

Carbon Isotope Chemostratigraphy of Carbonate Sequences and the Precambrian-Cambrian transition in NW Argentina

A.N. SIAL, V.P. FERREIRA, A.J. TOSELLI, F.G. ACEÑOLAZA, R. ALONSO AND M.A. PARADA

C-isotope stratigraphy is one of the most powerful tools in Precambrian chronostratigraphy, especially when sediments lack recognizable animal fossils (Kaufman, 1998). The $\delta^{13}\text{C}$ secular variation curve for marine carbonates in the Neoproterozoic (Hoffman et al. (1998) shows strong positive-negative excursions, four of the major ones interpreted as the stratigraphic position of ancient ice ages. In this study, we examined carbonates in NW Argentina that could, potentially, be proxies for the Precambrian-Cambrian transition, studying their $\delta^{13}\text{C}$ chemostratigraphy and comparing it to a global C isotope secular variation curve.

Geological setting .The Puncoviscana Fm. sl. is a complex sedimentary sequence of Upper Precambrian-Lower Cambrian age, outcropping in NW Argentina, from Tucumán to Salta and Jujuy. These rocks are highly deformed shales, sandstones, carbonates and conglomerates. In several localities, trace fossils of Tommotian age (*Oldhamia* facies) are abundant in clastic facies. The carbonates (Las Tienditas/Volcán Fms sensu Salfity et al., 1975) are intercalated in the clastic sequence and are composed of black limestones that show sparitic calcite with recrystallized organic matter, Fe sulfide grains, and lithic fragments (plag., chl., qz). According to Jezek (1990), these carbonates were deposited in marine tectonic ridges within shallow environments. In the Precordillera basin, San Juan province, a continuous sequence of carbonates with regressive characteristics developed from the Lower Cambrian to the basis of the Ordovician, at which point a transgressive stage started (Baláis *et al.*, 1984). Four large limestone-sandstone cycles have been recognized in the La Laja and Zonda Fms. These cycles were formed in an open, shallow platform, with clean and warm water with free circulation, by fluctuation of the sea level, which suffered an important lowering during the deposition of the high portion of the La Laja Fm. with the development of oolitic bars and supratidal dolomitic facies. The Pie de Palo range complex, east San Juan town, westernmost Sierras Pampeanas, has been regarded as part of the Precordillera basement. The west sector of this range is characterized by shallow sediments with the predominance of carbonates intercalated with magnesian and siliciclastic rocks, metamorphosed in the greenschist to amphibolite facies. Although a Late Neoproterozoic age for this complex has been suggested, U-Pb zircon data have indicated a Grenville age (e.g. Kay *et al.*, 1996).

Carbon and oxygen isotope chemostratigraphy Over 100 samples were taken along traverses, perpendicular to the strike of limestone layers, at a metric scale, from carbonates of the Las Tienditas Fm., from the Pie de Palo range complex and from La Laja Fm., Precordillera. CO_2 gas was extracted from powdered carbonates in a high vacuum line after reaction with 100% phosphoric acid at 25°C for one day (three days allowed, when dolomite was present). The CO_2 released, after cryogenic cleaning, was analyzed in a double inlet, triple collector SIRA II mass spectrometer and results are reported in δ notation, PDB scale, in permil (‰).

Las Tienditas Fm. Twenty three carbonate samples were stratigraphically collected from a 100m-thick exposure about 38 km SE from Salta in the Lerma Valley. $\delta^{13}\text{C}$ values between -1.6 and + 3.4 ‰_{PDB} have been found, the highest positive values observed at the basis of the section, and gradually decrease towards the top. About 15 m from the top, a negative

excursion (-1.6) is then observed. Oxygen isotopes exhibit strong oscillations at the basis of the Formation and gradually increase from -11.5 to -5‰_{PDB}, at the corresponding point where the lowest $d^{13}C$ value was observed. About 15 m from the top of this unit occur argillaceous levels, more thicker as one approaches the contact with the Puncoviscana Fm. The C- isotope curve of this Formation when compared to the one across the Precambrian-Cambrian boundary elsewhere suggest that Las Tienditas carbonates have registered such a transition about 15m from its top at the studied section.

(a) La Laja Fm., Precordillera Thirty five samples stratigraphically collected for ~700m of carbonates in this Formation along the Zonda Valley in the Chica de Zonda Range, display $d^{13}C$ from -2 to + 1 ‰_{PDB}. The lower portion (marly limestones) of the C-isotope curve shows much stronger oscillations, values varying from +1 to -2‰_{PDB}. This negative excursion is followed upsection by a slightly positive one (+0.5‰). For the next 100 m upsection, $d^{13}C$ values are progressively more negative and a well-defined anomaly (-2‰) is observed, -240m from the basis of the profile. From about 320m up, this profile exhibits little $d^{13}C$ variation (-0.5 to -0.1‰_{PDB}). This C-isotope profile for La Laja Fm., when compared to profiles for carbonates that registered the Vendian-Tommotian transition elsewhere (e.g. Magaritz, 1989; Magaritz *et al.*, 1991; Brasier *et al.*, 1994), suggests that such transition is recorded at the basis of this unit.

(b) **Pie de Palo Range complex** Carbonate rocks of this complex have been sampled in three localities: two of them in the La Petaca Creek (Ciampo Venato and Pozo) in the occidental side of the Range, and a third one, in the San Ceferino locality, in its southwestern portion. Each locality displays a different $d^{13}C$ chemostratigraphic profile. $d^{13}C$ in 10 carbonate samples from the Pozo locality are very close to 0.0‰_{PDB}, while 15 carbonate lens samples from Ciampo Venato yielded $d^{13}C$ values between -1.0 and 0.0 ‰_{PDB}. At San Ceferino, 11 carbonate samples exhibit $d^{13}C$ values from -1.4 to +1.3 ‰_{PDB}. These three C isotope profiles show a very narrow range of variation, atypical for Late Neoproterozoic sedimentary carbonates.

Conclusions Present C-isotope data suggest that the Precambrian-Cambrian transition was recorded by carbonates of the upper portion of Las Tienditas Fm, and at the lowest portion of the La Laja Fm. Little $d^{13}C$ variation, around zero, for carbonates of the Pie de Palo complex, is in better agreement with a Late Mesoproterozoic age, as proposed by several authors (e.g., Kay *et al.*, 1996). The Precordillera basin is interpreted as an exotic terrane detached from the Gondwana western side by strike-slip movement from a region between South America, Africa and Antarctica (SAFRAN, sensu Aceñolaza and Toselli, 1999). Other hypotheses propose the origin of Precordillera as a collisional event between the Occidentalia terrane (Dalla Salda *et al.*, 1992) or the detachment of a exotic terrane derived from Ouachita embayment of southern Appalachians (Astini *et al.*, 1995). More detailed C-isotopic work is necessary, however, to allow a chemostratigraphic comparison among Early Paleozoic carbonate sequences from the continents encompassed in these different hypotheses.

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