

CHEMOSTRATIGRAPHY OF THE MINA VERDÚN GROUP AND OTHER CEMENT-GRADE PROTEROZOIC LIMESTONE DEPOSITS IN URUGUAY

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INTRODUCTION

The Mina Verdún Group (MVG) was erected by Poiré et al. (2003) to include a sedimentary succession exposed in the homonymous mine, which is made up (from base to top) of (Fig. 2):

-Don Mario Formation: metapelites

-La Toma Formation: marls

-El Calabozo Formation: grey stromatolitic limestones

-Gibraltar Formation: dolomitic marls, red limestones and massive dolostones

Thickness of the succession at its stratotype reaches 285 m. An important feature of the thick (up to 170 m) limestones of El Calabozo Formation is the occurrence of a stromatolite assemblage composed almost exclusively by *Conophyton* (Fig. 2). These limestones are of considerable economic importance, because they constitute the basis of a large cement industry. A minimum age for the succession is provided by the unconformably overlying Las Ventanas Formation, which on the basis of acritarch biostratigraphy is assigned to the lower Ediacaran (635-575 Ma, Blanco & Gaucher, 2005). Gaucher et al. (2004d) assign the succession exposed in the Burgueño limestone Quarry, 40 km to the south of Mina Verdún, to the MVG. The succession exposed in the quarry, 150 m in thickness, includes (from base to top): metamarls, limestones, stromatolitic *Conophyton*-limestones and massive dolostones. At the stratotype and in Burgueño Quarry, conglomerates overly with erosional unconformity the MVG. These conglomerates, assigned to LVFm (Blanco & Gaucher, 2004, 2005), include a level of diamictites and breccias at the contact to the MVG, which has been recognized as a palaeokarst surface. The association of palaeokarst surfaces developed on top of carbonate successions and overlain by glacial diamictites is well known for a number of Neoproterozoic successions. Dropstones occur in laminated mudstones, associated with diamictites. However, no carbonates occur on top of the diamictites.

We carried out $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of carbonates and corresponding petrographic studies at two sections of the MVG and also on carbonates mined for the cement industry at La Plata Mine (ANCAP), with the aim of testing chemostratigraphic tools as an aid for the

exporation of cement-grade carbonates.

CHEMOSTRATIGRAPHY

MINA VERDUN GROUP

Mina Verdún Section. We collected 56 samples of carbonates and marls from quarry exposures and core material, and analyzed them for their C and O isotopic composition. A highly consistent pattern of secular $\delta^{13}\text{C}$ variations emerged, values ranging between -3.3 and $+4.0$ ‰ V-PDB (Fig. 2). Marls of La Toma Formation show negative $\delta^{13}\text{C}$ values at the base, beginning with a minimum of -3.3 ‰ V-PDB, steadily rising to positive values up to $+1.5$ ‰ V-PDB up section. Overlying limestones of El Calabozo Formation are characterized by remarkably constant positive $\delta^{13}\text{C}$ ratios within the narrow range between $+0.27$ and $+2.4$ ‰ V-PDB. Dolomitic marls, limestone-dolostone rhythmites and massive dolostones of the overlying Gibraltar Formation also exhibit exclusively positive values between $+0.15$ and $+4.0$ ‰ V-PDB, with a tendency toward heavier values up section. $\delta^{18}\text{O}$ values for the Mina Verdún section vary between -4.1 and -19.7 ‰ V-PDB. Whereas $\delta^{18}\text{O}$ values in El Calabozo Formation range from -9.1 to -19.7 ‰ V-PDB, the Gibraltar Formation exhibits higher values between -4.1 and -13.8 ‰ V-PDB, reflecting its mainly dolomitic composition. No correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is observed.

Burgueño Quarry section. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ crossplots of the 25 analyses performed there show a positive correlation between both parameters. This is indicative of thermal alteration of C isotopic composition of carbonates (Jacobsen & Kaufman, 1999). $\delta^{13}\text{C}$ varies between $+0.74$ and -0.60 ‰ V-PDB for the same stratigraphic interval sampled at the Mina Verdún section. Thus, $\delta^{13}\text{C}$ of carbonates is significantly shifted toward more negative values and stratigraphic variation in C isotopic composition lowered. $\delta^{18}\text{O}$ values are also more negative than in the Mina Verdún section, ranging between -20.7 and -15.1 ‰ V-PDB. Other indications that the mentioned differences are the result of metamorphic alteration are: (a) stromatolitic limestones in the Burgueño Quarry are distinctively decolorated,

showing light grey to white colour. The same lithologies are medium to dark grey in the Mina Verdún section, due to disseminated organic matter. (b) Intrusive granitoids of latest Ediacaran to Cambrian age crop out in the vicinity, namely the Pan de Azúcar Granite (559 ± 28 Ma, Rb-Sr) and Sierra de Animas syenites (520 ± 5 Ma Rb-Sr; Bossi et al., 1993). We envisage that magmatic activity and related hydrothermal alteration caused organic matter occurring in the succession to react with carbonates, thus lowering and homogenizing $\delta^{13}\text{C}$ values.

LA PLATA MINE (ANCAP)

Fourteen samples were collected just to the west of La Plata Mine (owned by the state company ANCAP), and their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ratios measured. Moreover, seven of these samples were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$, and their geochemistry studied by XRF. The analyzed section (Fig. 1) was chosen because it shows the least deformation and lowest thermal overprint of the nearby Minas Granite.

The structure of the area corresponds to an anticline (La Plata Anticline; Gaucher et al., 2004b), the core of which is occupied by banded siltstones typical of the Yerbal Formation (Gaucher, 2000). The flanks are made up of laminated limestones and limestone-dolostone rhythmites with variable amounts of silicates (up to 16.8% SiO_2). Colour of these carbonates range from dark gray to green and pink. Pink and reddish colours are probably due to thermal alteration of originally gray carbonates. $\delta^{13}\text{C}$ analyses show a consistent trend (Fig. 1) from positive (+1.8 ‰ V-PDB) to negative values (-2.0 ‰ V-PDB). The crossover occurs ca. 300 m above the contact with the underlying siltstones. Most of $^{87}\text{Sr}/^{86}\text{Sr}$ analyses show very radiogenic values indicative of resetting of this system. This is confirmed by both rather negative (<-10 ‰) $\delta^{18}\text{O}$ values and high Mn/Sr ratios between 4.0 and 9.0. One significant $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7077 was obtained in a very pure limestone (96 % CaCO_3), which is interpreted here as a good approximation to primary values (Fig. 1).

DISCUSSION

The section reflecting primary isotopic composition of carbonates of the MVG is its stratotype (Fig. 2). The $\delta^{13}\text{C}$ curve obtained, has the following salient features: (a) a small negative excursion at the base, followed by moderately positive values throughout the rest of the section; (b) moderate amplitude of $\delta^{13}\text{C}$ excursions of up to 5.5 ‰ (transition between La Toma and El Calabozo Formations); and (c) $\delta^{13}\text{C}$ values ranging between -3.3 and +4.0 ‰ PDB. This features strongly resemble the global C-isotopic curve (Kah et al., 1999) for the late Mesoproterozoic to early Neoproterozoic (Tonian), between 1300-800 Ma. Early Mesoproterozoic carbonates show isotopic invariance around 0 ‰ PDB, and late Neoproterozoic (Cryogenian-Ediacaran) successions are characterized by rapid, large-amplitude isotopic excursions and heavy $\delta^{13}\text{C}$ values between +4 and +12 ‰ PDB (Kah et al., 1999). Therefore, the Mina Verdún

Group was probably deposited in the late Mesoproterozoic to Tonian. So far, no correlations with other units in SW-Gondwana have been postulated. The Itaiacoca Group (SE-Brazil) contains lithologically very similar *Conophyton*-limestones. Siga Jr. et al. (2003, this symposium) consider an age close to 1.000 Ma as probable for that unit, on the basis of U-Pb SHRIMP dating of basic sills intruding the carbonates.

Regarding the stratigraphic assignment of the carbonate deposit of La Plata Mine, it has been proposed that it might be correlated with the MVG (Poiré et al., 2005; Masquelín, 2006). However, this is very unlikely, because: (1) limestones in La Plata Mine are non-stromatolitic; (2) no massive dolostones occur there, unlike the MVG (Gibraltar Formation); and (3) limestones of the MVG show no negative $\delta^{13}\text{C}$ excursions (Fig. 2), as recorded in La Plata deposit (Fig. 1).

On the other hand, Gaucher et al. (2004b) assign the La Plata deposit to the Polanco Formation of the Arroyo del Soldado Group. Our data supports this correlation, as shown by: (1) the stratigraphic succession exposed at La Plata Anticline, with banded siltstones at the base, passing into carbonates up section, is identical to the Yerbal-Polanco transition (Gaucher, 2000; Gaucher et al., 2004a, b); (2) non-stromatolitic, clastic limestones and limestone-dolostone rhythmites predominate, as in the Polanco Formation (Gaucher, 2000); (3) the lower Polanco Formation (Unit A) is characterized by positive values, passing into negative values up section (Unit B, Gaucher et al., 2004a), just as carbonates at La Plata Mine (Fig. 1); (4) the crossover from positive to negative values occurs 300 m stratigraphically on top of the underlying siltstones both in the Polanco Formation (Gaucher et al., 2004a) and at La Plata Mine; and (5) $^{87}\text{Sr}/^{86}\text{Sr}$ values around 0.7077 are typical of the upper Unit A of the Polanco Formation (Gaucher et al., 2004c). Differences between the typical Polanco Formation and carbonates of La Plata Mine include a different style of deformation and common pink and green colours for limestones at La Plata Mine, unfrequent in the Polanco Formation. However, as stated by Gaucher et al. (2004b), these differences can be readily explained by the thermal overprint generated by the nearby Minas Granite. Therefore, we conclude that carbonates of La Plata Mine belong to the Polanco Formation (Ediacaran).

CONCLUSIONS

1-A $\delta^{13}\text{C}$ curve is presented for the MVG, characterized by predominantly positive values and a moderate-amplitude, negative excursion near its base.

2-Whereas at Mina Verdún quarry primary isotopic values are preserved, $\delta^{13}\text{C}$ values obtained for the Burgueño Quarry denote considerable alteration due to the intrusion of the Pan de Azúcar Granite and Sierra de Animas Formation.

3-Age of the MVG is probably late Mesoproterozoic to Tonian (early Neoproterozoic).

4-On the basis of lithostratigraphy, C and Sr isotopic values and carbonate facies, we assign

limestones mined at La Plata deposit (ANCAP) to the Polanco Formation of the Arroyo del Soldado Group. On the same basis, an assignment to the MVG is ruled out.

5-The potential of C and Sr chemostratigraphy to identify prospective limestone horizons for the cement industry in thick carbonate successions is thus demonstrated.

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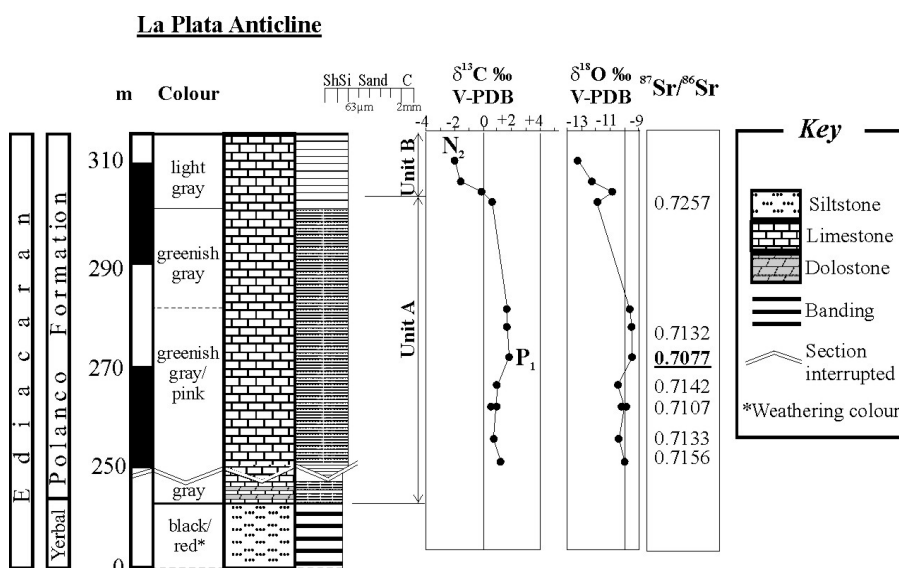


Fig. 1: Stratigraphic column and isotopic data for carbonates at the western flank of La Plata Anticline (site FPU 139: 34°24'58''S, 55°16'31''W), just to the W of the homonymous mine

Mina Verdún Group

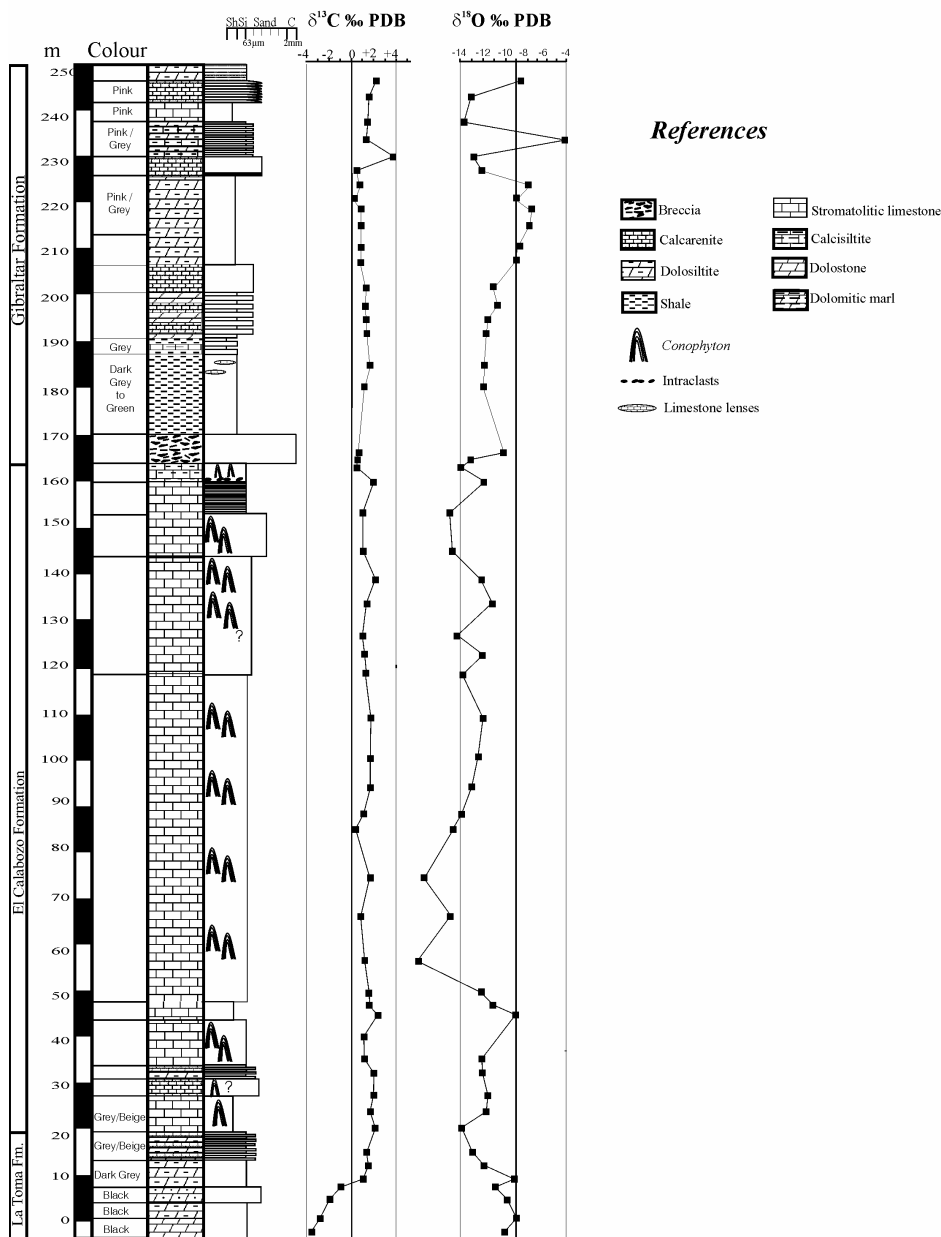


Fig. 2: Chemostratigraphy of the Mina Verdún Group at its stratotype, near the town of Minas (Mina Verdún, 34°22'23" S; 55°16'47" W).

RESUMEN

Se presenta una curva de $\delta^{13}\text{C}$ para el Grupo Mina Verdún (GMV) en su estratotipo cerca de Minas, caracterizada por valores negativos de hasta -3.3‰ V-PDB en la base (Formación La Toma), creciendo continuamente a valores positivos de hasta $+4.0 \text{‰ V-PDB}$ hacia la cima. Las calizas a *Conophyton* (Formación El Calabozo) muestran valores $\delta^{13}\text{C}$ restringidos entre $+0.27$ y $+2.4 \text{‰ V-PDB}$. Mientras en Mina Verdún se preservan los valores isotópicos primarios, las razones $\delta^{13}\text{C}$ en Cantera Burgueño muestran alteración importante debido a la intrusión del Granito Pan de Azúcar y Formación Sierra de Animas. $\delta^{13}\text{C}$ varía allí entre $+0.74$ y -0.60‰ V-PDB , con $\delta^{18}\text{O}$ más negativo que en Mina Verdún. Se analizó también la composición isotópica de calizas en Mina La Plata (ANCAP). Análisis $\delta^{13}\text{C}$ conforman una curva consistente desde valores positivos ($+1.8 \text{‰ V-PDB}$) a negativos (-2.0‰ V-PDB). Un valor $^{87}\text{Sr}/^{86}\text{Sr}$ de 0.7077 obtenido en calizas puras (96 % CaCO_3) se interpreta como el menos alterado y cercano a la razón primaria. En base a la litoestratigrafía, valores isotópicos de C y Sr y facies carbonáticas, confirmamos correlaciones previas de las calizas de Mina La Plata con la Formación Polanco del Grupo Arroyo del Soldado. Asimismo, se descarta una correlación con el GMV. Mientras la edad del GMV es probablemente Mesoproterozoico tardío-Toniano, las calizas cementeras de la Formación Polanco fueron depositadas en el Ediacarensis. Esto remarca el potencial de la quimioestratigrafía de C y Sr para identificar horizontes calcáreos prospectivos para la industria cementera.