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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.

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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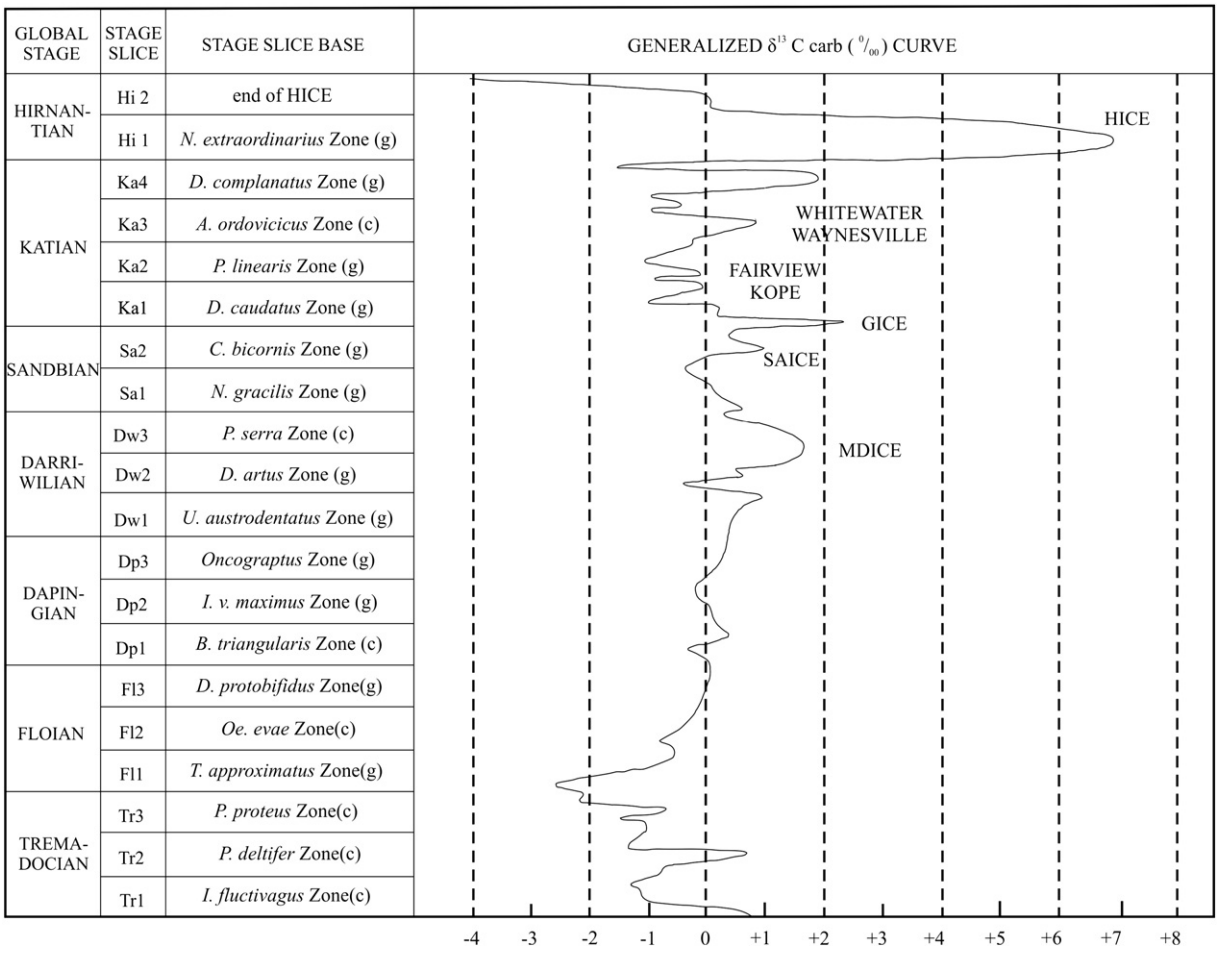

Fig. 1. Generalized $\delta^{13}C_{carb}$ curve and its relations to global stages and stage slices. Note the position of the MDICE in Stage Slices Dw2 and Dw3. Figure is slightly modified after Bergström et al. (2012).

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 $\delta^{13}C$ 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 $\delta^{13}C_{carb}$ records through substantial stratigraphic intervals. However, in two long and well-exposed sections, the San Juan Formation 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 approximately 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 unconformably 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 classification 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 separated 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