

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios discrimination applied to the main Palaeozoic carbonate sedimentation in Ossa-Morena Zone

Lo ratio $^{87}\text{Sr}/^{86}\text{Sr}$ aplicado a la discriminación de los episodios de sedimentación carbonatada en la Zona de Ossa-Morena

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Abstract: The carbonated sedimentation in Ossa-Morena Zone during the Palaeozoic is formed, at least, by two main episodes. However, some chronological questions remain open, due to lack of biostratigraphic data in some carbonates. Sr isotope analysis was performed in selected limestones and marbles of Ossa-Morena Zone, in order to discriminate the Sr signature of the two main carbonate sedimentation episodes. The Sr isotopic data from the analyzed carbonate show two clusters of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, one related with the Lower Cambrian and other with the Lower-Middle Devonian carbonates.

Palabras clave: Ossa-Morena Zone, carbonated sedimentation, $^{87}\text{Sr}/^{86}\text{Sr}$.

Resumen: La sedimentación carbonatada en la Zona Ossa-Morena durante el Palaeozoic está formado, por lo menos, por dos episodios principales. Sin embargo, algunas cuestiones cronológicas permanecen abiertos, debido a la falta de datos bio-estratigráficos en algunos carbonatos. Se han realizado análisis de isótopos de Sr en calizas y mármoles seleccionados de la Zona de Ossa-Morena, con el fin de discriminar la signatura de Sr de los dos episodios principales de sedimentación de carbonatos. Los datos isotópicos de Sr analizados en los carbonatos muestran dos grupos de relaciones $^{87}\text{Sr}/^{86}\text{Sr}$, uno relacionado con el Cámbrico Inferior y otros con los carbonatos de lo Devónico Inferior-Medio.

Key words: Zona de Ossa-Morena, sedimentación carbonatada, $^{87}\text{Sr}/^{86}\text{Sr}$

INTRODUCTION AND GEOLOGICAL SETTINGS OF OSSA-MORENA ZONE CARBONATES

The Palaeozoic carbonate sedimentation in Ossa-Morena Zone (OMZ) has been issue of discussion from various authors (e.g. Oliveira et al., 1991; Piçarra, 2000; Pereira et al., 2012; Araújo et al., 2013 and included references). However, it is unambiguous the presence, at least, of two different carbonate sedimentation episodes in this tectonostratigraphic zone:

(i) the first in the Lower Cambrian, related with the first pulses of Variscan Cycle (Moreira et al., 2014), is characterized by sequences of marbles (dolomite and calcite) or limestones, sometimes

with siliciclastic beds and interbedded metavolcanic rocks (e.g. Oliveira et al., 1991; Vera, 2004; Pereira et al., 2012; Araújo et al., 2013; Moreira et al., 2014). The Ovetian-Marianian age is constrained by paleontological data in Spain (Vera, 2004 and included references) and in Portugal (Alter-do-Chão-Elvas Domain; e.g. Oliveira et al., 1991; Araújo et al., 2013). However, in the sequences with absence of biostratigraphic data, the assigned age is based on lithostratigraphic correlations, such as the cases of Abrantes, Estremoz, Ficalho and Viana do Alentejo sequences (Oliveira et al., 1991). In Estremoz and Ficalho sequences, onto the carbonated sequences (mostly dolomitic marbles) appears a volcano-sedimentary complex with abundant calcitic marbles (Oliveira et al., 1991;

Araújo et al., 2013). Piçarra (2000) describes some crinoid fragments in the calcitic marbles in Ferrarias (according to the author, equivalent of Estremoz Marbles) and Ficalho, assigning at least an Upper Silurian or Devonian age for the calcite marbles contained in the volcano-sedimentary complex. Pereira et al. (2012) argue that these ages are not depositional, but results from sub-aerial exposure and remobilization of Devonian faunal material. The same authors obtain a 499.4 ± 3.3 Ma age (SHRIMP U-Pb zircon) in meta-rhyolites intercalated into dolomitic marbles from the Estremoz sequence, proposing a Middle-Upper Cambrian transition age. However, the stratigraphic position of the meta-rhyolite is uncertain with regard to the carbonate sequence and it is not interbedded in the marble sequence.

(ii) the second episode in the Lower-Middle Devonian, it seems to be represented only in Portugal, in the southernmost domains of OMZ, and it is related with a reef system. Machado et al. (2010) describe a calciturbiditic sequence (calcitic limestones) spatially associated to volcanic rocks with low-K tholeiitic to calc-alkaline geochemical signatures in Odivelas (Ferreira do Alentejo; Santos et al., 2013). The paleontological data from the calcitic limestones provides a Lower to Middle Devonian age (Oliveira et al., 1991; Machado et al., 2010 and included references).

The aim of this work is establish $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in marbles and limestones from different domains of OMZ, compare and correlate the obtained data with available data in previous works, in order to discriminate and achieve strontium isotopic patterns for the carbonate episodes and isotopic-stratigraphic correlation for Paleozoic OMZ carbonates.

THE $^{87}\text{Sr}/^{86}\text{Sr}$ RATIO

The ability to correlate and, in some cases, date sediments using strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) derives from the fact of this ratio value dissolved in the oceans has varied over the time, and these differences are preserved in carbonated sediments (McArthur, 1994; McArthur et al., 2012).

The $^{87}\text{Sr}/^{86}\text{Sr}$ variation has been caused by changing fluxes of Sr to the ocean, from two main sources: mantle and continental crust (McArthur, 1994). In middle ocean ridges the interaction between oceanic crustal rocks and seawater, related to hydrothermal circulation, generates a modification of Sr isotope ratio in seawater. The loss of Sr from seawater is replaced by leached Sr from middle ocean ridge rocks, decreasing the $^{87}\text{Sr}/^{86}\text{Sr}$ of marine seawater. On the other hand, the continental weathering supplies are higher than that of marine Sr. Indeed, addition of crustal Sr to the ocean therefore increases the $^{87}\text{Sr}/^{86}\text{Sr}$

of marine Sr. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater was always higher than 0,703 (minimum value of mid ocean ridge rocks) and generally lower than 0,713 (best estimated value to modern rivers; McArthur, 1994 and included references).

At the analytical precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that can be measured, which is ± 0.00002 , this ratio in seawater from worldwide localities are analytically indistinguishable. This uniformity is resulted from the residence time of Sr in the Ocean that is far longer than the time it takes currents to mix the oceans, so the oceans are thoroughly mixed on time scale that are short relative to the rates of gain and loss of Sr (McArthur, 1994). As such, it is assumed that the ocean has always been well mixed, as in present, and consequently is isotopically uniform with respect to $^{87}\text{Sr}/^{86}\text{Sr}$.

SAMPLES AND METHODS

37 samples of OMZ carbonated rocks were collected. The samples were characterized by conventional petrographic techniques, with special attention to textural and/or metasomatic (i.e. secondary dolomitization) features. After the conventional petrographic characterization, samples underwent specific preparation, such as cleaning and removing meteoric alteration surfaces followed by crushing, gridding and sieving, in order to obtain powdered carbonate samples smaller than 63 μm .

The detailed mineralogical composition of carbonates was analysed in X-Ray diffractometer (XRD) Bruker D8 Discover with DaVinci geometry and using a Lynxeye linear detector (Hercules Laboratory, University of Évora). The scans was collected from 2θ 3° to 75° , with steps of 0.005° and one second by step. The semiquantification of the phases abundances are done using the DIFFRAC.SUITE software from Bruker by the RIR-Reference Intensity Ratio (Hubbard et al, 1988 and included references).

The strontium isotope analyses was performed in the Isotopic Geology Laboratory (University of Aveiro) using a Mass Spectrometer Thermal Ionization (TIMS) with a VG Sector 54 spectrometer. The main procedure involve a first stage of rocks sample dissolution with HCl with some drops of HF and HNO_3 for the carbonates. Afterwards, the remaining solutions, including the carbonate leachate samples, were dried and redissolved in HCl and subject to conventional two-stage ion chromatography separation with cation exchange resins for Sr purification. This methodology should guarantee the non-carbonate fraction separation from the whole sample. After the carbonate concentration and purification in each sample the isotopic measurements $^{87}\text{Sr}/^{86}\text{Sr}$

ratios were performed by means of a thermal ionization mass spectrometry (VG Sector 54).

SUMMARY SAMPLE DESCRIPTION AND XRD ANALYZES

From the #37 analysed samples #21 are calcitic-dominated, #14 mostly dolomitic and #1 ankeritic (or dolomitic Fe-rich) carbonates and #1 is a sandstone with calcite cement. Some dolomitic carbonates show macro and microscopic textural evidences of secondary dolomitization, while others the dolomitization is regarded as "primary" due the nonexistence of textural/metasomatic features. In this cases is possible that the dolomitization results from diagenetic process.

The XRD analyses reveals variable carbonate contents in the analysed samples: #29 samples have more than 75% (#14 with more than 95%); #6 samples have 60-75% (ETZ-6A; VB-2; ALT-1; FIC-2; BEN-1; GQAB-37) and #2 samples (BA-3; BA-4) have less than 60%.

The remaining mineralogical component is mainly composed by silicates, generally quartz, muscovite and chlorite. Sometimes, plagioclase, K-feldspar, amphiboles and biotite are also present, as well some iron oxides. It is important to emphasize the presence of some clay mineral detected in XRD analysis, which could reveal some alteration of sample (GQAB-13; GQAB-27; GQAB-37; VIA-1; VIA-2), although the percentage is generally lower 3%.

$^{87}\text{Sr}/^{86}\text{Sr}$ RATIOS OF THE CARBONATED EPISODES: A DISCUSSION

The projection of $^{87}\text{Sr}/^{86}\text{Sr}$ values clearly shows the presence of two distinct clusters (Fig.1). One of them is only composed by the Odivelas limestones with $^{87}\text{Sr}/^{86}\text{Sr}$ lower than 0,70800. The lower values obtained could be related with the interaction between seawater and the host volcanics rock (Santos et al., 2013), or result from lower values of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater, which is typical for the Lower-Middle Devonian transition (McArthur et al., 2012). However, the reworked limestones with similar age (and genesis?) in the Cabrela Carboniferous Basin (Pereira et al., 2006) presents higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (0,70972), when compared with the Odivelas limestones. This may be the result of meteoric fluids interactions over the resedimentation of the Cabrela limestones inside this intracontinental basin. This fact also could explain the presence of dolomite-rich limestones in Cabrela Basin, since the Odivelas limestones are clearly calcitic (only two samples presents circa of 1% of dolomite).

The other cluster is composed by limestones and marbles attributed to Cambrian, and has

$^{87}\text{Sr}/^{86}\text{Sr}$ values higher than the Odivelas limestones (0,70825-0,70925; Fig.1). The Abrantes, Escoural, Viana do Alentejo and Estremoz marbles, affected by medium-high metamorphic grade, presents $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to the analyzed in the Vila Boim and Alentejo-Chão limestones, which have low metamorphic grade. This evidence seems to show that the metamorphic grade do not change significantly the primary signature of $^{87}\text{Sr}/^{86}\text{Sr}$. The dolomitic marbles and limestones from Estemoz, Assumar, Alter do Chão and Vila Boim displays similar $^{87}\text{Sr}/^{86}\text{Sr}$ values. The data are concordant with the Cambrian worldwide seawater values presented by McArthur et al (2012).

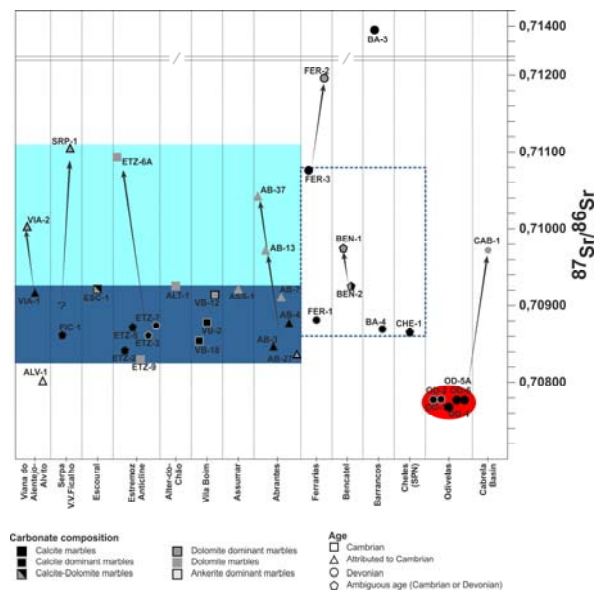


FIGURA 1. Projection of $^{87}\text{Sr}/^{86}\text{Sr}$ values, showing the presence of two distinct clusters, one of them composed by Odivelas Lower-Middle Devonian Limestones and the other one composed by Cambrian Carbonates. The arrows represents the effect of secondary dolomitization related to the interaction with meteoric fluids.

As mentioned to Cabrela limestones, the samples with macro evidences of secondary dolomitization (VIA-2, SRP-1; ETZ-6A; AB13; AB37) also presents highly values of $^{87}\text{Sr}/^{86}\text{Sr}$, comparatively to the calcitic and dolomitic limestones/marbles without evidences of secondary dolomitization. The Viana do Alentejo sample (VIA-2), sampled inside a marble centimetric fracture-filling dolomite (secondary dolomitization process) was collected as a control sample and shows high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values. This increment in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is interpreted as the result from the interaction between meteoric fluids/rock.

The Alvito Fe-rich carbonate (ALV-1) despite exposes textural evidences of metasomatic process, shows a lowest $^{87}\text{Sr}/^{86}\text{Sr}$ value and is regarded as an outlier. This require more data in order to understand the influence of ankeritic or

dolomite Fe-rich fluids in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during the metasomatism.

The Barrancos, Ferrarias and Bencatel limestones have low metamorphic grade and are attributed to Silurian-Devonian age (Piçarra, 2000). The $^{87}\text{Sr}/^{86}\text{Sr}$ data obtained for these limestones are distinct to the data obtained for the the Odivelas limestones and displays $^{87}\text{Sr}/^{86}\text{Sr}$ values partly similar to the values obtained from the limestones/marbles attributed to Cambrian (0,70860-0,71800). With exception to BA-3 sample (see discussion below), all these carbonates are NW-SE aligned, and their stratigraphic position is ambiguous. In Ferrarias, the carbonates are affected by intense fracturing and display several evidences of intense rock/fluid interaction. This may be justify the highly values observed in samples FER-2 and FER-3.

The BA-3 sample is the most impure "carbonate", with significant amounts of siliciclastic components and display the highest $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig.1). This higher value should be the result of the high siliciclastic component which may provide values that are not representative of Sr isotopic signature of seawater during the deposition. The interaction between silicate and carbonate components during the diagenetic process or the interaction rock/fluid dominated by crustal fluids can be invoked to justify this highest $^{87}\text{Sr}/^{86}\text{Sr}$ value.

FINAL CONSIDERATIONS

The differentiation is clear between two dissimilar events of carbonate sedimentation in OMZ based in the Sr isotopic signature of carbonates. This methodology could be applied to others OMZ domains without biostratigraphic data and allowing to correlate the different carbonates and assign the same age, based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. However, it is crucial use samples without meteoric or hydrothermal alteration, once the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio could be modified.

Although, this methodology is suitable applied to the Cambrian and Lower-Middle Devonian carbonated episodes, some doubts remain unresolved as regards to the age and origin of the Barrancos-Ferrarias-Bencatel carbonates, not being possible to differentiate this episode from the others.

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