Origin of fabric-selective dolomitization recognizable in the field: two case studies from Anisian carbonate rocks in the western Balkanides

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Abstract. The origin of dolomitized burrows (*Cruziana* ichnofacies) in limestones and dolomitic layers in limestone-dolostone ribbon rocks was studied on the basis of petrography, X-ray diffractometry, geochemical data and isotope signatures of the dolomites. Selective dolomitization of the burrows with a local source of Mg occurred in a near-surface setting from non-evaporitic solutions with low Mg/Ca ratio. The low-temperature precipitation of non-stoichiometric (with Ca excess) dolomite was microbially mediated and controlled by bacterial sulphate reduction. The carbon for dolomite formation was largely derived from seawater and/or dissolution of precursor carbonate sediments, and partly derived from the decomposition of organic matter. Selective dolomitization of primarily argillaceous carbonate layers in the ribbon rocks was mainly associated with an autochthonous source of Mg. Clay mineral transformations (*i.e.*, illitization of smectite) at intermediate burial depths supplied Mg ions for the formation of Ca-rich (locally ferroan) dolomite. However, differential diagenesis of the originally clay-rich and clay-poor layers may also have favoured early dolomite precipitation, whereupon contemporaneous seawater was the primary Mg source during shallow burial. The obtained results show that various factors control the formation of fine-grained, non-stoichiometric dolomite with macroscopically recognizable fabric-selective character of replacement.

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INTRODUCTION

Formation of dolomite and dolomitization patterns in carbonate rocks are controlled by several factors, including precursor mineralogy and grain/crystal size, porosity, permeability, source of Mg, character and delivery mechanism of the dolomitizing fluids, temperature, microbial activity, multiple dolomitization events, and recrystallization (*e.g.*, Murray and Lucia, 1967; Sibley, 1982; Bullen and Sibley, 1984; Mazzullo, 1992, 2000; Purser *et al.*, 1994; Machel, 1997, 2004; Warren, 2000; Armenteros, 2010; Gregg *et al.*, 2015; Ren and Jones, 2017). In certain cases, the resultant dolomite distribution clearly indicates selectivity with respect to former lithologies and textural components on macroscopic or microscopic scale. Examples of fabric-selective dolomitization recognizable in the field comprise dolomitic burrows, mottles, veins, layers in ribbon rocks, laminae in stromatolites, and dolomitized matrix in carbonate breccias/

conglomerates and nodular beds (*e.g.*, Gebelein and Hoffman, 1973; Morrow, 1978; Coniglio and James, 1988; Jones *et al.*, 1979; McHargue and Price, 1982; Demicco and Hardie, 1994; Chow and Longstaffe, 1995; Török, 2000; Dilliard *et al.*, 2010; Sharp *et al.*, 2010; Bertok *et al.*, 2011; Bayet-Goll *et al.*, 2015; Barale *et al.*, 2016).

This study is focused on two different types of selective dolomitization, which have been recognized macroscopically in Anisian carbonate rocks from Northwest Bulgaria. Dolomitized burrows in limestones and dolomitic layers in ribbon rocks were investigated on the basis of petrographic observations, XRD analysis, geochemical data and isotope signatures of the dolomites. The obtained results are used to interpret the origin of dolomitization in terms of relative timing, diagenetic setting, source of Mg, precursor mineralogy, character of the dolomitizing fluids, general temperature conditions, biological influence, and consequent alteration during burial.

GEOLOGICAL SETTING

The Triassic sedimentary rocks exposed in NW Bulgaria have been assigned to the Balkanide (facies) type of Triassic (Ganev, 1974; Chatalov, 1980). Lithostratigraphically, the Lower to Upper Triassic marine strata have been referred to as the Iskar Carbonate Group (Tronkov, 1981). This unit has maximum thickness of about 500 m and consists of limestones, dolostones, and minor amounts of siliciclastic rocks. The Iskar Carbonate Group overlies red-bed deposits of the Lower Triassic Petrohan Terrigenous Group (Tronkov, 1981) and is covered by variegated siliciclastic and carbonate deposits of the Upper Triassic Moesian Group (Chemberski *et al.*, 1974). The entire Triassic succession corresponds to a symmetrical second-order transgressive-regressive (T-R) stratigraphic cycle (Chatalov, 2013a). According to the Alpine tectonic model for Bulgaria proposed by Ivanov (2017), the Triassic rocks are exposed in the West Balkan Zone of the External Balkanides.

Biostratigraphic and sedimentological studies indicate that marine deposition occurred from the late Olenekian or early Anisian to the early Carnian (Tronkov, 1968, 1973; Ajdanlijsky *et al.*, 2018; see also Chatalov, 2017b) on a homoclinal carbonate ramp with local distal steepening, which evolved in the subtropical belt on the north-western shelf area of the Tethys Ocean (Čatalov, 1988; Chatalov, 2013a, 2018). Two main stages of the ramp development (retrogradational and progradational) produced two genetic units (transgressive and regressive) that are separated by a maximum flooding zone, *i.e.*, *Terebratula* Beds (Chatalov, 2013a, 2018). Subtidal, intertidal and supratidal facies were formed in several depositional environments of three ramp zones: inner ramp, mid-ramp, and outer ramp (Chatalov, 2013a, 2018; Chatalov *et al.*, 2015). Various environmental constraints of the ramp depositional system and controlling factors on its development have been recognized and thoroughly discussed (Chatalov, 2013a, 2018).

PREVIOUS RESEARCH

The distribution and petrographic characteristics of dolomitic rocks in the Triassic marine successions from NW Bulgaria have been described by many researchers (*e.g.*, Tronkov, 1960, 1968, 1973; Gnoevaya, 1965; Tronkov *et al.*, 1965; Chatalov, 1999a, 2009; Chatalov and Benatov, 2000; Chatalov and Stefanov, 2013). The presence of dolomitized burrows in the Zimevitsa (Chatalov *et al.*, 2001) and Zgorigrad members (Tronkov, 1976) of the Anisian Babina Formation (Tronkov, 1968) from outcrops in the Iskar River Gorge was reported by Chatalov *et al.* (2001) and Chatalov (2013a), respectively. Dolomitized marly matrix in nodular beds and dolomitic layers in ribbon rocks have recently been documented from ex-

posures of the Zgorigrad Member in the Vratsa Balkan (Chatalov, 2018).

Results from studies on dolomitization patterns and dolomite origin have been published in several works. First, Tronkov (1983) interpreted dolomicrites in the Opletnya Member (Olenekian–Anisian) of the Mogilata Formation (Tronkov, 1968; Assereto *et al.*, 1983) as chemically precipitated sediments in arid climate. Later, Chatalov (1994, 1997) presented petrographic and geochemical evidence for early diagenetic dolomitization of intertidal and supratidal deposits (including the dolomicrites) in the Opletnya Member. The origin of Olenekian and Anisian dolomites from a large area in the western Balkanides was investigated by Chatalov and Stanimirova (2001) on the basis of data from X-ray diffractometry. Field observations and laboratory techniques were used by Chatalov (2014) for genetic interpretation of Olenekian to Carnian dolostones exposed in the Elovitsa (Melyane) anticline. Penecontemporaneous dolomitization of Spathian peritidal deposits (Svidol Formation), including mimetic replacement of oolites, was described by Chatalov (1999b) and Chatalov *et al.* (2015).

MATERIALS AND METHODS

Field observations across the whole area with exposures of Triassic rocks in NW Bulgaria indicate that macroscopically recognizable selective dolomitization occurs in three lithostratigraphic units: the Opletnya Member, the Zimevitsa Member, and the Zgorigrad Member. These occurrences were studied in six stratigraphic sections from the Berkovitsa unit and Vratsa unit of the West Balkan tectonic zone (Fig. 1). The rock colours, stratification patterns, sedimentary structures, and textures were described, and the dolomitic lithology was tested with 5% solution of HCl. Forty-two samples were collected from selectively dolomitized burrows and dolomitic layers in ribbon rocks for further laboratory work. In addition, seven samples were taken from limestone layers of the ribbon carbonates.

Standard thin-sections for observation on transmitting light-microscope were prepared from all samples. A staining procedure with combined alizarine red S + potassium ferricyanide solution (Dickson, 1965) was applied to distinguish ferroan and non-ferroan calcite and dolomite phases. The flowchart proposed by Chatalov (2013b) was used for micropetrographic description of the dolostones, and the limestone textures were described, following the classification scheme of Folk (1962).

Fourteen powdered whole-rock samples were analysed by X-ray diffractometry, using TUR M62 diffractometer with filtered Co K_α radiation under operating conditions of 30 mA current and 40 kV voltage. The stoichiometry and degree of ordering of non-ferroan dolomite were determined by applying the standard techniques described by Chatalov and Stanimirova (2001) and Chatalov (2014). The samples were

Fig. 1. Exposures of the Iskar Carbonate Group (Lower–Upper Triassic) in parts of the Berkovitsa Unit and the Vratsa Unit of the West Balkan tectonic zone (data used from Tzankov *et al.*, 1991; Angelov *et al.*, 1992). Legend: 1 – Quaternary sediments, 2 – Jurassic rocks, 3 – Moesian Group (Carnian–Norian?), 4 – Rusinovdel Formation (Ladinian–Carnian), 5 – Milanovo Formation (Anisian–Ladinian), 6 – Babina Formation (Anisian), 7 – Mogilata Formation (Olenekian–Anisian) and Svidol Formation (Olenekian), 8 – Petrohan Terrigenous Group (Lower Triassic), 9 – Permian rocks, 10 – normal fault, 11 – reverse fault, 12 – thrust. Rectangles show location of the studied sections. Inset map: green – West Balkan Zone. The Alpine tectonic subdivision of Bulgaria is after Ivanov (2017).

scanned in the 4–80° 2 θ range with step size 0.02° aiming to detect the presence of other minerals (*e.g.*, clays).

Twelve powdered samples from the ribbon carbonates were reacted with 10% HCl (for the dolostones) and 5% HCl (for the limestones) to determine the acid insoluble residue. The same samples were also treated by classical chemical methods to analyse the Al content. For this purpose, they were dissolved in HClO₄+HF and Al was determined from the obtained solution by complexometric titration.

Six powdered whole-rock samples were analysed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of dolomite by using a method modified from McCrea (1950) and Rosenbaum and Sheppard (1986). The samples (~20 mg) were placed in Pyrex glass vials under vacuum and treated with 100% solution of H₃PO₄ for 45 min at 25 °C to remove calcite. Then, the samples were heated at 100 °C (± 1 °C) for

1 hour, and the extracted CO₂ was cryogenically purified in vacuum. The CO₂ was analysed with Finnigan Mat 253 spectrometer operating in dual inlet mode. The oxygen isotopic composition was corrected with phosphoric acid fractionation factor 1.00913 (Rosenbaum and Sheppard, 1986). The results are expressed in per mille values and reported relative to the V-PDB standard. The analytical precision is $\pm 0.1\%$ for both isotopes.

PETROGRAPHY

Dolomitized burrows

Selectively dolomitized burrows occur in an approximately 10 m thick interval of the Opletnya Member and also in several discrete beds of the Zimevitsa and

Zgorigrad members from exposures in the Berkovitsa Unit (Fig. 2). Macroscopically, the burrows are easily recognizable on weathered rock surface by their negative or positive relief and different colours (grey-yel-

lowish, beige, ochre, rusty) in the background of the light to dark grey micritic limestones (Fig. 3a–f). The dolomitized trace fossils have various lengths (from <1 cm to 12 cm), widths (from several mm to 1.6 cm),

Fig. 2. Vertical distribution of the macroscopically recognizable occurrences of fabric-selective dolomitization.

morphology (straight, curved, meandering, irregular, branched, U-shaped, Y-shaped), orientation (subhorizontal, inclined, subvertical), and cross-section (circular or elliptical). The burrows are mostly isolated but may locally be interconnected to form a dense network in the rock. In some cases, predominantly subvertical

burrows are developed below submarine discontinuities (Clari *et al.*, 1995) resulting from breaks in sedimentation (*i.e.*, marine omission surfaces).

In thin-sections, the host limestones show diverse textures (micrite, fossil-bearing micrite, biomicrite, pelintraomicrite, or biointraomicrite), while the bur-

Fig. 3. Selectively dolomitized burrows in micritic limestones of the Opletnya Member (a–c), the Zimevitsa Member (d, e), and the Zgorigrad Member (f): a, b) isolated and interconnected burrows showing pale ochre colour and positive relief, as well as various length, width, morphology, and orientation; c) burrows developed below submarine discontinuity surface (firmground); d, e) inclined to vertical, beige to rusty-coloured burrows with negative relief (arrows); f) isolated, yellowish-grey burrows with negative relief, showing various sizes and shapes.

row fills have textures of cryptocrystalline (<4 µm) to microcrystalline (4–32 µm) dolostones. The constantly sharp boundaries between the two lithologies are undulating (Fig. 4a), irregular, or rarely planar. Allochems (intraclasts, fossils, oncoids) in the limestones may be truncated at the contact (Fig. 4b), and calcitic bioclasts (e.g., bivalves) locally penetrate into the dolomitic burrow fills (Fig. 4c). Some burrows make protrusions into the limestone, which are commonly accompanied by incorporation of non-dolomitized clasts (Fig. 4d). Concentrations of small (<0.1 mm), moderately sorted dolomitized peloids (probably faecal pellets), or dark-coloured dolomicritic halos having variable thicknesses (diagenetic halos *sensu* Gingras *et al.*, 2004; see also Corlett and Jones, 2012) may be observed along the burrow periphery (Fig. 4e, f). Elsewhere, the contacts with the limestone are delineated by thin streaks of fine-grained pyrite (Fig. 4g), low-amplitude stylolites, or irregular strips of fine crystalline dolomite (Fig. 4h). The burrow fills consist of non-ferroan, predominantly subhedral and euhedral dolomite, while anhedral crystals are locally distinguished. The dolomite mosaics show homogeneous or heterogeneous crystal size (for example, larger euhedral crystals occur in more fine-grained dolomite matrix). The applied staining reactions do not reveal the presence of micritic or microsparitic calcite. Additional fabric features include scarce pyrite crystals, former irregular voids filled with fine to coarse crystalline drusy dolomite, and crosscutting dissolution seams, stylolites and calcite veinlets.

Limestone-dolostone ribbon rocks

The second type of macroscopically recognizable selective dolomitization occurs in an exposure of the Babina Formation, which is located north of Zgorigrad Village in the Vratsa Unit. An approximately 20 m thick interval in the uppermost part of the Zgorigrad Member (Fig. 2) includes heterolithic beds of grey limestones and ochre-coloured dolostones (Fig. 5a). The irregularly alternating layers in these ribbon rocks are continuous, lenticular, or pinching-out. They have various thicknesses (from several mm to 5–6 cm) and

sharp boundaries (planar, undulating, or irregular) that may be enhanced by stylolites. Dolostone lenses with length up to 13 cm, thickness up to 2 cm and subparallel orientation to the bedding planes show isolated occurrences in the limestone (Fig. 5b), thus resembling the flaser bedding in siliciclastic deposits (Reineck and Singh, 1980). Massive appearance is typical for both lithologies, but some dolostone layers display faint horizontal lamination, which is locally affected by soft deformation. Many limestone layers are cracked, disrupted, and/or brecciated (Fig. 5c). The vertical or oblique cracks have width of several millimetres and are commonly filled with dolostone material from adjacent layers. Predominantly pebble-sized limestone clasts showing various shapes, degree of roundness and orientation are embedded (*i.e.*, “float”) in the dolomitic matrix (Fig. 5d, e). The faint laminae in some dolostone layers bend around the larger limestone clasts (Fig. 5f).

Under the microscope, the two lithologically different types of layers in the ribbon rocks have mostly sharp boundaries (Fig. 6a). Only locally, scattered dolomite crystals and/or selectively dolomitized clasts occur in the limestone close to the contact (Fig. 6b). The limestone layers show textures of micrite (predominantly) or fossil-bearing micrite (rarely). The dolomite crystal size in the dolostone layers ranges from several µm to 50 µm, which defines the rocks as cryptocrystalline to extremely fine-crystalline dolostones that are clayey and calcareous to various degrees (Fig. 6c). The presence of brownish clay-sized material is best visible in vertical cracks of the limestone layers where an upwards gradation in the amount of replacive dolomite can be observed (Fig. 6d). The dolomite is non-ferroan and rarely ferroan (Fig. 6e), showing homogeneous or heterogeneous crystal size and euhedral, subhedral, or anhedral crystal shape. The limestone clasts and scarce calcitic bioclasts (crinoids, brachiopods, bivalves) in the dolostone layers may be dolomitized slightly (Fig. 6f, g). Some articulated brachiopod and bivalve shells are crushed as a result of mechanical compaction and filled with dolomite (Fig. 6h). The latter is probably a cement phase as inferred from its larger crystal size and absence of

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Fig. 4. Microphotographs of burrow-related dolomite: a) weakly undulating, sharp boundary between host limestone (ca) and dolomite-filled burrow (do); b) truncated allochems (large arrow) at the contact between dolomitic burrow and surrounding limestone; c) calcitic bivalve shell (large arrow) penetrating into dolomitic burrow fill; d) non-dolomitized clasts (large arrows) incorporated in dolomitic burrow from the adjacent limestone; e) small dolomitized peloids (large arrows) concentrated along the periphery of burrow fill; f) dolomicritic halo (large arrows) with variable thickness delineating dolomitized burrow; g) Contact between host limestone and dolomitic burrow marked by thin streak of fine-grained pyrite (large arrows); h) fine-crystalline dolomite developed along the periphery of dolomitic burrow. Note: Small red arrows indicate dispersed fine-grained pyrite. All thin-sections are stained and all microphotographs are in plane-polarized light.

Fig. 5. Selectively dolomitized layers in ribbon rocks of the Zgorigrad Member: *a*) heterolithic alternation of ochre-coloured dolostones and grey-coloured limestones. Note the variable thicknesses and sharp boundaries of vertically adjacent layers; *b*) dolostone lenses in limestone resembling the flaser bedding in siliciclastic deposits; *c*) cracked, disrupted, and brecciated limestone layers with dolomitic material filling the cracks and space between clasts; *d*) large pebble clast of limestone (green arrow) embedded in dolostone layer; *e*) numerous limestone clasts with various sizes, shapes, degree of roundness and orientation, “floating” in dolostone matrix; *f*) enlarged view of (*a*) showing flat limestone clast (green arrow) embedded in dolostone. Note: Red arrows indicate vague horizontal lamination, which is locally affected by soft deformation and bends around larger limestone clasts.

intercrystalline clay or calcite micrite in contrast to the surrounding rock matrix. Dissolution seams and low-amplitude stylolites are locally developed and occur preferentially in the dolostone layers with some dolomite crystals crosscutting these pressure solution features (Fig. 6i).

ANALYTICAL RESULTS

Data from the XRD analysis show great variations in the dolomite stoichiometry and degree of ordering with some overlapping between samples from the burrows and the ribbon rocks (Table 1). The burrow-related dolomite is non-stoichiometric (52.3–54.7 mole% CaCO_3 , average 53.33 mole% CaCO_3 , $n = 7$), and the degree of ordering ranges from 0.52 to 0.78 (average 0.65, $n = 7$). The dolomite of the ribbon rocks is more Ca-rich (53.9–56.0 mole% CaCO_3 , average 55.1 mole% CaCO_3 , $n = 7$), and the degree of ordering is in a more narrow range, from 0.55 to 0.65 (average 0.60, $n = 7$). Small amounts of calcite are recorded in most samples, while quartz, illite, and minor chlorite are detected only in samples from dolostone layers of the ribbon rocks.

The insoluble residue of dolomitic layers in the ribbon rocks shows values from 6.60% to 20.57% (average 10.78%, $n = 7$), and the Al_2O_3 content is between 0.38% and 2.17% (average 1.09%, $n = 7$). The insoluble residue of limestone layers in the ribbon rocks ranges from 1.80% to 3.22% (average 2.69%, $n = 5$),

and the Al_2O_3 content is between 0.04% and 0.11% (average 0.07%, $n = 5$).

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the burrow-related dolomite range from -0.69‰ to -1.15‰ (average -0.88‰ , $n = 3$) and from -4.42‰ to -5.58‰ (average -4.95‰ , $n = 3$), respectively. The dolomite in the ribbon rocks has $\delta^{13}\text{C}$ values between 1.24‰ and 1.67‰ (average 1.48‰ , $n = 3$), and $\delta^{18}\text{O}$ values between -6.73‰ and -8.02‰ (average -7.47‰ , $n = 3$).

INTERPRETATION AND DISCUSSION

Dolomitized burrows

The Anisian limestones with dolomitized burrows have been interpreted as shallow subtidal deposits in oxygenated, normal marine seawater of the inner ramp (Mogilata Formation) and mid-ramp (Babina Formation) zones (Chatalov and Vangelov, 2001; Chatalov, 2013a, 2018). The abundant micritic matrix in these rocks indicates deposition in poorly agitated settings, where predominantly deposit-feeding and suspension-feeding organisms burrowed into the muddy soft-ground, firmground, or hardground substrate. On the basis of their overall characteristics, the trace fossils can be assigned to the *Cruziana* ichnofacies with local overprinting by the substrate-controlled *Glossifungites* and *Trypanites* ichnofacies (see MacEachern *et al.*, 2007; Seilacher, 2007; Buatois and Mángano, 2011; Knaust *et al.*, 2012).

Table 1
Analytical data for the studied dolomites

Sample*	mole % CaCO_3	$\frac{\text{I}(015)}{\text{I}(110)}$	insoluble residue (wt. %)	Al_2O_3 (wt. %)	$\delta^{13}\text{C}$ (‰V-PDB)	$\delta^{18}\text{O}$ (‰V-PDB)
1-Bu	54.0	0.58				
2-Bu	53.0	0.52			-0.69	-5.58
3-Bu	52.3	0.71			-0.81	-4.42
4-Bu	54.7	0.57				
5-Bu	52.3	0.78				
6-Bu	53.2	0.64			-1.15	-4.84
7-Bu	53.8	0.73				
1-Rb-d	55.0	0.65	7.80	0.38		
2-Rb-d	54.7	0.63	6.60	0.42	1.24	-7.66
3-Rb-d	54.7	0.55	9.96	1.59		
4-Rb-d	55.7	0.57	8.91	0.59	1.53	-6.73
5-Rb-d	55.4	0.61	14.16	1.74		
6-Rb-d	56.0	0.59	20.57	2.17		
7-Rb-d	53.9	0.62	7.45	0.77	1.67	-8.02
8-Rb-l			2.65	0.08		
9-Rb-l			1.80	0.04		
10-Rb-l			3.22	0.11		
11-Rb-l			2.79	0.06		
12-Rb-l			2.99	0.08		

* Letters in the sample names indicate: Bu – dolomitized burrows, Rb – ribbon rocks, d – dolomitic layers, l – limestone layers.

Fig. 6. Microphotographs of dolomite in the ribbon rocks: *a*) sharp contact between clay-poor limestone layer (lm) and clay-rich dolostone layer (do); *b*) dolomite crystals dispersed in limestone (lm) close to the boundary with dolostone (do). Also note non-dolomitized clast (yellow arrow) in the dolostone and dolomitized clast (blue arrow) in the limestone; *c*) euhedral dolomite replacing clay-rich calcitic micrite; *d*) vertical crack in limestone layer showing gradual increase in the amount of dolomite (dl) upward from a clay-rich (cl) domain; *e*) ferroan dolomite in dolostone layer (upper part of the microphotograph); *f*) slightly dolomitized limestone clast in dolostone layer; *g*) non-dolomitized and poorly dolomitized skeletal debris in dolostone matrix; *h*) non-dolomitized crinoid (left) and brachiopod (arrow) bioclasts in dolostone layer. The articulated brachiopod shell is crushed as a result of mechanical compaction and filled with dolomite cement; *i*) low-amplitude stylolites developed in dolostone (do) and terminating at the contact with adjacent limestone (lm). Note that some dolomite crystals crosscut these pressure solution features. All thin-sections, except *a*, *f* and *i* are stained, and all microphotographs are in plane-polarized light.

Fig. 7. Cross-plot of stoichiometry vs. degree of ordering of the studied dolomites.

Dolomitization of the burrows occurred during the early diagenesis with a local source of Mg, which is evidenced by the fabric-selective character of replacement, sharp contacts with the host rock (with local truncation of allochems), incorporation of non-dolomitized clasts and bioclasts from the adjacent limestone, and crosscutting relationship with dissolution seams and stylolites. Moreover, the crypto- to microcrystalline dolomite with predominantly planar crystal faces suggests low-temperature (<50 °C) dolomite formation (Gregg and Sibley, 1984), *i.e.*, in a near-surface setting (*sensu* Machel, 1999). The variable Ca excess and degree of ordering (Fig. 7) further indicate early diagenetic origin from non-evaporitic, dolomitizing solutions with lower Mg/Ca ratio (Lumsden and Chimahusky, 1980; Sperber *et al.*, 1984; Kaczmarek and Sibley, 2011). The Middle Triassic dolomitized burrows are similar to other studied ex-

amples from the geological record in terms of petrographic features (Morrow, 1978; Rao, 1990; Gingras *et al.*, 2004; Rameil, 2008; Corlett and Jones, 2012; Baniak *et al.*, 2014; Baldermann *et al.*, 2015), as well as dolomite stoichiometry and degree of cation ordering (Morrow, 1978; Rao, 1990; Baldermann *et al.*, 2015). On a broader scale, the small crystal size and Ca-rich composition of the burrow-related dolomite characterize the so-called organogenic (Compton, 1988), or microbially mediated (Petrash *et al.*, 2017), low-temperature dolomites from modern and ancient peritidal, shallow-marine and deep-sea environments (Mazzullo, 2000).

Burrowing substantially alters the physical and chemical character of sediment substrates and may control the formation of low-temperature dolomite and the selective dolomitization of burrows (Gingras *et al.*, 2004). Modification and redistribution of the grain size is caused by movement and digestion activities of burrowing organisms (Bromley, 1996). Reduction of the substrate grain size creates larger surface area of the sediment particles and greater number of nucleation sites that may favour dolomitization (Chow and Longstaffe, 1995; Zenger 1996). Conversely, increase of the grain size would lead to higher porosity and permeability, and hence provide a conduit for the circulation of dolomitizing fluids. Biochemical modification of burrowed substrates is related to the incorporation of concentrated organic matter in the form of mucous and/or faecal material (Petrash *et al.*, 2011, and references therein) providing a microenvironment for bacterial colonization (Gingras *et al.*, 2004). According to the model proposed by Gingras *et al.* (2004), the microbial oxidation of organic matter close to the sediment–water interface, *i.e.*, in the oxic zone, produces CO₂, which may enhance carbonate dissolution during the early diagenesis. The presence of free sulphate ions further inhibits kinetically the dolomite formation and lowers the Mg/Ca ratio by bonding with Mg²⁺ ions. In the anoxic zone, however, the reaction between NH₃ (released from the breakdown of proteins in organic

matter) and H_2O raises the pH of ambient seawater, which, in turn, increases the activity of the carbonate ion. Under such reducing conditions, SO_4^{2-} ions are consumed by sulphate-reducing bacteria, leaving a high Mg/Ca ratio. Metal enrichments in the organic burrow lining and interstitial (marine) water provide a source of Mg for dolomitization (Mirsal and Zankl, 1985). By raising the pH in interstitial pore water, sulphate-reducing bacteria decrease the solubility of metals, resulting in increased metal concentrations in the burrows (Corlett and Jones, 2012). Thus, the combination of reducing conditions, elevated pH, and low sulphate levels favours the precipitation of dolomite in burrows during the early diagenesis.

In the case studied, the presence of disseminated fine-grained pyrite in the burrow fills implies that bacterial sulphate reduction was an important control on the dolomite formation (*e.g.*, Berner *et al.*, 1985). Another clue is the non-ferroan composition of the dolomite, considering that sulphate-reduction dolomites are generally Fe-poor because available iron is rapidly incorporated into sulphide minerals and/or bound to organic substrate (Mazzullo, 2000; Macquaker *et al.*, 2014; Petrash *et al.*, 2017). Furthermore, the carbon isotope values ($\delta^{13}\text{C}$) of the burrow-related dolomite (Fig. 8) are typical for peritidal and shallow subtidal dolomites precipitated during sulphate reduction (Mazzullo, 2000). The recorded $\delta^{13}\text{C}$ signatures are slightly depleted in comparison to the carbon isotope values of Middle Triassic seawater based on brachio-

pods (Veizer *et al.*, 1999; Korte *et al.*, 2005). These data indicate that the carbon for dolomite formation in the burrows was largely derived from seawater and/or dissolution of precursor carbonate sediments, and partly derived from the decomposition of organic matter (*cf.* Gingras *et al.*, 2004; Corlett and Jones, 2012). The slightly depleted $\delta^{13}\text{C}$ compositions may reflect dolomite precipitation, either during early sulfate reduction (*i.e.*, prior to maximum ^{12}C enrichment in pore fluids) or in sediments with relatively small amount of organic matter (Compton 1988; Mazzullo, 2000).

The interpretation of $\delta^{18}\text{O}$ from dolostones is controversial because $\delta^{18}\text{O}$ values of dolomite are influenced by many variables, including the isotopic composition of dolomitizing fluids, temperature, kinetics, and dolomite stoichiometry (see Swart, 2015; Ren and Jones, 2017, and references therein). The recorded oxygen isotope signatures of the burrow-related dolomite are depleted in comparison to the estimated values of Middle Triassic marine dolomite, if an equilibrium ^{18}O enrichment of 2.6‰ in low-temperature dolomite relative to calcite $\Delta^{18}\text{O}_{\text{dol-cal}}$ ($\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{calcite V-PDB}}$) is assumed (Vasconcelos *et al.*, 2005). This difference suggests that the original oxygen isotope values were reset with increasing burial and temperature as a result of recrystallization (*e.g.*, Mazzullo, 1992; Kupecz *et al.*, 1993; Machel, 1997). Such conclusion is consistent with the statement of Machel (2004) that most dolomites formed in near-surface settings tend to recrystallize during burial due to their thermodynamic instability in conditions of increasing temperature and pressure and changing fluid composition. In this case, possible petrographic evidence for recrystallization includes the heterogeneous crystal size of the dolomite in some burrows (*i.e.*, mixed crypto- to microcrystalline texture, coarser euhedral crystals in more fine-grained matrix) and the presence of non-planar crystal boundaries (see Rott and Qing, 2013).

The fine-crystalline dolomite forming irregular strips along the periphery of some burrows is interpreted as a result of late diagenetic formation and was probably derived from dissolution of crypto- to microcrystalline dolomite of the burrow fills (see Gingras *et al.*, 2004).

Limestone-dolostone ribbon rocks

Some macroscopic characteristics of the dolostone layers, *e.g.*, small thickness, stratiform pattern and preserved laminations, along with the fine crystal size, planar crystal faces, non-stoichiometry (with Ca-excess) and moderate degree of ordering of the dolomite (Fig. 7), may indicate that low-temperature dolomitization occurred syndepositionally or in the early diagenesis, *i.e.*, in a near-surface setting. Thus, a possible origin of the dolomite can be related to penecontemporaneous, microbially mediated dolomitization in shallow-marine to supratidal and hemi-

Fig. 8. Cross-plot of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ of the analysed dolomites. The isotope values for Middle Triassic marine calcite are from Korte *et al.* (2005). The estimated $\delta^{18}\text{O}$ values for Middle Triassic marine dolomite are based on equilibrium ^{18}O enrichment of 2.6‰ in low-temperature dolomite relative to calcite $\Delta^{18}\text{O}_{\text{dol-cal}}$ (Vasconcelos *et al.*, 2005). The outlined field for Middle Triassic late diagenetic dolomites of the western Balkanides is from Chatalov (2014). Note: The used symbols are the same as in Figure 7.

pelagic to pelagic environments (*sensu* Machel, 2004), or dolomite formation in hypersaline settings (*e.g.*, sabkha). Ancient ribbon carbonates have been reported from a wide spectrum of depositional environments, *e.g.*, from peritidal to deep subtidal (see Chatalov, 2017a, 2018, and references therein). Field and micropetrographic evidence have recently been presented that the carbonate rocks of the Zgorigrad Member from the Vratsa region were deposited in a mid-outer ramp setting developed on a distally steepened part of the ramp profile (Chatalov, 2018). Therefore, penecontemporaneous organogenic or hypersaline dolomitization in such slope environment is an unlikely scenario.

Several petrographic features of the dolostone layers in the ribbon rocks imply strong lithologic control on the dolomitization process. The sharp contacts with the limestone layers, the incorporation of non-dolomitized or slightly dolomitized limestone clasts, the presence of unreplaced calcitic bioclasts in the dolomitic matrix, and the rare appearance of selectively dolomitized clasts in the limestone layers close to the contact with the dolostone layers all indicate that the dolostones had a different mineralogy compared to the limestones prior to the dolomitization event. Furthermore, the presence of calcite micrite and clay-sized siliciclastic material between the dolomite crystals and the gradation from non-dolomitized clay-rich domains to strongly dolomitized domains in crack fills of the limestone layers suggest that the dolostones consisted primarily of variable amounts of CaCO_3 and clay minerals. This conclusion is supported by the preferential development of dissolution seams and low-amplitude stylolites in the dolostone layers, which points to higher clay content relative to the limestone layers (Bathurst, 1987; Aharonov and Katsman, 2009). In addition, the insoluble residue and Al content in the dolostones show significantly higher values (with proportional increase) in comparison with the limestones (Fig. 9), and the XRD analyses of bulk dolostone samples reveal the common presence of illite and minor chlorite (*cf.* Török, 2000). The originally different mineralogical composition of the limestone and dolostone layers is also indicated by unequivocal evidence for their differential diagenesis under shallow burial conditions (*i.e.*, Westphal *et al.* 2000). Thus, the ductile behaviour of the dolostone layers (deformed lamination, crack fills in the limestone layers, randomly “floating” limestone clasts) and the brittle deformation of the limestone layers (cracking, disruption, brecciation) can be explained by earlier lithification of the latter while the primarily argillaceous carbonate layers were still unconsolidated (see McHargue and Price, 1982; Coniglio and James, 1988; Demicco and Hardie, 1994). *In situ* fragmentation of early lithified limestone layers and subsequent deformation of ribbon sediments may result from: a) seismic shocks and resultant gravity-induced movements (Kullberg *et al.*, 2001); b) compaction, fluidization, and expulsion of

Fig. 9. Cross-plot of acid insoluble residue vs. Al content in dolostone layers and limestone layers of the ribbon rocks.

pore water during shallow burial (Kwon *et al.*, 2002); or c) combined influence of an external triggering force and burial compaction (Chen *et al.*, 2009). In this study case, the presence of slumps in the vertical interval with ribbon rocks and some other evidence for gravity-driven transport in the Zgorigrad Member (Chatalov, 2018) suggest that an oversteepened slope must have particularly favoured the early ductile and brittle deformation (*cf.* Sherman *et al.*, 2001) of the argillaceous and pure carbonate layers, respectively, while further deformation took place in shallow burial conditions.

The selective dolomitization of originally clay-rich carbonate layers by non-stoichiometric dolomite, together with the presence of unreplaced allochems and variable amounts of argillaceous calcitic matrix, implies a local and limited source of Mg for the dolomite formation. It has widely been demonstrated that argillaceous carbonate rocks are commonly dolomitized (Kahle, 1965; McHargue and Price, 1982; Gregg, 1988; Demicco and Hardie, 1994; Ali, 1995; Glumac and Walker, 2002; Carnell and Wilson, 2004; Li *et al.*, 2016). In a seminal paper, McHargue and Price (1982) proposed a hypothesis that diagenetic transformation of smectite to illite during burial may supply Mg ions for late-stage dolomitization. The illitization of smectite takes place over a broad temperature range from 50–60 °C to 140–180 °C (Pollastro, 1993; Milliken, 2003) and is accompanied by the release of metal ions to the pore fluid (Boles and Franks, 1979; Awwiller, 1993). It has particularly been suggested that Fe and Mg are released at temperatures >100 °C, presumably up to about 125 °C (Boles and Franks, 1979). Clay min-

eral transformations have been interpreted as a major control on dolomitization in argillaceous carbonates (McHargue and Price, 1982; Gregg, 1988; Ali, 1995; Glumac and Walker, 2002) and limestones adjacent to shales (Mattes and Mountjoy, 1980; Gawthorpe, 1987; Srinivasan *et al.*, 1994; Suchý *et al.*, 1996; Sabbagh Bajestani *et al.*, 2018), but also in sandstones (Śliwiński *et al.*, 2016) and volcanoclastic rocks (Zhu *et al.*, 2017). In this case, several lines of evidence support the assumption that illitization of smectite during burial supplied Mg ions for dolomitization of the ribbon rocks, *e.g.*, the selective replacement of argillaceous carbonate layers and the presence of illite (vs. absence of smectite) in the dolostones. Furthermore, the local formation of ferroan dolomite was most probably related to release of Fe ions during the illitization process, and thus reflects reducing (*i.e.*, burial) conditions during the dolomitization (Taylor and Sibley, 1986; Gregg, 1988; Glumac and Walker, 2002). The presence of anhedral dolomite crystals suggests formation above the critical roughening temperature (CRT), which is estimated to be between 50 °C and 100 °C, while the formation of euhedral to subhedral dolomite above the CRT may have been controlled by impurities (*i.e.*, clays) that stabilized crystal faces (Gregg and Sibley, 1984; Sibley and Gregg, 1987). The crushed brachiopod and bivalve shells (filled with dolomite cement) and the crosscutting stylolites and dissolution seams (truncated by some dolomite crystals) indicate that the dolomitization post-dated the mechanical compaction and occurred prior to and during the chemical compaction of the primarily argillaceous carbonate layers. Therefore, the relative timing of the dolomitization process can be interpreted as related to intermediate burial depths, *i.e.*, from 600–1000 m to 2000–3000 m (*sensu* Machel, 1999), which is consistent with the presumption that clay mineral transformations supplied Mg ions for the dolomite formation. The recorded oxygen isotope values ($\delta^{18}\text{O}$) of the dolomite are considerably lower than the predicted values for dolomite derived from Middle Triassic seawater (Fig. 8) and may attest to high-temperature dolomite formation (*sensu* Allan and Wiggins, 1993), *i.e.*, corresponding to the temperature range of smectite illitization. It is noteworthy that similar oxygen isotope values were reported from dolomitized layers of Cambrian and Ediacaran ribbon rocks by Glumac and Walker (2002) and Li *et al.* (2016), respectively.

Recently, Li *et al.* (2016) questioned the well-established hypothesis of McHargue and Price (1982) by studying the Mg isotope compositions of dolomite in Ediacaran ribbon rocks from South China. A numerical model calculation indicated that clay mineral transformation cannot provide sufficient Mg for dolomitization of the argillaceous layers, and instead Li *et al.* (2016) speculated that contemporaneous seawater might be the primary Mg source. These authors proposed a kinetic model, in which early differential

diagenesis of the clay-rich and clay-poor layers promotes Ca–Mg exchange between them, and as a result elevated pore-water Mg/Ca ratio in the clay-rich layers favours dolomite formation. Similarly, in an earlier study of Cambrian ribbon rocks, Glumac and Walker (2002) suggested that dolomitizing fluids may at first be provided by diffusion of overlying seawater and dissolution of some of the host carbonate sediments, and subsequently by compaction and expulsion of pore water from the argillaceous carbonate layers, with trapped seawater and ions adsorbed on clay-mineral surfaces serving as the Mg source. According to Glumac and Walker (2002), additional Mg ions for the dolomite formation may be supplied by release of structural water from clay minerals during the late diagenetic illitization of smectite. In the case studied, the possible role of seawater in the dolomitization process is implied by the measured $\delta^{13}\text{C}$ values of the dolomite, which point to seawater-derived pore fluids. If so, the dolomitization of the argillaceous carbonate layers may have been a continuous process related to changing diagenetic conditions and different sources of Mg during shallow and deep burial. In conclusion, it may be inferred that the observed variations of the dolomite amount in the Anisian ribbon rocks reflect: a) variations in the distribution, amount and composition of clay minerals in the primary sediments (McHargue and Price, 1982); and/or b) the efficiency of Mg supply through ion exchange between lithologically different layers plus rapid termination of dolomitization during the early differential diagenesis (Li *et al.*, 2016). Also, the preservation of calcian dolomite must be attributed to a semi-closed diagenetic system with low water/rock ratio (Lumsden and Chimahusky, 1980; Sperber *et al.*, 1984), in which the impermeable limestones prevented the supply of allochthonous Mg ions during deep burial.

CONCLUSIONS

Two different types of fabric-selective dolomitization are recognized macroscopically in Anisian carbonate deposits from Northwest Bulgaria. The dolomitization of burrows in limestones occurred during the early diagenesis with a local source of Mg from non-evaporitic solutions with low Mg/Ca ratio. The low-temperature precipitation of non-stoichiometric (with Ca excess) dolomite was microbially mediated and controlled by bacterial sulphate reduction. The carbon for dolomite formation was largely derived from seawater and/or dissolution of precursor calcareous sediments, and partly derived from the decomposition of organic matter. The selective dolomitization of primarily argillaceous carbonate layers in limestone-dolostone ribbon rocks was mainly associated with an autochthonous source of Mg. Conversion of smectite to illite at intermediate burial depths supplied Mg (and locally Fe) ions for the formation of Ca-rich dolomite. However,

differential diagenesis of the clay-rich and clay-poor layers may also have favoured early dolomite precipitation, whereupon contemporaneous seawater was the primary Mg source during shallow burial. This study demonstrates that various factors control the formation of fine-grained, non-stoichiometric dolomite with fabric-selective character of replacement recognizable in the field.

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