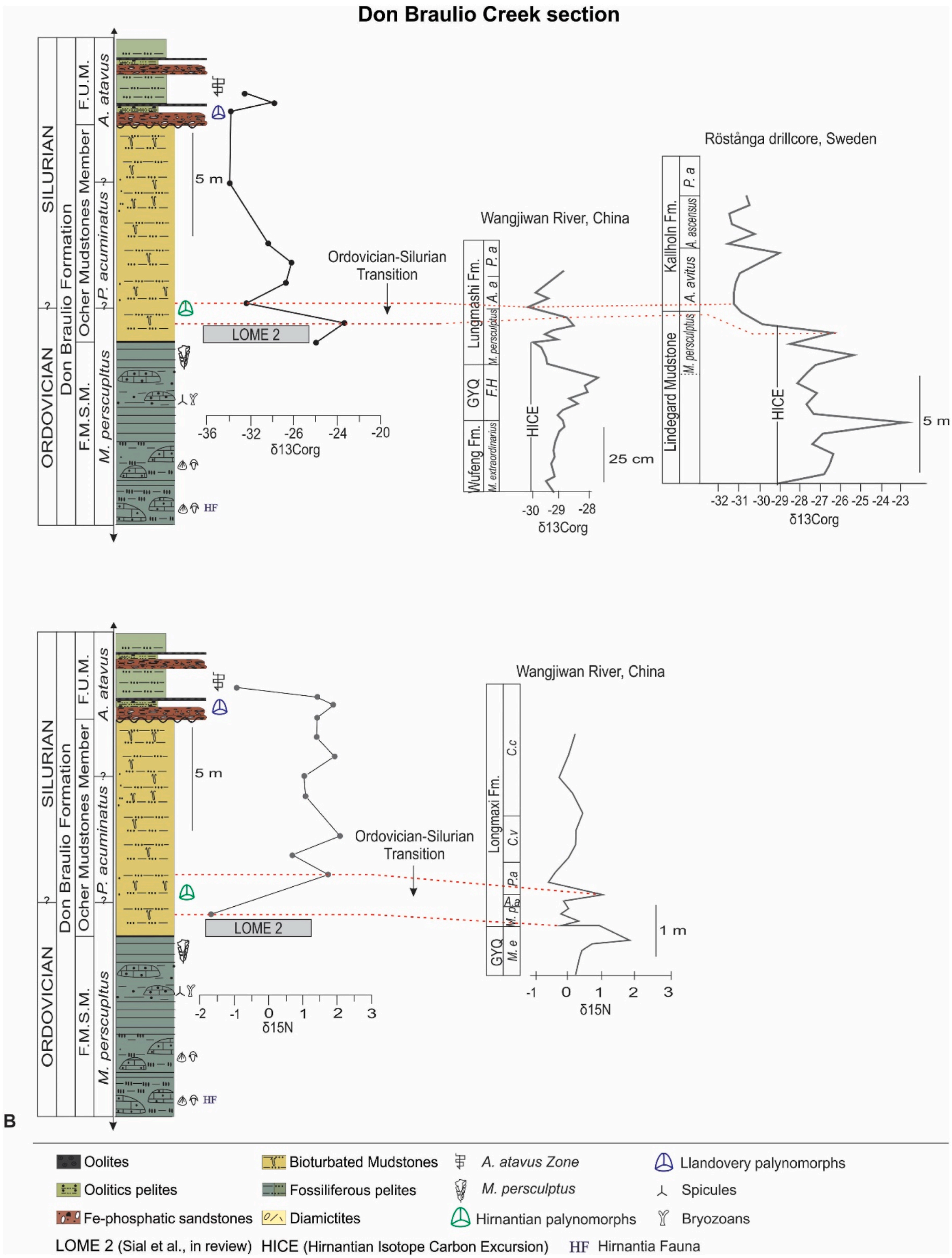

Fig. 5. The stratigraphic position of the Ordovician–Silurian Transition in the lower part of the Ocher Mudstone Member was determined based on the δ^{13}Corg and δ^{15}N curves of Sial et al. (2017a), the record of palynomorphs (Gómez, 2022; Gómez et al., in review). The stratigraphic position of the LOME event is taken from Sial et al. (2022). The isotopic correlation with the localities of Wangjiwan, Hubei Province (South China) (Luo et al., 2015) and Röstånga drillcore (Sweden) (Bergström et al., 2014) is shown.

result of the reworking of glacial deposits as a consequence of the sea-level rise, coeval with the gradual disappearance of the early Hirnantian glacial record (Peralta and Carter, 1999).

In the La Chilca section, a Hirnantian succession made up of a basal carbonate breccia, paraconformably covered by Hirnantian fossiliferous pebbly mudstone, is considered a correlative of the Don Braulio Formation, which underlies shallow marine deposits of La Chilca Formation (Astini and Benedetto, 1992) (Fig. 6). It is noted that in the Central

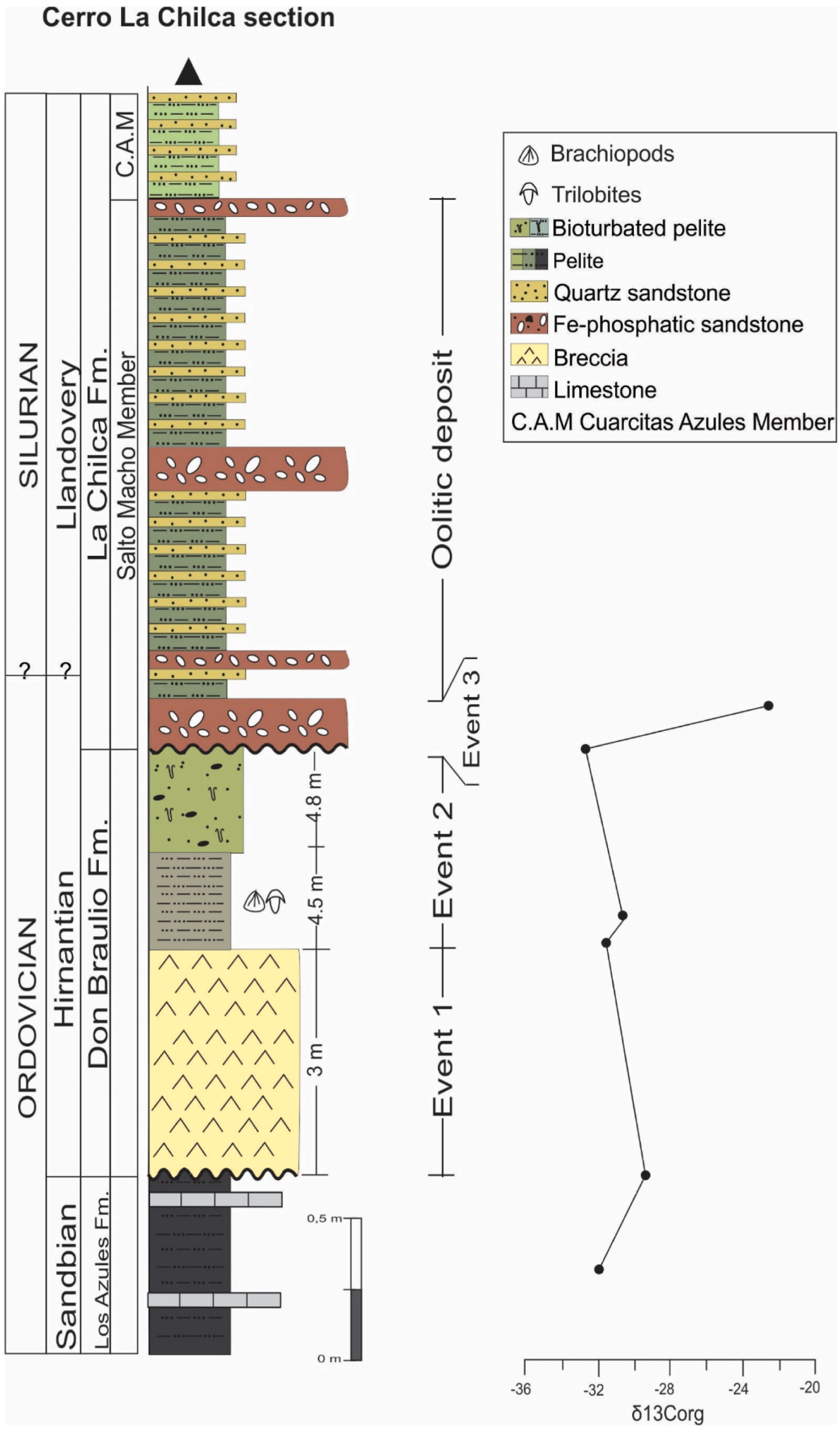

Fig. 6. Stratigraphic section of Cerro La Chilca showing the $\delta^{13}C_{org}$ isotopic curve from the top of Los Azules Formation up to the basal strata of La Chilca Formation (Sial et al., 2017a, 2017b). The location of the Ordovician–Silurian boundary is inferred due to the lack of biostratigraphic records in the basal part of La Chilca Formation.

Precordillera, similar deposits have been mentioned in the Talacasto area (Asurmendi et al., 2018).

Gómez (2022) pointed out the stratigraphic correlation between the basal diamictite of the Don Braulio Formation at the Villicum section and the breccia of Don Braulio Formation at Cerro La Chilca section, considering them as a result of the first Hirnantian transgressive pulse (Figs. 4, 8–9). This author proposed the link of the diamictite with the Transitional Benthic Fauna TBF1 in the sense of Wang et al. (2019), which thrived immediately after the End-Ordovician Mass Extinction (EOME), as proposed by Brenchley and Newall (1984), linked to the first

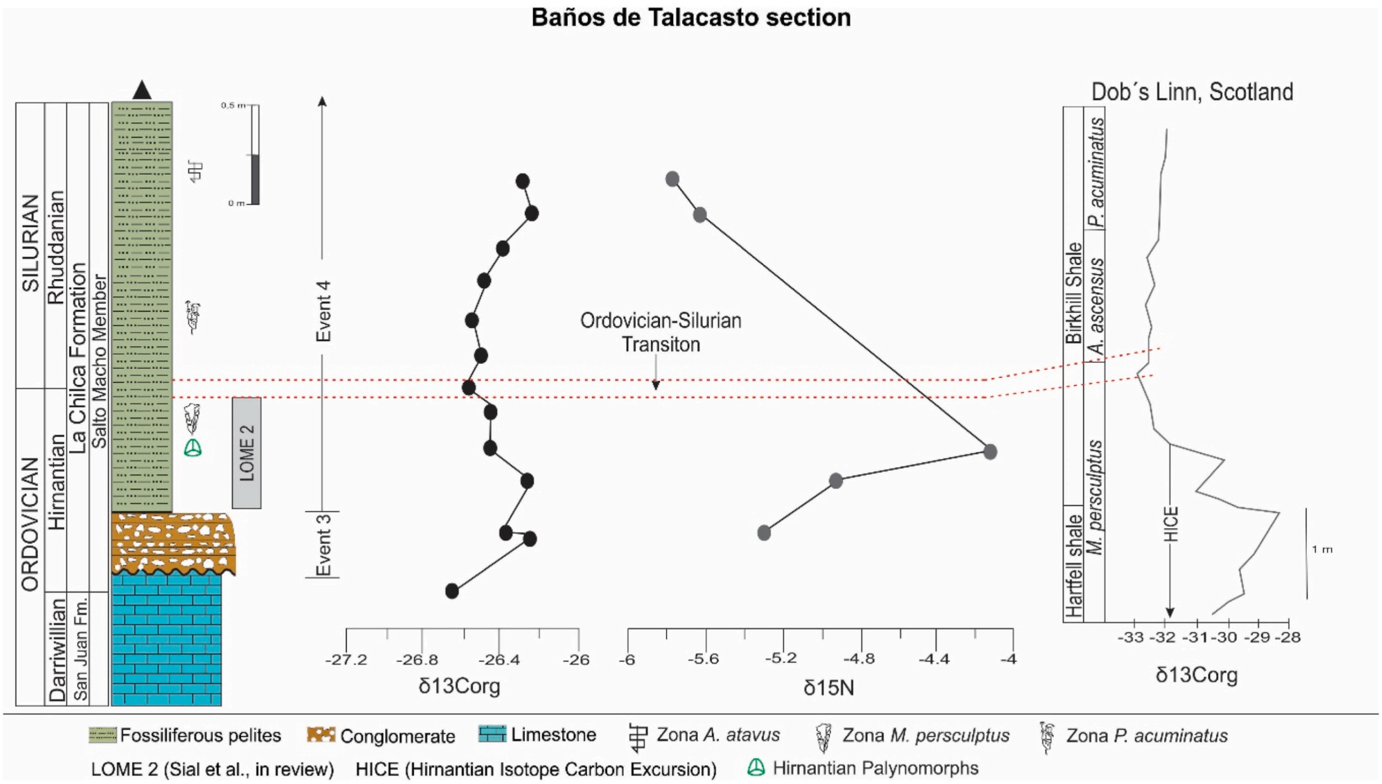

Fig. 7. Stratigraphic section of the Los Baños de Talacasto locality showing the position of Hirnantian and Rhuddanian graptolite levels, and the isotopic curves of $\delta^{13}C_{org}$ and $\delta^{15}N$ (modified from Cuerda et al., 1988a; Sial et al., 2017a; Gómez et al., 2021a), and palynomorphs (Gómez et al., in review). The isotopic correlation of this section with Dob's Lin section in Scotland, GSSP of the base of the Silurian, is shown (modified from Underwood et al., 1997). The stratigraphic position of the OST in the lower part of the Salto Macho Member is based on the record of the *M. persculptus* and *P. acuminatus* zones (Cuerda et al., 1988a).

extinction pulse of the Late Ordovician Mass Extinction (LOME) (Sheehan, 2001; Finnegan et al., 2012; Zou et al., 2018). Besides, the Event 1 is assigned to the lower Hirnantian (Gómez, 2022), being coeval with the occurrence of the *M. extraordinarius* Zone (Fig. 9), according to Wang et al. (2019).

A relationship between the basal diamictite plus TBF 1 and the *M. extraordinarius* Zone was inferred from regional stratigraphic and biostratigraphic analyses carried out by Gómez (2022) in Central and Eastern Precordillera. This relationship is reinforced by biostratigraphic correlation with the *M. extraordinarius* Zone registered in black shales of the Alcaparrosa Formation in the Western Precordillera (Brussa et al., 1999), and with the *A. superbus* Zone in the lower part of the Trapiche Formation in the Guandacol area (Albanesi et al., 1995). Moreover, the upper Member of the Empozada Formation, Mendoza Precordillera, bearing "Ashgillian" conodonts (Heredia and Beresi, 2004), and graptolites of the *Dicellograptus complanatus* and *Dicellograptus ornatus* Zones (Mitchell et al., 1998) is probably correlatable as well.

According to the continental stratigraphic correlation model proposed for the Ordovician–Silurian Transition of South America by Gómez (2022), the basal diamictite of the Don Braulio Formation correlates with equivalent deposits of the Zapla Formation from northwestern Argentina, Cancañiri Formation in Bolivia, San Gabán Formation in Peru, El Cambur Formation in Venezuela, and Rio Ivaí Group in the Paraná Basin of Brazil (Fig. 3).

3.2. Event 2- lower-middle Hirnantian (lower-middle M. persculptus Zone)

This event took place during the middle to upper Hirnantian, embracing the lower-middle *M. persculptus* Zone, and is witnessed in the type section of the Don Braulio Formation, where the basal diamictite is paraconformably covered (erosive surface) by a thin polymictic conglomeratic level with a maximum thickness of 15 cm, at the base of a transgressive fossiliferous sandstone and pelite shallow-water succession of 12 m thick. This succession bears two fossiliferous levels with brachiopods of the *Hirnantia* Fauna (Benedetto, 1986), associated with trilobites and bivalves, and to the top a monospecific assemblage of *Metabolograptus persculptus* (Fig. 4) registered by Peralta and Baldis (1990). This succession is linked to a second transgressive pulse coeval with the Transitional Benthic Fauna TBF 2 (Fig. 9), as defined by Wang et al. (2019), and assigned to the middle-upper Hirnantian (Gómez et al., 2022). On the other hand, this event also occurs in the Central Precordillera, where TBF 2 is registered in the Don Braulio Formation at the Cerro La Chilca and the Cerro del Fuerte sections (Figs. 4 and 8), in agreement with the biostratigraphic data provided by Huang et al. (2019).

In accordance with the tecto-sedimentary model proposed by Gómez (2022) for the Hirnantian evolution of the Villicum and Cerro La Chilca depocenters, the connection among them would have allowed the development of coeval deposits to biofacies TBF 2. This would have favored the postglacial expansion of the shelf to the West, and the deepening of the basin to the North in the Cerro del Fuerte and the Cerro Potrerillos depocenters (Sánchez et al., 1991; Rickards et al., 1996; Benedetto, 1999).

In this scenery, the sea level rise and consequent transgression triggered a change in the biota, evidenced by the record of the TBF2 biofacies, indicating the passage from cold to temperate water conditions. The TBF2 record would be related to a global increase in temperature and widespread anoxia during the middle Hirnantian (Wang et al., 2019) (Fig. 9). At the Cerro La Chilca section, the Hirnantian brachiopod fauna of the Don Braulio Formation is related to TBF 2 and the $\delta^{13}C_{org}$ curve indicates a positive excursion (Sial et al., 2017a), consistent with the late stage of the glacial event, and also with the Hirnantian Carbon Isotopic Excursion (HICE) as proposed by Finney et al. (1999), Gong

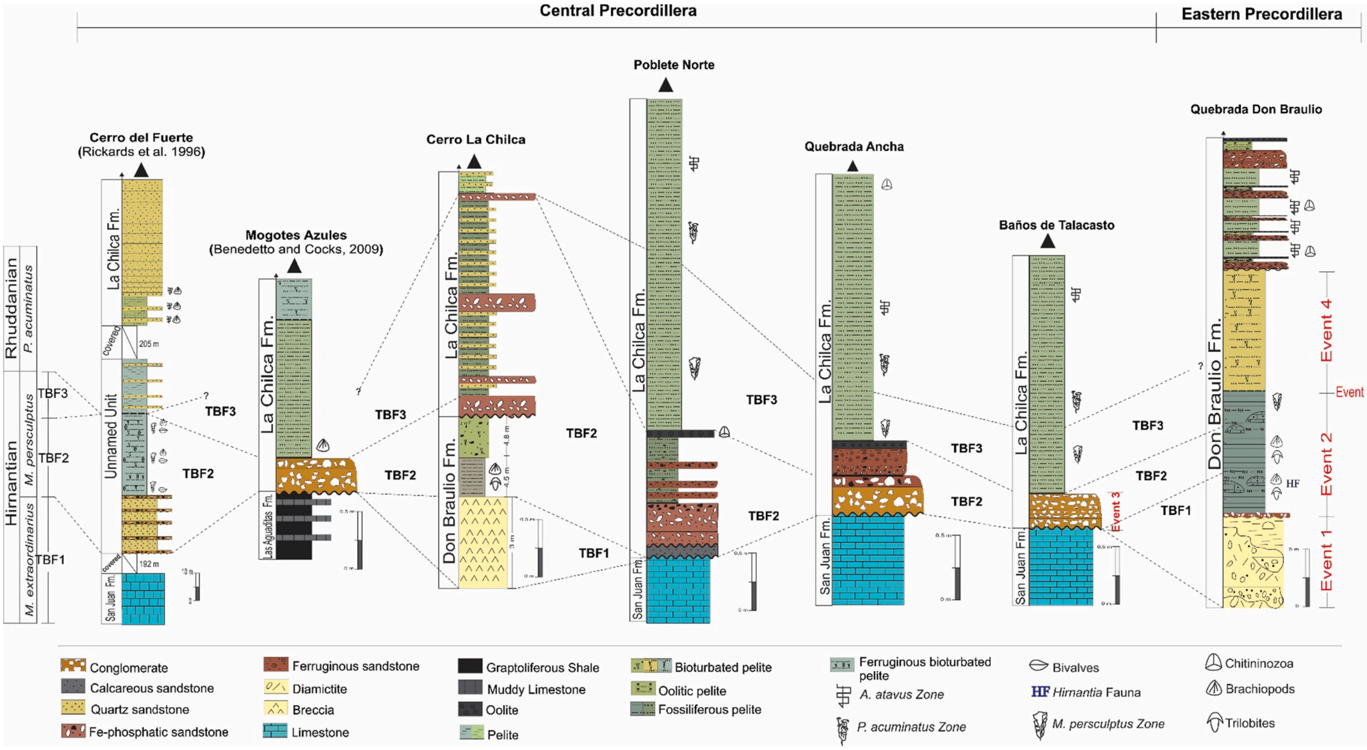

Fig. 8. Biostratigraphic correlation of the Hirnantian TBF1-3 biofacies in the Central and Eastern Precordillera, considering the *M. persculptus, P. acuminatus* and *A. atavus* zones (Baldis et al., 1984; Peralta, 1986; Cuerda et al., 1988a; Peralta and Baldis, 1990; Rickards et al., 1996; Lenz et al., 2003; López et al., 2020; López and Kaufmann, 2023), associations of palynomorphs (Volkheimer and Pöthe de Baldis, 1980; Melendi and Volkheimer, 1982; García-Muro and Rubinstein, 2015), brachiopods of the Hirnantian Fauna (Benedetto, 1986, 1987, 1990; Astini and Benedetto, 1992; Benedetto and Cocks, 2009) and trilobites of the *Dalmanitina-Eohomalonotus* fauna (Baldis and Blasco, 1975; Peralta, 1997), and the global correlation proposed by Wang et al. (2019) and Huang et al. (2019).

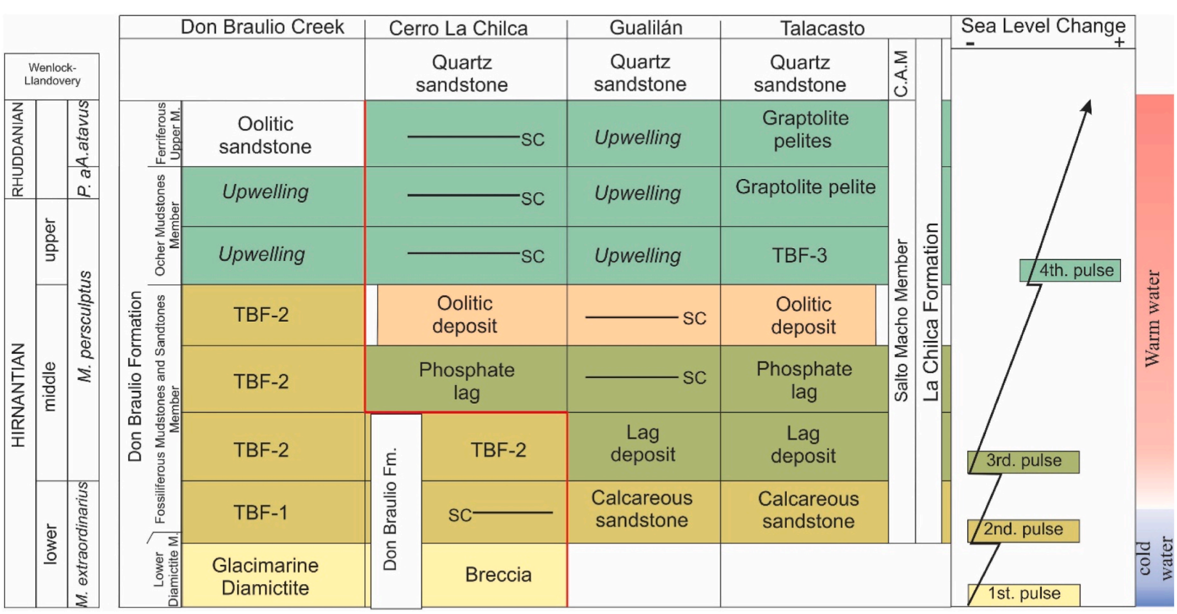

Fig. 9. Integrated litho-biostratigraphy of the of the Hirnantian-Llandovery for the Quebrada de Don Braulio in the Eastern Precordillera and the Talacasto, Gualilán and Cerro La Chilca sections at the Central Precordillera. The relationship between the Transitional Benthic Faunas (TBFs) 1–3 and the lithofacies of the Don Braulio and La Chilca formations allow the recognition of four transgressive pulses and the passage from cold to temperate/warm water in the Hirnantian–Rhuddanian postglacial interval. The *M. extraordinarius* Zone and TBF3 are inferred on the basis of biostratigraphic correlations at regional and global scales. SC, sharp contact.

et al. (2017), Wang et al. (2019), Bergström and Goldman (2019). According to our observations, this behavior of the $\delta^{13}C_{org}$ curve is consistent with the litho-biofacies that characterize the lower part of the Don Braulio Formation, in the Villicum and Cerro La Chilca sections (Figs. 5 and 6).

3.3. Event 3- upper Hirnantian (middle-upper M. persculptus Zone)

This event is well-represented in the Central Precordillera by the transgressive basal cherty pebbly conglomerate of La Chilca Formation (Rolleri, 1947, in Gómez et al., 2022), Hirnantian in age (Cuerda et al., 1988a) and its correlatives Los Bretes Formation and lower pelites of the Tambolar Formation (Peralta et al., 1997; Peralta, 2013) (Fig. 2C and E, 7, 8). This conglomerate is absent in the Eastern Precordillera, however reworked and well-rounded chert clasts are found in the Llandoverian deposits of the Upper Ferriferous Member of the Don Braulio Formation (Fig. 4).

From the Río San Juan to the Gualilán area, the conglomerate overlies erosively (paraconcordance) Early Ordovician open sea limestones of the San Juan Formation and Late Ordovician siliciclastic successions at Cerro La Chilca and Río Jáchal areas and around. The erosive surface at the base of the conglomerate is thought to be a Wave Ravinement Surface (wRs), and the conglomerate as a lag deposit, as a result of the transgressive event (Gómez et al., 2022). A lithofacies change is indicated by the deposition of a coeval phosphate lag toward the north, at the Poblete Norte section (Fig. 2F and 9), below Hirnantian strata bearing palynomorphs (Gómez et al., 2021a; Gómez, 2022) and graptolites of the *M. persculptus* Zone (López and Kaufmann, 2023).

3.4. Event 4: Hirnantian-early Llandovery (upper M. persculptus-P. acuminatus zones)

At the Talacasto area, a transgressive pulse is witnessed in the Los Baños de Talacasto and Poblete Norte sections. Herein, the conglomerate is paraconformably covered by 30 cm thick transgressive phosphate and Fe-phosphate beds, containing Hirnantian palynomorphs (Gómez et al., 2021a; Gómez, 2022). These beds are succeeded by a 12 m thick graptolite-rich succession bearing the Hirnantian *M. persculptus* and Rhuddanian *A. acuminatus* zones indicating the Ordovician–Silurian Boundary (Cuerda et al., 1988a; López et al., 2020; López and Kaufmann, 2023) (Fig. 7). This succession contains scattered phosphate-rich concretions and, based on litho- and biostratigraphic features, correlates with the Ocher Mudstone Member of the Don Braulio Formation at the Villicum section. This would also, include the Ordovician–Silurian Boundary (Peralta, 1993a) and is interpreted as a result of upwelling processes (Gómez et al., 2021b). In addition, equivalent deposits are observed in the lower part of La Chilca Formation in the Gualilán section, with no fossil record to date (Peralta and Páez, 2017) (Fig. 9).

In the Eastern Precordillera, the Ocher Mudstone Member of the Don Braulio Formation spans the Hirnantian-Rhuddanian interval, and consequently, the occurrence of the Ordovician–Silurian Boundary (OSB) is inferred in the succession. This member is dominated by yellowish to greenish bioturbated mudstone, its basal contact is transitional with the underlying Hirnantian deposit containing the *Hirnantia* Fauna, and to the top graptolites of the *M. persculptus* Zone occur. This unit is paraconformably covered by ironstone and pelite intercalations bearing graptolites of the *A. atavus* Zone (Peralta, 1993a) and palynomorphs (Volkheimer and Pöthe de Baldis, 1980) indicating an early Llandovery age.

In the Ocher Mudstone Member positive $\delta^{13}C_{org}$ (−28.7‰) and $\delta^{15}N$ (1.7‰) typical of the Ordovician–Silurian transition have been recorded by Sial et al. (2017a, b), noting that most positive values are characteristic of a glacial stage. According to the data provided by Gómez (2022), the probable Ordovician–Silurian Boundary could be placed between 0.75 and 3 m from the base of the Ocher Mudstone Member (Fig. 5).

4. Discussion

The four transgressive pulses recognized as part of the Late Ordovician and Early Silurian postglacial events are related to the timeline of event as described herein, which show tecto-sedimentary control and sea level changes (Sánchez et al., 1991), as a result of the tilting and deepening of the basin northwards and by the action of the Tambolar structural highs in the Central Precordillera (Bracaccini, 1949; Peralta, 2013; Peralta and Páez, 2017; Peralta and Gómez, 2022) and the Villicum-Zonda arch in the Eastern Precordillera (Padula et al., 1967; Peralta, 1993b).

4.1. Eastern Precordillera

In the Villicum depocenters, in the lower Hirnantian (*M. extraordinarius* Zone), due to the post-glacial sea level rises (Event 1), glacial deposits would have been reworked by the waves and carried out onto the shelf as a debris flow and deposited as a glaciomarine diamictite (Peralta and Carter, 1990; Peralta, 1993a, b; Astini and Buggisch, 1993). This deposit erosively overlays the La Cantera Formation (Sandbian) at the Don Braulio section but also La Pola Formation (Sandbian-Katian) at the La Pola section, considered as an erosive relict of the Late Ordovician glaciation (Astini, 2001a, 2001b). A possible pre-TBF1 extinction suggests that volcanogenic gases caused greenhouse and warming around the Katian-Hirnantian boundary, which led to an expansion of a pre-existing deep-water oxygen minimum zone and productivity collapse (Bond and Grasby, 2020).

A second sea level rise (Event 2) spanning from lower to middle Hirnantian is characterized by the transgressive basal conglomerate with outsized clasts, and shallow water deposits of the Fossiliferous Mudstone and Sandstone Member of the Don Braulio Formation. This succession bears the TBF2 biofacies (Hirnantia Fauna, *M. persculptus* Zone), which would represent an initial stage of faunal recovery, immediately after EOME (Wang et al., 2019), and probably related to the first LOME (Sheehan, 2001; Finnegan et al., 2012; Zou et al., 2018).

The continuous sea-level rise through Event 2 would have favored the passage from TBF1 to TBF2 suggesting the change from cold to temperate water conditions. The recognition of TBF2 would be related to a global increase in temperature and generalized anoxia during the middle Hirnantian. In the middle-upper Hirnantian, the proposal of a LOME 2 suggests a renewed volcanism that stimulated warming and anoxia, causing the second extinction pulse (Bond and Grasby, 2020). In contrast, the single pulse model proposes that despite biodiversity losses, particularly in dominant brachiopods, its magnitude was remarkably smaller than predicted, with only several critical elements of the Hirnantian fauna being extinct. At the same time interval, other groups experienced modest radiation rather than extinction (Wang et al., 2019).

In the Villicum depocenter, during the upper Hirnantian, a basin deepening is recorded (Event 4), in which palynomorph assemblages indicated terrigenous contributions into marine deposits. The interaction between the eustatic sea level rise and glacial flows would have generated a short-term local upwelling plume, as result of oxygenated thermohaline currents. This process originated the stratification of ocean waters and significant changes in sedimentation and biological activity (Cooper et al., 2012), and biota (TBF3). This type of upwelling is produced by a substantial dampening of the effect of wind stresses on currents under the sea ice (Kämpf and Chapman, 2016). In this environment, the winds were directed towards the Gondwanan paleopole controlling the distribution of surface water currents around North Africa, predominantly landward. Consequently, any upwelling would have been restricted to relatively north-south oriented coastline and developing as a local phenomenon (Armstrong et al., 2005). Isotope data in the basal part of the Ocher Mudstone Member suggest a drastic shallowing phase in the Hirnantian–Rhuddanian transition, in accordance with the model provided by Finney et al. (1999).

In the Llandovery, *A. atavus* Zone, the relative lifting of the Villicum block would have generated shallowing with short-time regressive pulses (Astini, 1992) in a high-energy coastal area influenced by freshwater (Gómez et al., 2021a). This would have allowed the development of oolitic bars, interspersed with inner shelf pelites, bearing Llandoverian graptolites of the *A. atavus* Zone (Peralta, 1985) and palynomorphs (Volkheimer and Pöthe de Baldis, 1980; Pöthe de Baldis, 1997).

The Lower Silurian ironstone deposits of Precordillera are a valuable tool as paleoclimate and paleoenvironmental indicators, but also for correlation to regional scale, as occur with correlative deposits of the Northwest Argentina (Lipeón Formation), the North-Patagonian Massif (Sierra Grande Formation), and similar deposits found in Bolivia (Kirusillas Formation) and Brazil (Vila María Formation) (Fig. 3).

Various authors discussed the models of Fe provenance for ironstone deposits. Based on early models, Bayer (1989) and Astini (1992) suggest that the sediments-rich in iron are transported from temperate to cold waters seas during transgressive periods, and then processes of concentration, dissolution, and subsequent precipitation occur during the event. A similar model was proposed for the Lipeón Formation in NOA by Bossi and Viramonte (1975).

Matheson et al. (2022) suggested that the Paleozoic ironstone deposits would have formed from iron-enriched deep ocean hydrothermal fluids. The iron-rich waters would have been delivered by coastal upwelling currents along the continental margins. Analyses of rare earth elements in iron ooids are needed to determine the origin of the Fe and P contributions of hydrothermal fluids from mid-ocean ridges. It is also possible that Fe enrichment could have resulted from weathering of exposed rocks during regression stages, as suggested by Oggiano and Mameli (2006) as an origin of the ironstone seems to fit a regression regime. In the Eastern Precordillera, the relationship of the ironstone deposits with Late Ordovician post-glacial event suggests that the ferruginous rocks could have been linked to a cold to temperate climate as a result of the paleolatitudinal position (30° and 45° SL) in western Gondwana (Van Houten, 1985; Astini, 1992; Ferreti, 2005). This provenance model can be correlated with similar platform deposits recorded in Italy and Austria (Ferreti, 2005; Oggiano and Mameli, 2006).

4.2. Central Precordillera

Considering a possible connection between the depocenters of Cerro La Chilca and Villicum during the lower Hirnantian (Gómez, 2022) and the tilting and deepening of the basin northwards, the first sea level rise is evidenced by the basal carbonate breccia of the Don Braulio Formation at the Cerro La Chilca section. This breccia is thought to be a stratigraphic equivalent of the basal diamictite of the Don Braulio Formation at the Villicum range. In the Talacasto area, the transgressive surface (TS) at the base of La Chilca Formation represents a stratigraphic hiatus spanning from the Darriwilian? to lower Hirnantian.

The subsequent sea level rise (Event 2) records a delay in the transgression and slow sedimentation towards southern part of the basin, which in the Poblete Norte section is represented by the calcareous sandstone lithofacies that erosively overlies (TS) the Early Ordovician limestone of the San Juan Formation. The delay could be a consequence of the basin tilting and deepening towards the north. Towards the central part of the basin, the connection of the Cerro La Chilca and Villicum depocenters would have allowed the extension of the postglacial platform in a westerly direction and basin deepening to the north. This is consistent with the record of the TBF2 biofacies at the Cerro La Chilca section, and the TBF2 biofacies and lithofacies and deeper environments at the Cerro del Fuerte and Cerro Potrerillo depocenters (Sánchez et al., 1991; Rickards et al., 1996; Benedetto, 1999).

At the Cerro La Chilca, Talacasto, Portezuelo de Tambolar, and Cerro Blanco de Pachaco sections, the third transgressive event records the retreat of the shoreface, causing a wRs-type surface and deposition of a transgressive lag (Event 3), and suggesting maximum deepening. A sedimentation change is indicated by the phosphate lag at Cerro La Chilca, Poblete Norte, and Quebrada Ancha sections. This lithofacies represents a sedimentary condensation in the stage of the maximum transgression of the third pulse (Gómez and Fernández, 1992).

The tilting of the Central Precordillera basin and the Tambolar uplift would have allowed the development of localized ferruginous deposits during the middle Hirnantian. These deposits would have been generated from a clastic trap (Brookfield, 1971), with deep facies in the Cerro La Chilca section and shallow facies in the Talacasto area (Gómez, 2022). From a paleogeographic point of view, TBF2 faunas in high-latitude regions of Gondwana appear above glaciomarine diamictites. This litho-biostratigraphic relationship is coincidental with iron-rich deposits during the middle-upper Hirnantian, formed in the first stages of the postglacial transgression (Van Houten, 1985).

In the Talacasto area, during the fourth sea level rise (Event 4, Upper Hirnantian− Rhuddanian), inner shelf deposits bearing the TBF3 biofacies has been recorded. This is evidenced by: a) the transition between the *M. persculptus* and *P. acuminatus* biozones (Baldis et al., 1984; Cuerda et al., 1988a; López et al., 2020), and b) the record of Hirnantian palyno association (Gómez et al., 2021a). The persistence of this transgressive pulse is evidenced by the graptolite-rich succession of the Salto Macho Member of La Chilca Formation, but also by the record of the *P. acuminatus* and *A. atavus* zones (Cuerda et al., 1988a; Lenz et al., 2003; López et al., 2020).

5. Conclusions

For the first time, a detailed litho-biostratigraphic correlation study is applied to establish the timeline of four events in the Ordovician–Silurian Transition of the San Juan Precordillera. With this purpose, paleobiologic (benthic faunas, graptolites and palynomorphs assemblages), diagnostic sedimentary deposits (glaciomarine diamictite, ironstone, transgressive lag, Fe-phosphate lag, and upwelling rocks), isotope data (C, N), and stratigraphic unconformities (erosive and flooding surfaces) were analyzed in four sections of the Central Precordillera at Los Baños de Talacasto, Poblete Norte and the Cerro La Chilca, and in the Eastern Precordillera at the Don Braulio section of the Villicum range. Besides, additional sections from the Central Precordillera (Tambolar, Gualilán and Rio Escondido), were considered for correlation.

Four events have been recognized as follow:

Event 1, is represented by the first transgressive pulse, evidenced by the basal diamictite of the Don Braulio Formation in the Villicum range, and by the basal carbonate breccia of this formation in the Cerro La Chilca section. This event is assigned to the lower Hirnantian, and by regional stratigraphic and biostratigraphic correlation in the Precordillera of San Juan and Mendoza coeval with the occurrence of the *M. extraordinarius* Zone.

Event 2, is evidenced by the second transgressive pulse, represented in the Eastern Precordillera by the Fossiliferous Sandstone and Mudstone Member of the Don Braulio Formation, bearing the TBF1 *Hirnantia* Fauna, the second TBF2 brachiopod association, trilobite fauna, and to the top *M. persculptus* Zone. On the other hand, in the Central Precordillera, at the Cerro La Chilca section, this event is evidenced by the Fossiliferous Sandstone and Mudstone Member bearing the TBF2 brachiopod Fauna, correlative to that of the Don Braulio section. This event corresponds to the middle-lower part of the *M. persculptus* Zone, and the TBF2 record would be related to a global increase in temperature and general anoxia during the middle Hirnantian.

Event 3, is related to the third transgressive pulse, only evidenced in the Central Precordillera by the transgressive basal cherty pebbly conglomerate of La Chilca Formation, and the coeval phosphate lag deposits. The conglomerate is overlain by a graptolite-rich pelite succession, which includes the Ordovician–Silurian Boundary (OSB). In accordance with the bio-stratigraphic data, this event is assigned to upper Hirnantian, middle-upper part of the *M. persculptus* Zone.

Event 4, is represented in the Eastern Precordillera by the fourth transgressive pulse related to the upper *M. persculptus* Zone and the *P. acuminatus* Zone. This event is evidenced by a lower sedimentation rate of upwelling deposits, and the record of Hirnantian palynomorphs in the Ocher Mudstones Member of the Don Braulio Formation. In the Central Precordillera is witnessed by the correlative graptolite-rich pelite succession of La Chilca Formation in the Talacasto area with the TBF3 biofacies. Short-term regressive intervals recognized in the Upper Ferriferous Member of the Don Braulio Formation would indicate the final stage of the Llandoverian postglacial transgression. It should be noted that at the Don Braulio section, the palynological record and isotope data are useful tools to infer the Ordovician–Silurian Boundary. In this way, the Ordovician–Silurian Boundary could be placed between 0.75 and 3 m from the base of the Ocher Mudstone Member. At the Central Precordillera, in the Cerro La Chilca section, no diagnostic fossils have been recorded to date in the Ordovician–Silurian Transition. On the other hand, in the Baños de Talacasto and Poblete Norte sections, the Ordovician–Silurian Boundary is well-defined based on the graptolite record, which correlates with the isotope data. This allows correlation with the Southern China and Sweden, where the OST is isotopically and biostratigraphically well-defined.

In the studied sections, the relationship between bio-chemostratigraphic and sedimentary features, including diagnostic deposits, Transitional Benthic Fauna and isotope excursions, reveals that paleoenvironmental changes through the Ordovician–Silurian Transition are linked to sea level changes (four transgressive pulses), and the passage from cold to temperate/warm waters (postglacial).

CRediT authorship contribution statement

J.C. Gómez: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **S.H. Peralta:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **A.N. Sial:** Writing – review & editing, Validation, Investigation, Jessica Gómez, Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **M.M. di Pasquo:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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