

STRONTIUM ISOTOPE COMPOSITION OF TRIASSIC
COASTAL AND SHALLOW MARINE CARBONATES IN
THE WESTERN BALKANIDES, NW BULGARIA

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Abstract

Whole-rock samples of Triassic coastal and shallow marine carbonates were analyzed for their Sr isotope signatures and trace element concentrations were measured in order to assess the possible impact of diagenetic alteration. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Anisian to lower Carnian calcite micrites reproduce the global Triassic seawater variations fairly well. The recorded higher values can be explained by an influence from detrital aluminosilicate phases and a minor postdepositional alteration. The samples of tidal-flat dolomicrites from the base of the Anisian show no significant diagenetic overprint but have considerably more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signatures compared to the global Sr isotope curve that corresponds to the Triassic (Mesozoic) maximum. These anomalously high values may have resulted from some interaction between the dolomitizing brines and the underlying fluvial siliciclastics (Buntsandstein facies), but more likely from the high $^{87}\text{Sr}/^{86}\text{Sr}$ river waters discharged from a silicate-dominated drainage basin to the coastal area at the beginning of the Middle Triassic. This study demonstrates that bulk micrite can be used as a proxy for seawater $^{87}\text{Sr}/^{86}\text{Sr}$ after proper sample selection and diagenetic screening. It also suggests that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ancient carbonates precipitated in coastal settings should be interpreted with caution, considering the possible influence of continentally-derived fluids.

Key words: marine micrites, tidal-flat dolomicrites, Anisian–Carnian, Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ curve, riverine input

Introduction. Marine minerals (e.g., carbonate, sulphate, phosphate) can incorporate dissolved strontium (Sr) from ambient seawater and record its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the time of precipitation. The $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the oceans has varied through time reflecting fluctuations in the balance of two major Sr sources: riverine input of radiogenic Sr from continents and submarine hydrothermal flux of unradiogenic Sr [1, 2]. The Sr isotopic signature of marine deposits can be used as a tool for stratigraphic correlation as the residence time of Sr in the ocean ($\sim 10^6$ yr) is much longer than the mixing time of oceanic water masses ($\sim 10^3$ yr) [3]. It can also serve as a proxy for understanding the evolution of the Earth system, e.g., periods of glaciations, mountain building, enhanced submarine hydrothermal activity and major volcanic eruptions, as well as changes in the submarine groundwater discharge, ocean crust alteration and total land area [2]. For Paleozoic and Mesozoic deposits, the most useful samples have proven to be brachiopods and belemnites but other macrofossils and conodonts have also been studied with various degree of success [1]. Bulk carbonate Sr isotope analysis appears to be the only practical option in fossil-free strata [4–7], although diagenetic alteration and/or contamination from detrital aluminosilicates remain persistent threat for misreading the geological record. Micrites are considered to be particularly suitable to use as a proxy for seawater $^{87}\text{Sr}/^{86}\text{Sr}$ because they typically have low porosity and permeability, which can effectively reduce the pore fluid circulation and thus postdepositional alteration [4, 5].

This paper presents Sr isotope ratios in calcitic and dolomitic micrites from Middle to Upper Triassic coastal and shallow marine rocks exposed in NW Bulgaria. The main purpose is to compare the Sr isotope signature of stratigraphically well-dated deposits with the global Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ curve and to contribute to the discussion on possible reasons for isotope fluctuations.

Geological setting. Surface exposures of Triassic sedimentary deposits in NW Bulgaria occur mostly in the West Balkan Tectonic Zone (Fig. 1). They belong to the Balkanide (facies) type of Triassic and the entire Triassic succession corresponds to a second-order T-R stratigraphic cycle. The marine rocks are lithostratigraphically referred to as Iskar Carbonate Group which consists of limestones and dolostones plus some marls, shales and sandstones having total thickness up to ~ 500 m. These sediments were mainly deposited on a homoclinal ramp with local distal steepening that developed in the subtropical belt on the NW shelf of the Tethys Ocean. According to biostratigraphic data, the carbonate sedimentation started in the early Anisian [8] and persisted into the early Carnian [9], producing inner ramp facies (tidal flat, lagoon, shoal) and mid- to outer ramp facies (storm-influenced, slope) with significant contribution of lime mud [10]. Two main stages of the ramp development are distinguished – deepening (retrogradational depositional trend) and shallowing (progradational depositional trend).



Fig. 1. Surface exposures of Triassic marine rocks, i.e., Iskar Carbonate Group (shown as brown patches), in the West Balkan Tectonic Zone (shown in mauve) and sample locations (1 Gintsi 43°11'N 23°10'E, 2 Zgorigrad 43°17'N 23°53'E, 3-7 Sfazhen 43°09'N 23°42'E, 8-10 Cheshmichki dol 43°44'N 226°94'E)

Sample selection and methods. More than 100 samples from aphanitic limestones were initially collected in eleven stratigraphic sections of the Iskar Carbonate Group [10]. Standard thin-sections were prepared aiming to screen for rocks that predominantly consist of calcite micrite, i.e., have $\leq 1\%$ allochems, contain only small amount of terrigenous admixture (less than 5%), and are devoid of veinlets, stylolites, void filling spar, dolomite (as verified by XRD) and other authigenic minerals. Trace element concentrations (Sr, Mn, Fe) were analyzed (for method details see CHATALOV [10]) in order to assess the degree of diagenetic alteration. Lastly, six whole-rock samples of micrites from two key sections were selected for Sr isotope analysis (Fig. 1). They originate from carbonate strata having early Anisian to early Carnian age (Table 1). Additionally, four samples of dolomicrites were taken from the base of the Anisian (where pure micritic limestones are lacking) in three sections. These samples were preliminarily screened following the same petrographic criteria and then analyzed for trace elements. The stoichiometry and cation ordering of the dolomites were determined by XRD analysis using TUR M62 diffractometer with filtered Co K α radiation at Sofia University “St. Kliment Ohridski”.

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Strontium isotope and trace element data for the analyzed whole-rock samples (1-Sv, 2-Sv, 3-Sv, 4-Sv – dolomicrites, 5-Mg, 6-Mg, 7-Ba, 8-To, 9-Sh, 10-Ch – calcitic micrites)

sample No.	sample No. [10]	litho-stratigraphy	chrono-stratigraphy	section	$^{87}\text{Sr}/^{86}\text{Sr}$ (NBS-987)	2σ error	Sr ppm	Mn ppm	Fe ppm	Mn/Sr
1-Sv		Svidol Fm	base of Anisian	Gintsi	0.709022	0.000004	140	188	2280	1.34
2-Sv		Svidol Fm	base of Anisian	Zgorigrad	0.708731	0.000005	210	307	2184	1.46
3-Sv		Svidol Fm	base of Anisian	Sfrazhen	0.708891	0.000005	181	215	1845	1.19
4-Sv		Svidol Fm	base of Anisian	Sfrazhen	0.708537	0.000005	166	233	2699	1.40
5-Mg	4-M-IV	Mogila Fm Opletnya Mb	Anisian (Aegean)	Sfrazhen	0.708239	0.000007	713	165	875	0.23
6-Mg	8-M-IV	Mogila Fm Opletnya Mb	Anisian (Bithynian)	Sfrazhen	0.708167	0.000007	1060	116	528	0.11
7-Ba	15-B-IV	Babina Fm Zimevitsa Mb	Anisian (Pelsonian)	Sfrazhen	0.708110	0.000005	945	131	892	0.14
8-To	4-T-VIII	Toshkovdol Fm	Anisian/Ladinian	Cheshmichki dol	0.708036	0.000004	589	57	490	0.10
9-Sh		Shirokaplanina Fm	Ladinian (Fassanian)	Cheshmichki dol	0.708003	0.000004	510	83	583	0.14
10-Ch	10-Ch-VIII	Cheshmichka Fm	Carnian (Julian)	Cheshmichki dol	0.707838	0.000004	528	108	646	0.20

For the Sr isotope analysis ~ 500 μg of WR powder was first subjected to weak (0.4 M) acetic acid leaching, following the protocol of METODIEV et al. [11]. Then the leached powders were dried, re-dissolved in UpA grade HNO_3 acid and processed via standard micro-column separation techniques using Eichrom Sr spec resin. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured on Thermo-Scientific Triton-series Thermal Ionization Mass Spectrometer at the University of Leeds, UK. To attain maximum accuracy, the ^{88}Sr signal was bracketed between 5 and 8 V, delivering internal precision (2σ ; $n = 200$) between 4 and 7×10^{-6} . $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized for fractionation to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. All $^{87}\text{Sr}/^{86}\text{Sr}$ data have been normalized to NBS-987 value of 0.710248 [12]. Repeated analysis of the previously studied belemnite (pure carbonate) internal standard YCB ($n = 9$) processed together with the Triassic rocks produced $^{87}\text{Sr}/^{86}\text{Sr}$ values only 19 ppm higher when compared with the literature values [12] and only 8 ppm higher from the previous runs of YCB at the same lab and via the same column separation technique and with the same reagents and blanks.

Analytical results. The Sr isotope and trace element dataset is provided in Table 1. The limestone samples show $^{87}\text{Sr}/^{86}\text{Sr}$ ratios varying in a relatively narrow range (0.707838–0.708239), while the dolostone samples have much higher values that reach up to 0.709022. The stratigraphic variations of the Sr isotope ratio are shown in Fig. 2A. They outline an upsection decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ trend, i.e., sharply through the Anisian and then more gradually to the lower Carnian. The measured trace element concentrations are 510–1060 ppm (Sr), 57–165 ppm (Mn), 490–892 ppm (Fe) in the calcite micrites, and 140–210 ppm (Sr), 188–307 ppm (Mn), 1845–2699 ppm (Fe) in the dolomicrites. The calculated Mn/Sr ratio ranges from 0.10 to 0.23 for the micrites and from 1.19 to 1.46 for the dolomicrites. The dolomite stoichiometry and cation ordering vary from 52.6 to 55.0 mole% Ca and from 0.44 to 0.65, respectively.

Interpretation and discussion. The most extended $^{87}\text{Sr}/^{86}\text{Sr}$ dataset of the Triassic was provided by KORTE et al. [13] and different parts of the Triassic interval on the global Phanerozoic $^{87}\text{Sr}/^{86}\text{Sr}$ curve were refined in several additional studies [14,15]. The Early Triassic rate of increase of marine $^{87}\text{Sr}/^{86}\text{Sr}$ over time was the fastest in the Phanerozoic [1] and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios around the Olenekian–Anisian boundary were the highest in the Mesozoic, forming the so-called Triassic (Mesozoic) maximum [15] (Fig. 2A). This sharp rise is considered to be a direct response to high riverine flux of Sr due to enhanced continental weathering that was caused by combination of anomalous warming, intensified hydrological cycle and loss of vegetation cover during the Early Triassic [13,14]. A rapid decline in the marine $^{87}\text{Sr}/^{86}\text{Sr}$ composition followed during the Middle Triassic mainly as a result of reduced continental weathering and continued until the early Carnian when the $^{87}\text{Sr}/^{86}\text{Sr}$ values started to gradually rise again [13,14].

The limestone samples analyzed in our study reproduce fairly well the global Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ variations (Fig. 2A) [1], and hence we interpret the measured

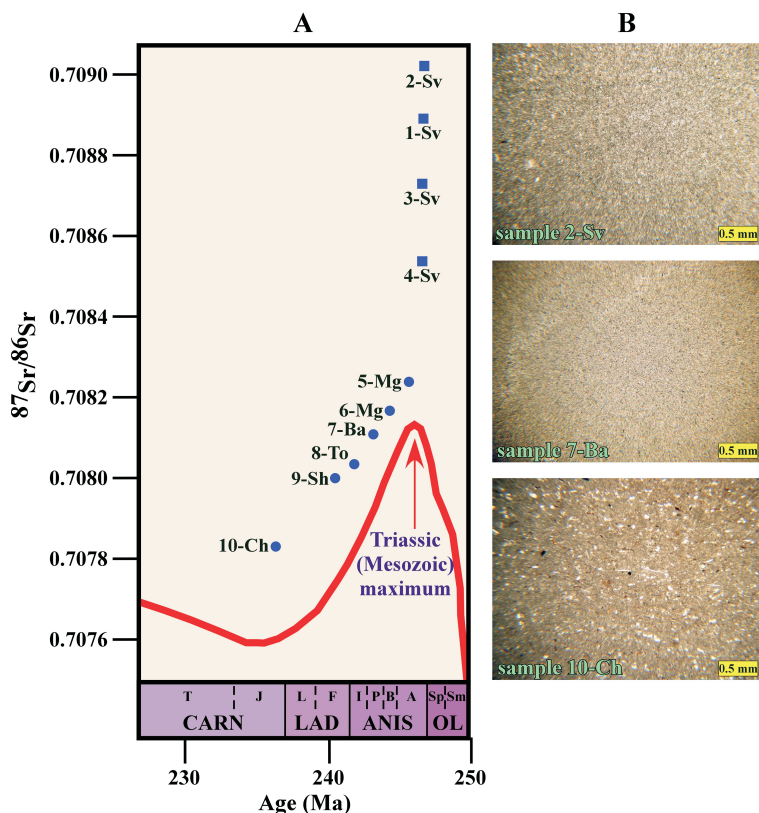


Fig. 2. A. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of whole-rock samples from the Iskar Carbonate Group (limestone – circles, dolostone – squares). The red line denotes the global marine Sr isotope calibration curve of MCARTHUR et al. [1]. The age of the sampled lithostratigraphic units is based on AJDANLIJSKY et al. [8] and TRONKOV [9]. Abbreviations: Sv – Svidol Fm, Mg – Mogila Fm, Ba – Babina Fm, To – Toshkovdol Fm, Sh – Shirokaplanina Fm, Ch – Cheshmichka Fm. B. Microphotographs of calcitic micrites and dolomicrites. Note the presence of detrital grains in sample 10-Ch

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios as largely retaining the pristine composition of Middle to early Late Triassic seawater. The higher values may be explained by some diagenetic alteration and/or influence from detrital aluminosilicate phases. The degree of diagenetic alteration of bulk marine carbonate is assessed by applying various screening criteria (petrographic, trace element, isotopic) which are generally similar to those used for fossils [3–6,16]. Since diagenetic alteration commonly causes depletion in Sr and enrichment in Mn and Fe, all our samples can be classified as well preserved by having $\text{Sr} > 500$ ppm, $\text{Mn} < 200$ ppm, $\text{Fe} < 1000$ ppm, and $\text{Mn}/\text{Sr} < 0.25$. Furthermore, the obtained $^{87}\text{Sr}/^{86}\text{Sr}$ values show poor covariation with these diagenetically sensitive proxies (Fig. 3) and thus indicate insignificant

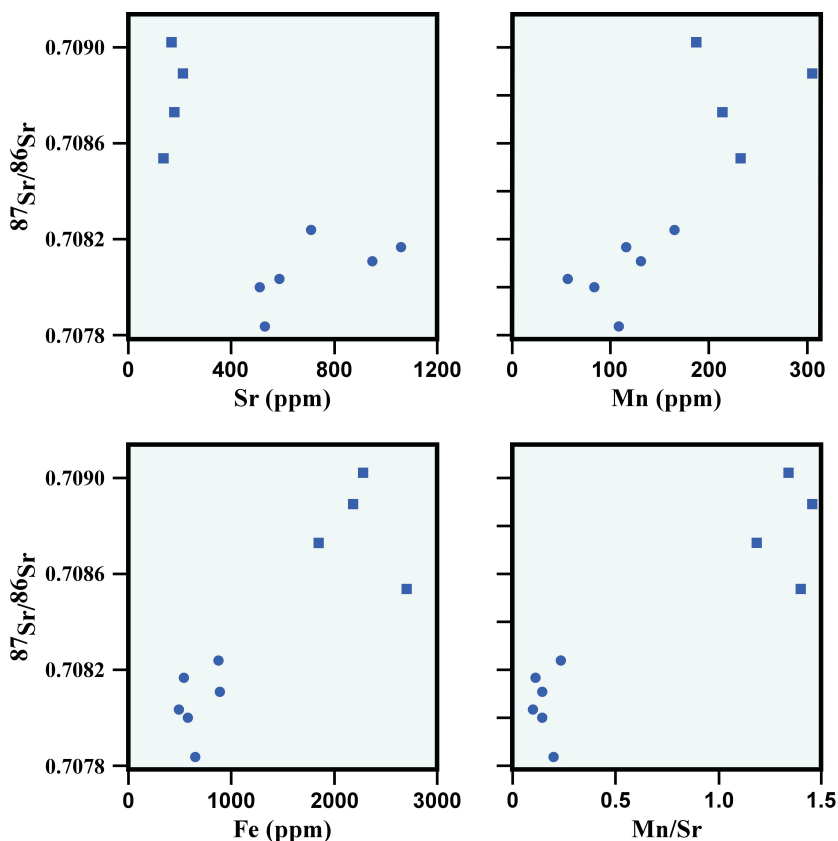


Fig. 3. Crossplots of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio versus trace element contents and Mn/Sr ratio. Symbols are the same as in Figure 2

postdepositional overprint [5, 6, 16]. The more radiogenic Sr isotope signatures could rather be due to the presence of terrigenous K-bearing minerals (clays, feldspars, mica) because the greatest deviation from the global Triassic $^{87}\text{Sr}/^{86}\text{Sr}$ curve is recorded in two samples (9-Sh, 10-Ch) that have the highest amount of siliciclastic admixture (Fig. 2B).

The samples of dolomicrites from the base of the Anisian show considerably higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to the global Sr isotopic curve which corresponds to the Triassic (Mesozoic) maximum (Fig. 2A). These deposits were formed in a tidal flat environment (during the Tethyan transgression) where lime muds were penecontemporaneously dolomitized from evaporated seawater [17]. The anomalously radiogenic Sr isotope values may reflect significant contamination from detrital silicates, substantial diagenetic alteration, or strong influence of a non-marine fluid source. The first possibility seems unlikely because the dolostones contain very low amount of siliciclastics similarly to the Anisian limestone samples (Fig. 2B). Evidence from trace element analysis may be ambiguous for assessing

the diagenetic alteration because dolomite has a higher preference for Fe and Mn and a lower preference for Sr compared to calcite. Various thresholds for the Mn/Sr ratio have been proposed in the literature but values <2 are generally considered to reflect little to no alteration [3]. In our case, all of the dolostone samples have Mn/Sr <1.5 and thus reveal no significant diagenetic overprint, consistent with the relatively low Fe and Mn contents plus a lack of covariance between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and trace element compositions (Fig. 3). Furthermore, there is no petrographic evidence for recrystallization of the dolomicrites, e.g., increase in crystal size and non-planar crystal boundaries, and the same conclusion is inferred from the dolomite nonstoichiometry and low to moderate cation ordering.

The $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of carbonate minerals precipitated in coastal and shallow marine environments can be influenced by freshwater discharge [18, 19]. In general, freshwater is enriched in radiogenic Sr by continental weathering and modern rivers have an elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.711 [2]. However, on a regional and local scale, the Sr isotope signatures of river water primarily reflect the Sr isotopic signatures of outcropping bedrocks in the drainage area [20]. For example, BENITO et al. [19] demonstrated the strong effect of weathered and eroded silicate-dominated rocks on the Sr isotope composition of Lower Cretaceous marginal-marine carbonates even in the case of low alluvial detrital input and high marine influence. The anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ values in the lowermost Anisian tidal-flat dolomites probably resulted from some interaction between the dolomitizing brines and the underlying Lower Triassic siliciclastics which have varying thickness in the western Balkanides. More importantly, these red-bed sediments (referred to as Buntsandstein facies) were deposited in a large fluvial system and the river water discharged to the coastal area at the beginning of the Middle Triassic was thus enriched in radiogenic Sr. If Upper Paleozoic rocks were exposed at that time in the catchment basin, this also contributed to the riverine input of radiogenic ^{87}Sr , because present-day exposures in the study area include predominantly diverse types of granitoids and siliciclastic deposits. Ultimately, the high but differing $^{87}\text{Sr}/^{86}\text{Sr}$ values of the dolomicrites may also reflect the temporal influence of other factors, e.g., variable influx of seawater into the tidal flat environment and submarine groundwater discharge.

Conclusions. The present pilot study on the Sr isotope signatures of Triassic carbonates from NW Bulgaria reveals that the whole-rock samples of shallow marine micritic limestones largely retained the pristine composition of Middle to early Late Triassic seawater, hence suggesting that diagenetically screened bulk micrite can be successfully used as a proxy for seawater $^{87}\text{Sr}/^{86}\text{Sr}$ fluctuations. In addition, it is demonstrated that the lowermost Anisian tidal-flat dolomicrites broadly reflect the influence of continentally-derived fluids (riverine input) with influx of more radiogenic Sr, thus highlighting that caution is needed when interpreting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ancient carbonates precipitated in coastal settings, including those with low siliciclastic admixture and little diagenetic overprint.

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