Efects of secondary late dolomitization on $^{87}Sr/^{86}Sr$ isotopic ratio; examples from Ossa-Morena Zone carbonates

Efeito do processo de dolomitização secundária na razão isotópica $^{87}Sr/^{86}Sr$; exemplo dos carbonatos da Zona de Ossa-Morena

Moreira, N.[1,2 *], Pedro, J.[1,3], Santos, J.F.[4], Inês, N.[5], Araújo, A.[1,3], Dias, R.[1,2,3], Ribeiro, S.[4], Romão, J.[6], Mirão, J.[3,7]

[1] Earth Sciences Institute (ICT), Pole of the University of Évora, Rua Romão Ramalho, nº 59, 7000-671 Évora, Portugal; *moreira@estremoz.cienciaviva.pt

[2] LIRIO- Escola de Ciências e Tecnologia da Universidade de Évora (ECTUE), Pólo de Estremoz da Universidade de Évora, Convento das Maltezas, 7100-513 Estremoz, Portugal.

[3] Departamento de Geociências da ECTUE; Colégio Luís António Verney, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal.

[4] GeoBioTec, Departamento de Geociências and Laboratório de Geologia Isotópica, Universidade de Aveiro, 3810-193 Aveiro, Portugal;

[5] PARTEX - OIL AND GAS, Partex Services Portugal. Rua Ivone Silva, 6 – 1º, 1050 – 124 Lisboa, Portugal;

[6] UGCG, Laboratório Nacional de Energia e Geologia, Estrada da Portela, Apartado 7586 - Zambujal, 2720 Alfragide, Portugal;

[7] Laboratório HERCULES, Instituto de Investigação e Formação Avançada, Largo Marquês de Marialva, 8, Palácio do Vimioso, 7000-089 Évora, Portugal

Resumo

A razão $^{87}Sr/^{86}Sr$ é usada em estratigrafia com intuito de correlacionar e, em última instância, datar eventos de sedimentação carbonatada marinha. A variação da razão isotópica $^{87}Sr/^{86}Sr$ ao longo da escala do tempo geológico aliada ao facto desta razão isotópica poder considerar-se uniforme em todo o oceano num determinado momento geológico, abre uma temática para a investigação e caraterização da sedimentação carbonatada e o seu ambiente de sedimentação. Desta forma, é importante perceber as limitações inerentes à utilização desta razão isotópica como método de correlação de episódios carbonatados. No presente trabalho, analisam-se um conjunto de amostras de carbonatos Câmbricos (ou atribuídos ao Câmbrico) da Zona de Ossa-Morena, amostrados em diversos sectores. Os carbonatos amostrados apresentam graus metamórficos distintos, sendo caracterizada a sua lito-facies bem como a presença de processos dolomitização tardia (i.e. pós-metamórfica). Os dados mostram que os processos de dolomitização tardia provocam um incremento significativo das razões $^{87}Sr/^{86}Sr$, quando comparados com os carbonatos (mármores ou calcários) calcíticos presentes nas mesmas unidades.

Palavras-chave: Razão isotópica $^{87}Sr/^{86}Sr$; Zona de Ossa-Morena, Dolomitização, Sedimentação Carbonatada, Câmbrico

Abstract

The $^{87}Sr/^{86}Sr$ ratio is usually used in stratigraphy to correlate and even date marine carbonate sedimentation events. The variation of the $^{87}Sr/^{86}Sr$ isotopic ratio along the geological time scale combined with the fact of this isotopic ratio could be considered uniform in all ocean at a given geological moment, opens a thematic for the investigation and characterization of carbonate sedimentation and as well it sedimentation environment. Therefore, it is important to understand the inherent limitations to the use of this isotope ratio as a method of correlation. For the present work, the Cambrian (or Cambrian attributed) carbonates from the Ossa-Morena Zone were sampled in several sectors. These samples present distinct metamorphic features and their litho-facies were been characterized, as well as the presence of late dolomitization processes (i.e. post-metamorphic). The data show that the late dolomitization processes induce a significant increase of the $^{87}Sr/^{86}Sr$ ratio, when compared with the calcitic carbonates (marbles and limestones) collected in the same units.

Keywords: $^{87}Sr/^{86}Sr$ isotopic ratio, Ossa-Morena Zone, Dolomitization, Carbonated sedimentation, Cambrian

Introduction

The $^{87}Sr/^{86}Sr$ isotopic ratio of seawater changed during geological time (McArthur et al., 2012 and included references). This variation results from changes in the fluxes of strontium to the ocean, from the two main sources: mantle and continental crust (McArthur, 1994; Veizer et al., 1999). The hydrothermal circulation in middle ocean ridges induces the interaction between oceanic crust and seawater, generating a modification of strontium isotopic ratio in the seawater. In this case, the loss of strontium from seawater is replaced by leached strontium from middle ocean ridge rocks, decreasing the $^{87}Sr/^{86}Sr$ of marine seawater (McArthur, 1994). However, when the strontium from the continental weathering prevails over the marine one, the $^{87}Sr/^{86}Sr$ ratio from seawater increases (McArthur, 1994).

During marine carbonate sedimentation, the $^{87}Sr/^{86}Sr$ signature of seawater was preserved in these carbonates. Thus, the $^{87}Sr/^{86}Sr$ ratio could correlate and, in some cases, date the marine carbonates resulting from the same carbonated event, preserving the seawater $^{87}Sr/^{86}Sr$ fingerprint (Veizer et al., 1999; McArthur et al., 2012 and included references). However, several processes could modify the primary $^{87}Sr/^{86}Sr$ signature of these carbonates. In the present study, it was tested the effect of secondary dollomitization in the $^{87}Sr/^{86}Sr$ signature of carbonates from Ossa-Morena Zone.

Material and Methods

19 samples collected in the Cambrian (or Cambrian attributed) sucessions of OMZ (Oliveira et al., 1991; Moreira et al., 2015) were analyzed. The samples were cleaned, removing all the products of meteoric alteration, and subsequently milled in jaw crushers. In order to concentrate the carbonate component, sample powders were sieved in steel mesh sieve and only the finer component (smaller than 63 µm) was analyzed.

The mineralogical composition of the carbonated rocks and the composition of the analysed powder rocks were obtained by conventional petrographic studies and X-ray diffraction (XRD). A Bruker D8 Discover difractometer was used (Hercules Laboratory, University of Évora). The same powdered samples were analyzed to obtain the $^{87}Sr/^{86}Sr$ isotope ratio, using a Thermal Ionization Mass Spectrometer, VG Sector 54, Laboratory of Isotopic Geology (University of Aveiro).

Petrographic and XRD studies

The studied samples were characterized based on petrographic and XRD studies. The XRD analysis reveal a variable carbonate content:

- more than 95% of carbonates – GQAB-3, GQAB-7, ASS-1, ETZ-2, ETZ-3, ETZ-5, ETZ-7, VIA-1 samples;
- ranging between 95 and 80% – GQAB-4, GQAB-13, GQAB-27, ETZ-9, VIA-2;
- less than 80% of carbonate content – GQAB-37, VB-2, VB-12, VB-18, ALT-1, ETZ-6A samples.

Concerning the carbonate species, calcite is the unique species in samples GQAB-3, GQAB-4 ETZ-2, ETZ-5 and VIA-1, whilst samples VB-2, VB-18, ETZ-3, ETZ-7 are calcite-rich carbonates with less than 2% of dolomite. Samples GQAB-7, GQAB-13, GQAB-37, ASS-1, ALT-1; ETZ-9 and ETZ-6A present dolomite as the only carbonate species and samples GQAB-27, VB-12 and VIA-2 have also calcite. The non-carbonate fraction is mainly composed of quartz, micas and chlorite, sometimes with clay mineral, titanite, orthose, albite and zeolites.

The petrographic characterization shows seven distinct carbonate lithofacies:

1) Extremely pure calcite marbles (calcite > 80%), with granoblastic inequigranular textures (Fig. 1A). The calcite has type II twins, showing pervasive recrystallization (Passchier and Trouw, 2005). The non-carbonated component is mostly composed of quartz – GQAB-3, GQAB-4, ETZ-2, ETZ-3, ETZ-5 and ETZ-7;

2) Fine-grained impure grey limestones (calcite=60-70%), with significant quartz, chlorite and epidote content (25-35%) and some sericite, amphibole, feldspars and opaque minerals – VB-2 and VB-18;

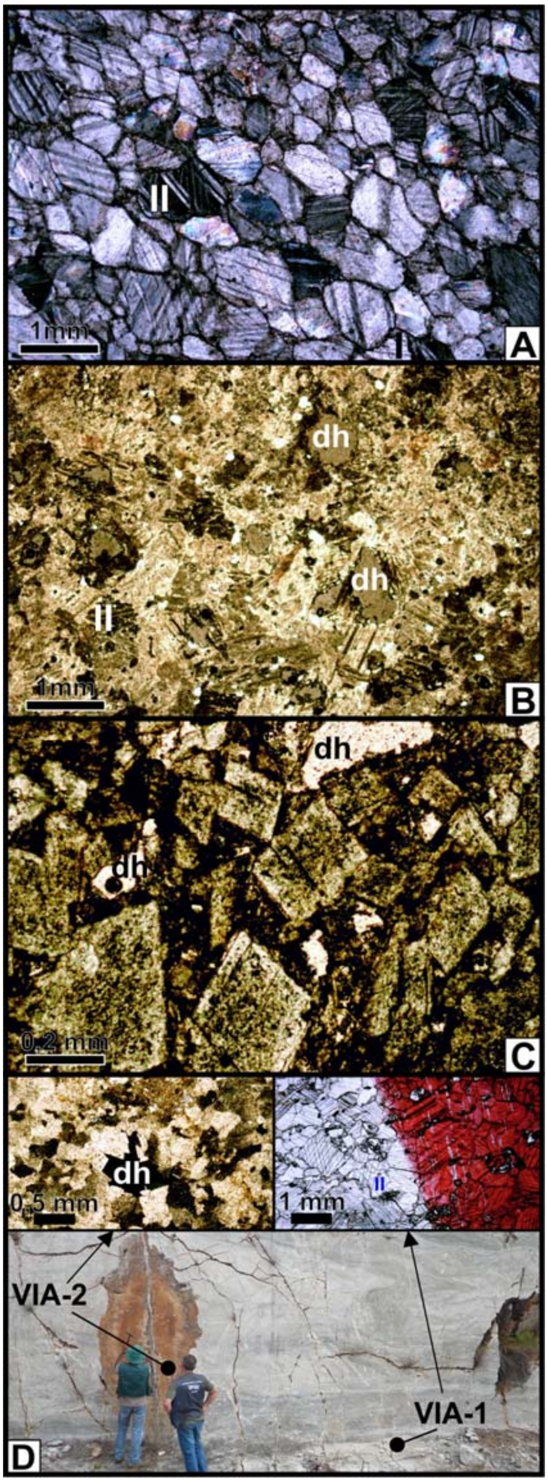

Fig. 1 – Main features of selected carbonated samples (dh – dissolution hole; I – twin type I; II – twin type II): (A) Extremely pure marble from Estremoz Anticline, with type I and II twins in calcite (ETZ-2 sample); (B) Two generations of dolomite, the first formed prior to metamorphism with recrystallized type II twins and the second one overgrowing and partially replacing the first generation (GQAB-13 sample); (C) Dolostone resulting from the total substitution of primary carbonate, showing dissolution holes and euhedral zoned crystals of dolomite, with cloudy core and clear edges (ETZ-6A sample); (D) Field relations between non dolomitized marble (VIA-1) and secondary dolostone (VIA-2).

3) Extremely pure calcite marble (calcite > 85%), with intense recrystallization, type II and III (and IV?) twins, and a coarse-grained (centimetric to millimetric) granoblastic texture. Olivine, epidote, brucite(?), K-feldspar and quartz were recognized – sample VIA-1;

4) Dolomite marbles (dolomite=80-90%) with granoblastic inequigranular texture. The dolomite predates the metamorphism (possibly diagenetic), showing evidence of recrystallization of dolomite crystals (type I or II twins). There is no evidence of pervasive late dolomitization – GQAB-27 and ETZ-9;

5) Fine grained impure dolostones (dolomite=65-75%) with two generations of dolomite: one syn-diagenetic (or primary?) with some recrystallization (type I twins) and a second generation with fine-grained cloudy late dolomite (sometimes subhedral to euhedral), associated to dissolution and growing over the earlier dolomite – VB-12 and ALT-1. Similar features are emphasized in samples ASS-1, GQAB-7 and GQAB-13, but in these cases the earlier dolomite crystals show type II twins. The primary dolomite is almost absent in sample GQAB-13 (Fig. 1B);

6) Dolostones characterized by pervasive dissolution and late dolomitization with abundant cloudy euhedral to subhedral dolomite (GQAB-37 and ASS-1). There is no evidence of early recrystallized dolomite. Frequently, the late dolomite shows internal zonation enhancing more than one episode of growth (Fig.1C).

7) Sample VIA-2 is a secondary dolostone growing in relation with a fracture (Fig. 1D). It is characterized by dolomite, with no recrystallization, presenting millimetric late calcite veins. Several dissolution holes are recognized and secondary dolomite, sometimes euhedral and zoned, is pervasive.

$^{87}Sr/^{86}Sr$ data on OMZ carbonated rocks

The calcite and calcite-rich carbonates have minimum $^{87}Sr/^{86}Sr$ value of 0,708420 (ETZ-2), maximum of 0,709169 (VIA-1) and median of 0,708716. The dolomite and dolomite-rich carbonates show greater spreading of $^{87}Sr/^{86}Sr$: minimun 0,708299 (ETZ-9); maximum 0,710933 (ETZ-6A); median 0,709182 (table 1).

Table 1 – $^{87}Sr/^{86}Sr$ isotopic data from studied samples.The grey cells represent the dolomite carbonates.

Sector	Sample	$^{87}Sr/^{86}Sr$	2σ
Abrantes and Assumar	GQAB-3	0.708471	0.000014
	GQAB-4	0.708773	0.000026
	GQAB-7	0.709106	0.000014
	GQAB-13	0.709716	0.000024
	GQAB-27	0.708366	0.000021
	GQAB-37	0.710410	0.000017
	ASS-1	0.708866	0.000024
Alter-Do-Chão – Elvas Sector	VB-2	0.708777	0.000013
	VB-12	0.709136	0.000030
	VB-18	0.708538	0.000021
	ALT-1	0.709227	0.000024
Estremoz Anticline	ETZ-2	0.708420	0.000033
	ETZ-3	0.708610	0.000033
	ETZ-5	0.708716	0.000027
	ETZ-6A	0.710933	0.000021
	ETZ-7	0.708741	0.000027
	ETZ-9	0.708299	0.000023
Viana do Alentejo	VIA-1	0.709169	0.000023
	VIA-2	0.710030	0.000021

Efect of dolomitization

The $^{87}Sr/^{86}Sr$ values in calcite carbonates are generaly lower than in the dolomite ones. However, the two samples with recristalization and no evidence of secondary dolomitization (GQAB-27, ETZ-9) contain similar values to those recorded in the calcite carbonates from the same sectors (Fig.2). These dolomite carbonates could be diagenetic, thus incorporating the $^{87}Sr/^{86}Sr$ ratio of the Cambrian seawater. The calcite marble from Viana do Alentejo (VIA-1) have slightly higher ratio value than the other calcite marbles, which may result from the HT metamorphism.

In turn, all the dolomite marbles and dolostones with evidence or pervasive dolomitization show an increase of $^{87}Sr/^{86}Sr$ ratio in relation to the non-dolomite carbonates. The increase is greater when the dissolution and late dolomitization is pervasive and completely obliterates the primary textures. The samples with some evidence of late dolomitization and dissolution, but preserving the primary recrystallized textures, show intermediate $^{87}Sr/^{86}Sr$ values. The dolomitization could result from interaction with fluids that have previously circulated through continental crustal rocks, which are enriched in ^{87}Sr and consequently display higher $^{87}Sr/^{86}Sr$ ratio (McArthur, 1994).

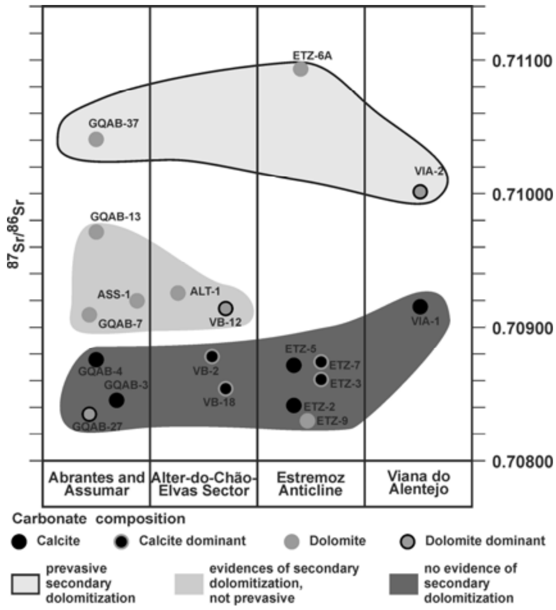

Fig. 2 – Plot of $^{87}Sr/^{86}Sr$ data of sampled OMZ carbonates, emphasizing the increase of isotopic ratio related to secondary dolomitization.

Acknowledgements

N. Moreira acknowledges Gulbenkian Fondation for the financial support ("Programa de Estímulo à Investigação 2011") and the FCT PhD grant (SFRH/BD/80580/2011). This work is a contribution to the project ALT20-03-0145-FEDER-000028, funded by Alentejo 2020 through the FEDER / FSE / FEEI. The authors acknowledge the FCT funding to the GeoBioTec (UID/GEO/04035/2013) and to ICT (UID/GEO/04683/2013) and by COMPETE POCI-01-0145-FEDER-007690.

References

McArthur, J.M., 1994. Recent trends in strontium isotope stratigraphy. *Terra Nova,* 6:331-358.

McArthur, J.M., Howarth, R.J., Shields, G.A., 2012. Strontium Isotope Stratigraphy. In: Gradstein, F.M., Ogg, J.G., Schmotz, M.D., Ogg, G.M. (Ed.), A Geologic Time Scale 2012 (7), Elsevier, pp 127-144.

Moreira, N., Pedro, J., et al., 2015. The Neoproterozoic-Cambrian transition in Abrantes Region (Central Portugal); Litostratigraphic correlation with Cambrian Series of Ossa-Morena Zone. *Géologie de la France*, 2015(1), 101-102.

Oliveira, J.T., Oliveira, V., Piçarra, J.M., 1991. Traços gerais da evolução tectono-estratigráfica da Zona de Ossa Morena, em Portugal: síntese crítica do estado actual dos conhecimentos. *Comun Serv Geol Port* 77, 3-26.

Veizer, J., Ala, D., et al., 1999. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. *Chemical Geology*, 161, 59-88.