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Isotope studies of carbonate rocks of La Luna Formation (Venezuela) to constrain the oceanic anoxic event 3 (OAE3)

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ABSTRACT

^{87}Sr/^{86}Sr ratios, δ^{13}C, and δ^{18}O determinations performed on 30 bulk carbonate rocks are presented to constrain the isotope characteristics regarding Oceanic Anoxic Event 3 in the La Luna Formation, Maracaibo Basin. The samples were collected along a 22 m profile in San Miguel region (Merida State, Venezuela). The exhibited ^{87}Sr/^{86}Sr ratios are between 0.707659, at the base, and 0.707733 at the top of studied section, corresponding estimated younger numerical ages than the inferred ages dated as Santonian (85.8–83.5 Ma) based on occurrence of *Dicarinella asymetrica*. The obtained ^{87}Sr/^{86}Sr ratios are certainly higher than expected for Santonian sea Sr and they are attributed to regular riverine strontium fluxes in the restricted (gulf-like) Maracaibo Basin. The values of δ^{18}O data between −3.76‰ and −11.76‰ are distributed in two distinct clusters in a same way and coherent as for δ^{13}C data which are in a range between −1.75‰ and −13.87‰. One of the clusters $\delta^{13}C = -2.5 \pm 1.0$‰ and $\delta^{18}O = -10.0 \pm 1.5$‰), illustrate the homogeneous marine deposition under tropical conditions, while the other, more variable, probably could reflect the cyclicity of temporally changes in Pacific versus Atlantic Ocean circulation with cooling water or cooling trend climate. These δ^{13}C values around −2.5 ± 1.0‰ do not fit with the significant carbon isotope excursion as expected for the oceanic anoxic event (OAE) and support the work hypothesis that Coniacian–Santonian anoxic event (denominate as OAE3) is not a global one.

1. Introduction

The secular variation of ^{87}Sr/^{86}Sr ratios during Paleogene and Cretaceous based in marine carbonates are well established after few excellent works, e.g.:. DePaolo and Ingram (1985),Mcarthur et al. (1992),Jones et al. (1994). The precise and reliable values for the ^{87}Sr/^{86}Sr ratios permit infer the ages and perform high resolution stratigraphy that is similar to that of other techniques used in age correlations.

The use of Sr-Sr ratios to constrain depostional ages in marine carbonate rocks is obviously related to well preserve samples with minimum of extraneous strontium. As extraneous can be understood all anomalous Sr (different isotopic composition of the prevalent sea Sr) incorporated during or later by some diagenetic alteration, for example. In a general way the presence of extraneous Sr led to higher values of ^{87}Sr/^{86}Sr ratios, mainly in internal basins which can be influenced by continental and more radiogenic Sr carried by rivers. The opposite situation is also valid as is observed in the Black Sea (Major et al., 2006). The nature of contamination and extent of diagenetic alteration can be evaluated by usual stratigraphic methods or modern instrumental techniques which include SEM, cathode luminescence, X ray diffraction etc.

Carbon and oxygen isotopes can also be used as geochemical proxies when involve carbonates in general. Their usage for different purposes was prior to studies involving Sr. The isotopic ratios of both elements are expressed as δ‰ (simply δ^{13}C or δ^{18}O) which are per mil differences compared usually with a standard carbonate designed VPDB (Craig, 1957). They are used in various branches of science. Particularly in geosciences constitutes an

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excellent tool for stratigraphy studies and palaeoclimatology. The temperature in the past (Epstein et al., 1953), anoxic events, isotopes markers, freshwater or sea mollusk shells, sea excursions, etc., are examples of application using carbonate samples.

$\delta^{13}C$ data in limestones of marine basins are in a narrow range (±2‰) and fairly uniform. Usually the results along a profile are assigned by negative and/or positive excursions, as well as in ^{18}O which could reflect temporal variations in environmental conditions, temperature essentially. Regarding the carbon data, the positive excursions are in general marked to increased rate of organic-rich sediment burial and, hence, sequestering the lighter ^{12}C isotope. Other possible minor causes are raised phytoplankton productivity and preservation of organic matter under anoxic conditions (<0.5 ml of dissolved O_2/L) which are known abbreviated in the literature as AOE (Anoxic Oceanic Event). Three anoxic events are currently mentioned as occurred during Cretaceous. The Coniacian-Santonian oceanic event designated as OAE3 is thought to be the last one (Arthur and Schlanger, 1979; Jenkyns, 1980) and documented in La Luna Formation (Perez–Infante et al., 1996). The ^{12}C sequestering, as mentioned above, results in residual CO_2 reservoir enriched in ^{13}C (Jones and Jenkyns, 2001). Notwithstanding, the exact correlation of enrichment of heavier carbon isotope and marine events of carbon rich sediments burial is complex because high values in ^{13}C usually persist after ending an anoxic event (Jenkyns and Clayton, 1997; Menegatti et al., 1998). Rey et al (2004) based on sedimentological, micropaleontological and geochemical evidence proposed that the La Luna Formation was deposited under anoxic/dysoxic conditions in a tropical epicontinental sea on the northwest South America margin that it may provide insights into factors that influenced the sedimentation and controlled the accumulation of organic-rich deposits at decimeter and meter scales during the youngest of the Cretaceous oceanic anoxic events (OAE). Concerning the anoxic events Arthur et al. (1990) suggest that are global episodes of deposition and preservation of organic matter, and Jones and Jenkins (2001) postulate that most probable explanation is increased rates of hydrothermal activity, which in turn led to several processes including enhanced CO_2 outgassing, global warming and makes surface ocean waters more productive during certain period. Other similar explanations are proposed by Nadin et al. (1997). Generally, according to Koutsoukos et al. (1991) the anoxic event are episodic of short duration by changes in paleogeography, leading to changes in the water circulation and sea level, for example. With regards to the Maracaibo Basin is thought that the oceanic Caribbean–Colombia plateau generated at shallow depth and close to Proto Caribe passage restricted the circulation of cooler and richer oxygen Pacific water to the warmer Atlantic Ocean (Kerr, 2005) and expanding the extent of oceanic anoxy. The maximum of sea ingression and anoxy is not yet precised. Until now are assumed as occurred between Turonian (91 Ma) and Campanian (74.5 Ma).

In this paper stable isotopes of Sr, C and O in carbonate rocks recovered in San Miguel section of La Luna Formation are applied to recognize the potentialities of such isotopes for validate or no the sedimentary evolution and the presence of AOE3 as discussed in some previous works performed by conventional techniques of this formation in the Maracaibo Basin in Venezuela (e.g.: Rey et al., 2004 and references therein).

1.1. Geological setting

Along the western South American the La Luna Formation and the equivalent Navay Formation in the Merida Andes area (Upper Cretaceous) of Maracaibo Basin are the most representative Cretaceous sedimentation and broadly recognized as the main oil field of Venezuela. The Maracaibo Basin and adjacent modern provinces are shown in Fig. 1.

The adjacent provinces are result of compression and transpression between Caribbean and Pacifico Plates occurred during Tertiary. The basin is limited by Sierra Perija at west, by Oca fault at north, by Merida Andes at eastern, and by Boconó fault at southwestern, occupying an area of 52000 km^2. The siliciclastic and carbonate rocks were deposited in a tropical epicontinental sea and are exposed at the edges of Maracaibo basin, Venezuela, and also in Colombia (Middle and Upper Magdalena basin), Ecuador (Santiago basin) and in Peru (Huallanga basin). The Maracaibo Basin is a Cretaceous restricted deep (gulf-like) basin connected to a passive margin. It began with a formation with rifts filled by lacustrine and fluvial sediments and volcanic rocks during the Latte Jurassic. During the Early Cretaceous this region evolved to a passive continental basin, which it was covered by a the Upper Cretaceous foreland basin (Parnaud et al., 1995; Erlich et al., 1999a, b).

The overall stratigraphy in Maracaibo Basin (Fig. 2) consists of continental Jurassic lacustrine, fluvial and volcanics rocks (La Ge Group and La Quinta Formation units) followed by Cretaceous sedimentation with basal continental sandstones and shales (Rio Negro Fm.) of Neocomian age. These units are covered by Barremian to Maastrichian shelf sedimentation with deposits of carbonates, sandstones and shales and some local phosphates. La Luna Fm., represented by inner to middle shelf carbonates, is deposited from Santonian to Campanian (Rey et al., 2004). Upper Campanian to Maastrichian Mito Juan and Colon formations overly the La Luna Fm and Esquinas Member and correspond to marine coarser-grained sedimentary rocks and shale, respectively. These formations are deposited during the transition from a passive (La Luna Fm.) to an active margin (Cooney and Lorente, 2009).

1.2. Stratigraphy of the La Luna Formation at San Miguel section

La Luna Formation was originally called as La Luna Limestones by Garner (1926). Hedberg and Sass (1937) named as La Luna Formation who described as constituted by thin and high density layers of black to gray bituminous limestones and impure limestones of variable thickness. The blackish limestones at the base are predominant and whitening to the top is described as the main feature. In the Trujillo and Lara (Venezuela States) the La Luna Formation is ticker (100–300 m) and Renz (1959) proposed the subdivision in 3 members: La Aguada, Chejendé and Timbetes. Other details of La Luna on these areas and thin sections were described by Hedberg (1931) and Ford and Houbold (1963). A typical section is located at Quebrada La Luna, in the borders of Serra Perijá Mountains and 26 km NW of Villa do Rosario in the Zulia State.

The La Luna Formation (Cenomanian to Campanian) is constituted mostly by fine-grained limestones with some calcareous shale and large original TOC values calculated in a range from 2.5 to 10.8 wt% (Talukdar and Marcano, 1994; Alberdi-Genolet and Tocco, 1999). In general, the layers of uniform and monotonous carbonate deposits varies in thickness in a range between 1 to up to 50 cm. Veins and black chert nodules, discoidal and elipsoidal concretions of varied size between 10 and 80 cm are common in the formation and most of concretions are macrofossils of ammonite type. According to many authors cited by Rey et al. (2004), this formation was deposited under anoxic to dysaerobic conditions on a broad marine outer shelf.

In the whole section (see Fig. 3) can be recognized two informal stratigraphic units. The lower unit is dominated by very compacted black marstones with carbonate concretions and very thin siliceous beds, while in the upper one is characterized by limestones with a 1 m thick of a glauconitic phosphate bed known as Tres Esquinas