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Early-diagenetic dolomitization of Middle Triassic platform/ramp carbonates driven by geothermal convection in the Bükk Mts. (North Hungary)

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Abstract: Shallow marine carbonates of the Anisian Hámor Dolomite Formation in the Bükk Mountains, NE Hungary were studied to determine the mechanism and controlling factors of the dolomitization. Petrographic features, along with C and O stable isotope properties of the investigated rocks, indicate near-surface/shallow burial dolomitization of the shallow, subtidal–peritidal carbonate succession. This occurred via long-term circulation of relatively low-temperature fluid of sea-water origin. Geothermal convection may have been the driving force of this circulation. For application of this model, we need to assume that segmentation of a previously-established shallow ramp had already initiated in the Western Neotethys earlier in the middle Anisian. Unfortunately, we have only indirect evidence of this in the studied area. Still, the structural evolution and the related paleogeographic setting may have been the basic controlling factors of the pervasive early diagenetic near-surface/shallow burial dolomitization of the Hámor Formation. The coarse crystalline dolomite cement in the fractures and pores was precipitated from relatively high temperature (cc. 170 °C) water. Comparing the stable isotope values of the bulk rock and the fracture-occluding dolomite cement phase suggests a host-rock buffered fluid flow probably in the Late Cretaceous deformation phase.

Keywords: carbonate platform, dolomitization, stable isotopes, Middle Triassic, Bükk Mountains

Introduction

Petrographic features and geochemical characteristics of a predominant part of the dolomite rocks suggest that they were formed via replacement of precursor carbonates in various diagenetic settings (e.g., Tucker & Wright 1990; Budd 1997; Machel 2004; Pearce et al. 2013). However, despite the remarkable efforts of generations of researchers, there is no general model for the explanation of large-scale dolomitization of marine carbonate rocks, and thus the mechanism of the dolomite-forming processes is still rather enigmatic. This is why case studies which focus on determining the nature and mechanism of the dolomite forming processes are of particular importance. Results of investigations of Anisian-dolomitized shallow marine successions in the Bükk Mts., NE Hungary is presented in the current paper.

At the beginning of the Middle Triassic, widely-extended carbonate ramps came into being along the western termination of the large embayment of the Panthalassa Ocean, i.e., the later Neotethys Ocean. During the Middle Anisian, a westward opening of the Neotethys Ocean developed in the area of the later Alpine–Carpathian–Dinaric region. The related extensional tectonics led to the onset of dissection of large carbonate ramps predominantly from those areas, which were located in the proximity of the spreading axis. Here, fault-bounded basins were formed, whereas on the footwall blocks, shallow marine conditions prolonged, i.e., isolated carbonate platforms came into being. (Haas et al. 1995; Budai & Vörös 2006; Budai et al. 2017). In some of these ramps the shallow marine carbonate sediments were affected by partial to complete dolomitization, while in others, no or only slight dolomitization took place.

Only one dolomite formation plays a significant role in the geological build-up of the Bükk Mountains: the Anisian Hámor Dolomite, which has never been studied from the aspect of dolomitization (Less et al. 2002; Pelikán et al. 2005).

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In the current paper, we present the results and interpretation of our petrographic and geochemical studies, which were carried out on samples taken from selected localities. In addition to this, we compare the results of the current investigations in the Bükk Mountains with those gained from our previous studies as well as published results of others on carbonate platforms of similar age and development (Haas et al. 2014, 2017, 2021). This provides us with a better understanding of the mechanisms and main controlling factors of their dolomitization.

Geological setting

The Bükk Mountains are located in Northeast Hungary. Their Pre-Cenozoic rocks belong to the Bükk Unit, which is one of the structural units of the Mid-Hungarian Megaunit (Fig. 1a) – a shear zone between the ALCAPA and Tisza Megaunits, consisting of displaced elements of South Alpine and Inner Dinaridic origin (Kovács et al. 2000; Haas et al. 2012, 2013). According to relevant paleogeographic reconstructions (e.g., Haas et al. 1995; Gawlick et al. 1999; Gawlick 2000; Schmid et al. 2008; Kovács & Haas 2010), during the Middle Triassic, the area of the Bükk Units, as well as the Sana-Una and Jadar Units of the Inner Dinarids were located near the western termination of the Neotethys Ocean on the Gondwana-related continental passive margin of Pangea known as Adria (Fig. 2). In the Bükk Mts., Upper Carboniferous marine shales and limestones are the oldest rocks exposed on the surface (Fig. 1b). They are overlain by a Middle Permian succession made up of fine terrestrial siliciclastics and evaporites of sabkha facies. Shallow marine limestone was formed in the Late Permian (Pelikán et al. 2005). The lower part of the Lower Triassic (lower Induan) is made up of shallow marine oolitic limestone (Gerennavár Limestone Fm.) followed by a shallow ramp succession characterised by alternation of fine siliciclastic and carbonate rocks (Ablakoskővölgy Fm. – upper Induan to Olenekian). The uppermost member of this formation (Újmassa Member) consists of dark grey to black thin-bedded nodular or laminated limestone. It was formed on the outer ramp near the storm wave base in oxygen depleted and occasionally in anoxic environments (Hips & Pelikán 2002; Pelikán et al. 2005).

The Ablakoskővölgy Formation is overlain concordantly by the Hámor Dolomite Formation (Fig. 3). This cc. 400 metre-thick formation is widely extended in the Bükk Mts., and it is exposed in several core drillings (Less et al. 2002; Pelikán et al. 2005). The light to dark grey dolomite succession commonly shows cyclic alternation of 1–2 m thick beds of bioclastic and/or oncoidal wackestone-packstone texture, as well as centimetre to decametre thick stromatolite layers or beds containing rip-up clasts of stromatolites, microbial nodules, and/or cm-sized oncoids (Haas et al. 2012; Pelikán et al. 2005). The sedimentological features of the succession suggest alternating shallow subtidal and peritidal depositional conditions in ramp/platform setting. Based on foraminifera (*Endotriadella wirzi, Trochammina almtalensis, Earlandinita oberhauseri, Haplofragmella inflate, Meandrospira deformata*) and dasycladalean algae, the largest part of the Hámor Formation can be assigned to the Pelsonian substage, although the lower part of the formation likely involves the Lower Anisian (Velledits 2004; Pelikán et al. 2005). In the north-eastern segment of the mountains, the upper cc. 50 m thick part of the formation consists locally of grey bioclastic limestone with fragments of colonial corals and reef-derived clasts (Nyavalyás Limestone Member; Pelikán et al. 2005). It is a Steinalm-type ramp carbonate succession containing a rich dasycladalean alga flora (*Physoporella pauciforata pauciforata, Ph. pauciforata undulata, Teutloporella peniculiformis*) and foraminifera assemblage (*Diplotremina astrofimbriata, Pilammina densa, Trochammina almtalensis*) of Pelsonian age (Velledits 2004).

The Hámor Formation is overlain unconformably by terrestrial deposits of the Sebesvíz Formation. In the northern part of the Bükk, unsorted, poorly-rounded dolomite and claystone clasts occur in a red clay matrix in the basal part of the tens of metre-thick succession. It is followed upward by polymictic breccia and conglomerate beds with red clay interbeds. Based on the texture and microfossils of the dolomite clasts, they are derived from the Hámor Dolomite. Scarce occurrence of small pelagic limestone clasts (wackestone with radiolarians and sponge spicules) has also been reported (Velledits 2004). In the southwestern part of the mountains (core Felsőtárkány Ft-7), the Hámor Dolomite is covered by volcanic tuff and tuffaceous marl, as well as siltstone with light grey lacustrine calcareous marl intercalations (Velledits 2004). Acidic and neutral products of continental volcanic activity (dacite and rhyolite lava rocks and pyroclasts and basaltic andesite to andesite lava rocks – Szentistvánhegy Metavolcanics Formation) occur above the terrestrial deposits (Haas et al. 2012). Recent U–Pb data indicate cc. 240 Ma (Ladinian) age of the volcanism (Gál et al. 2018; Németh et al. 2023). As a result of extensional tectonics, a segmented topography came into being – carbonate platforms and intraplatform basins were developed (Velledits 2006). From the Ladinian to the latest Triassic, kilometre-thick platform carbonates (Bükkfennsík Limestone) were formed on the submarine highs, whereas laminated limestone and radiolarite (Várhegy Fm.), cherty limestone (Felsőtárkány Limestone), fine siliciclastic sediments (Vesszős Fm.), and carbonates (Hegyestető Fm.) were deposited in the basins (Csontos 2000; Velledits 2004; Pelikán et al. 2005).

The Upper Triassic formations are overlain by a Middle Jurassic succession, which is made up of pelagic basin and redeposited slope deposits (Haas et al. 2013). The Paleozoic and Mesozoic formations were affected by very low to low-grade metamorphism in the Early and Late Cretaceous (Árkai 1983; Árkai et al. 1995). The strongly-deformed and slightly metamorphosed pre-Cenozoic formations were covered by Upper Eocene to Miocene sequences, which have now been almost completely eroded in the inner part of the mountains (Pelikán et al. 2005).

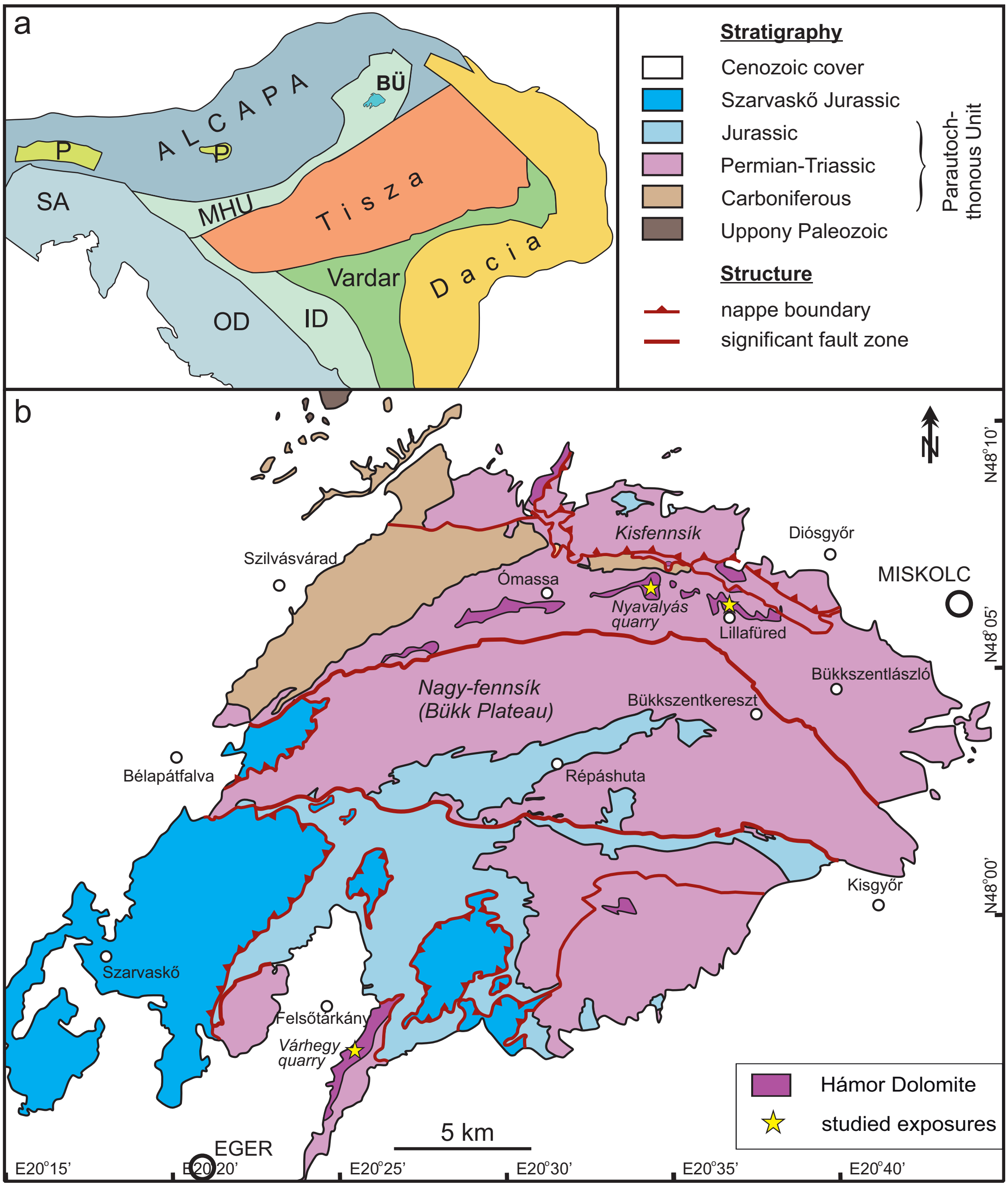

Fig. 1. a — Tectonic position of the Bükk Unit in the Alpine–Carpathian–Dinaridic system (after Kovács et al. 2011). **b** — Simplified geological map of the Bükk Mts.showing the sampling sites of the Hámor Dolomite (from Németh et al. 2023).

Material and methods

For petrographic investigations and stable C and O isotope measurements, three localities were sampled. We collected samples from the lower and middle yard of the Várhegy quarry near Felsőtárkány (Figs. 3, 4; N47°57'54", E20°26'04"), which is the largest exposure of the Hámor Dolomite in the southwestern part of the Bükk Mts. We took samples along a 4 m thick section from the upper yard of the Nyavalyás quarry close to Lillafüred (Figs. 3, 4; N48°06'35", E20°34' 58"), which is a representative exposure of the Hámor Dolomite in the northeastern part of the Bükk Mts. A few samples were taken from small outcrops of the Nyavalyás Member near the upper yard of the Nyavalyás quarry (N48°06'38", E20°34'34"). We collected samples at Lillafüred (Figs. 3, 4; N48°06'23", E20°37'14") from tectonically-fractured rocks assigned to the basal part of the Hámor Formation.

Thin sections were prepared from every samples. The classification of Folk (1959) was applied for the crystal size assignment. Cathodoluminescence (CL) microscopy was performed on a few of the polished thin sections using a MAAS-Nuclide ELM-3 cold-cathode luminoscope at the Department of Geology, Eötvös Loránd University. Determination of textural features of the samples was followed by the selection

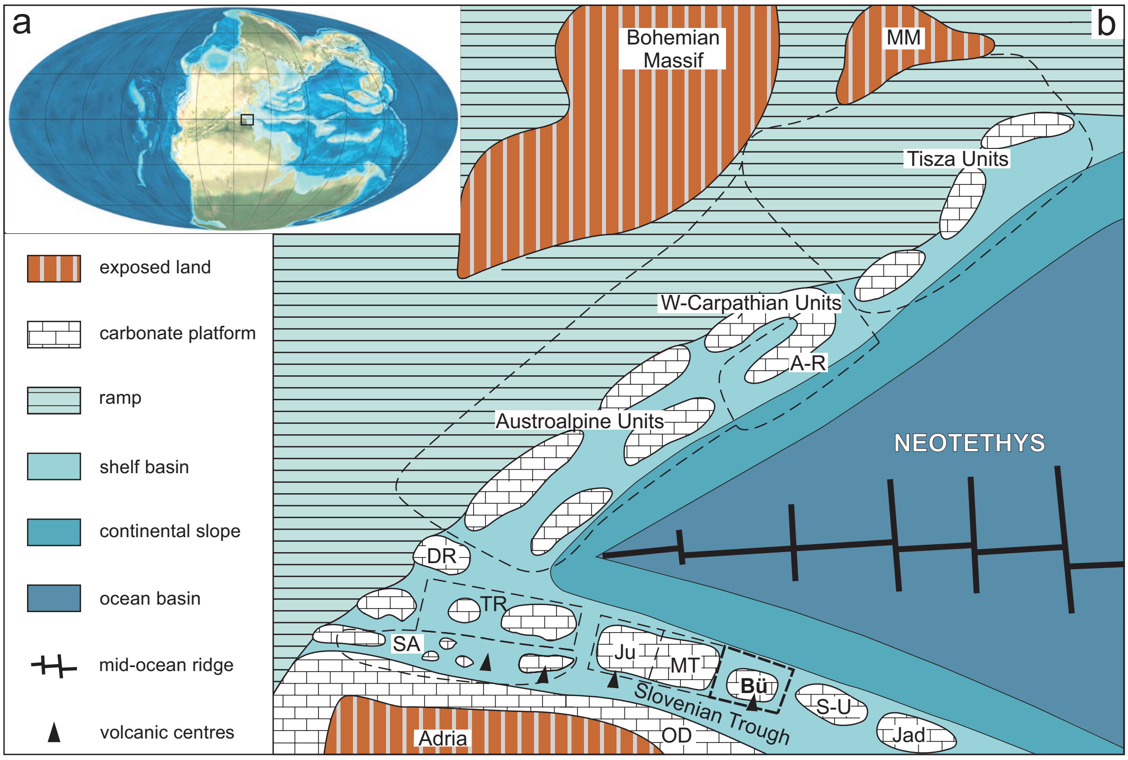

Fig. 2. Paleoglobe (**a**) and paleogeographic position of the Bükk Unit (Bü) on the Neotethys shelf (**b**) during the Middle Triassic (from Budai et al. 2017). A–R – Aggtelek–Rudabánya units (Steinalm-type ramp); DR – Drau Range; Jad – Jadar Blocks (Steinalm-type ramp); Ju – Julian Alps; MM – Malopolska Massive; MT – Mid Transdanubian unit; SA – South Alpine units (Camorelli, Dosso dei Morti, Albiga and Upper Serla Platforms); S-U – Sana-Una unit (Steinalm-type ramp); TR – Transdanubian Range unit (Tagyon and Kádárta Platforms).

of pure phases for stable isotope analysis. This was carried out by a hand-held dental drill of 1 mm in diameter. Stable carbon and oxygen isotope analyses were performed at the Institute for Geological and Geochemical Research (Budapest, Hungary) using a Finnigan delta plus XP mass spectrometer (Thermo Fisher Scientific, Bath, UK). The stable C and O isotope compositions of micro-drilled powders of dolomite samples were determined using the continuous flow technique (Spötl & Vennemann 2003) and dolomite reaction conditions, described by Rosenbaum & Sheppard (1986). All samples were measured at least in duplicate, and the mean values are in the traditional δ notation in parts per thousand (‰) relative to Vienna Pee Dee Belemnite (VPDB). Reproducibility is better than ±0.1 ‰ for $\delta^{13}C$ and ±0.1 ‰ for $\delta^{18}O$.

For the clumped isotope analysis, mm-size crystals were extracted from an open vug. Clumped stable isotope analyses of dolomites were performed at the Isotope Climatology and Environmental Research Centre (ICER), Institute for Nuclear Research (ATOMKI, Debrecen, Hungary) on a Thermo Scientific™ 253 Plus 10 kV mass spectrometer, after phosphoric acid digestion at 70 °C using a Thermo Scientific Kiel IV automatic carbonate device. The applied reaction time was 2200 seconds. 110–130 µg aliquots of each dolomite sample measurement was replicated at least 11–12 times and measured alongside carbonate standard samples (ETH1, ETH2, ETH3, IAEA-C2 and NIST-SRM88b

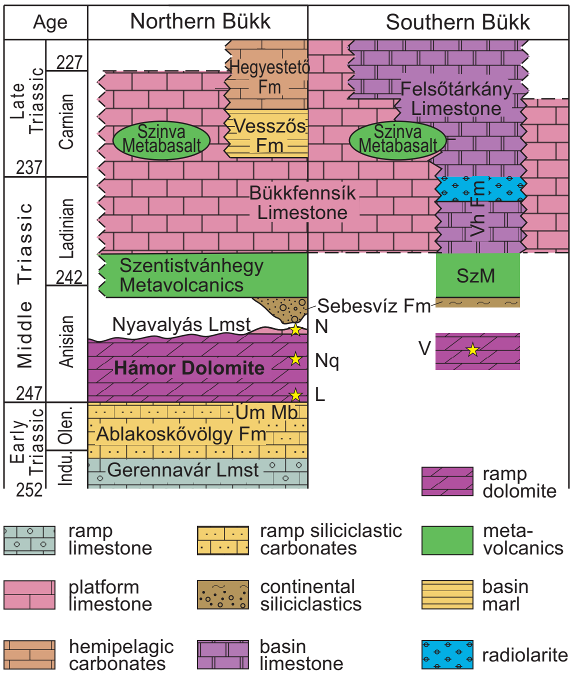

Fig. 3. Stratigraphic column of the Lower Triassic to Carnian formations of the Bükk Mts. (from Haas et al. 2001). Yellow stars show the position of the samples taken for microfacies and stable isotope studies: L – Lillafüred (Hámor Lake); Nq – Nyavalyás quarry, N – Nyavalyás outcrops, V – Várhegy quarry (Felsőtárkány).

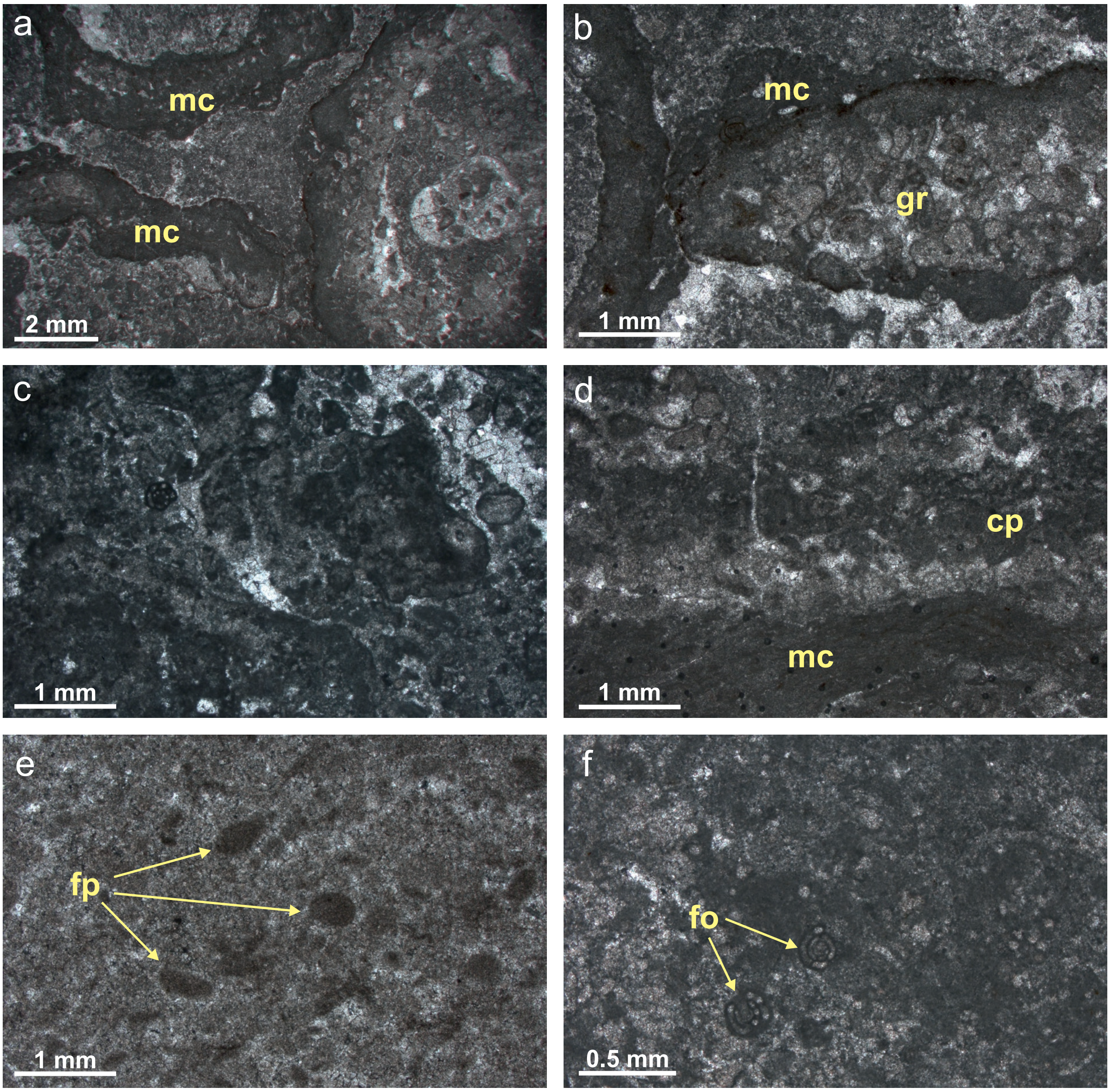

Fig. 4. Photomicrographs of the samples taken from middle part of the Hámor Dolomite in the Várhegy quarry, Felsőtárkány. **a** — Oncoids and fragments of microbial crusts (mc) in very-fine to fine crystalline peloidal matrix. An oncoid with gastropod nucleus is visible in the right side of the picture (sample VA3). **b** — Microbially encrusted (mc) grapestone (gr; sample VA3). **c** — Very fine- to fine-crystalline clotted matrix with medium-crystalline pore filling cement (sample VA2). **d** — Very fine-crystalline microbial crust with vague wavy lamination (mc) is visible in the lower part of the picture that is separated from the overlying clotted peloidal lamina (cp) by a thin fine- to medium crystalline horizon (sample VA2). **e** — Faecal pellets (fp) in very fine-crystalline clotted matrix (sample VA1). **f** — Foraminifera (fo) in very fine- to fine-crystalline clotted matrix; both the foraminifera and the matrix consist of dolomite (sample VA1).

as a dolomite monitoring sample). Data evaluation, standardization, and analytical error propagation of Δ_{47} clumped-isotope measurements were carried out using the CO_2 Clumped ETH PBL replicate analysis method, implemented in Easotope software (John & Bowen 2016) using the revised IUPAC parameters for ^{17}O correction (Brand et al. 2010). Δ_{47} results are given in the I-CDES90 scale (Intercarb-Carbon Dioxide Equilibrium Scale; Bernasconi et al. 2021), and apparent temperatures in °C were calculated based on the Δ_{47}-temperature calibration from Bonifacie et al. (2017), with temperature uncertainties propagated from the 1σ standard error (SE) of the Δ_{47} value.

Results

Petrography and microfacies

A predominant part of the cc. 400 metre-thick Hámo Formation was the subject of complete pervasive dolomitization, except for its uppermost part (Nyavalyás Member), which is made up predominantly of limestone, but with totally or partially-dolomitized intervals.

The Várhegy quarry at Felsőtárkány (Figs. 1b, 3) exposes the middle part of the Hámor Dolomite. The grey to dark grey rocks usually exhibit well- to moderately-preserved depositional fabrics; however, poorly-preserved fabrics occasionally occur as well. These rocks are usually made up of mm to cm-sized grains (oncoids, grapestones, microbial nodules, intraclasts commonly with microbial coating, fragments of gastropods and foraminifera – Fig. 4a, b, c, d); very fine to fine crystalline dolomite occurs among the grains. Clotted fabric characterised by massive occurrence of tiny peloids was also observed locally (Fig. 4e, f). The succession is punctuated by sheet or wavy-laminated stromatolite intercalations (Fig. 5a). They usually exhibit an excellently-preserved fabric characterised by alternation of clotted micrite/microsparite and fenestral-pore rich laminae (Fig. 5b, c, d). Stromatolite-derived, rip-up clasts from inbreccia horizons were also encountered (Fig. 5e). In some cases, a network of cracks and tiny vugs with fine to medium crystalline cement fill could be observed. The wider fractures and the mm to cm-sized mouldic/vug pores are filled by medium to coarsely crystalline dolomite cement (Fig. 5f).

The lowermost part of the Hámor Dolomite is exposed in the studied outcrop near the south-eastern termination of Lake Hámor at Lillafüred (Figs. 1b, 3). The light to medium grey, fine-crystalline dolomite is fabric destructive, commonly brecciated, and usually densely dissected by cracks and fractures filled by white dolomite cement (Fig. 6a, b). In some cases, it is visible that the cm-sized breccia clasts are bounded by cracks (Fig. 6c). The small vugs and narrow fractures are occluded by fine to medium crystalline dolomite cement. The cm-sized dissolution pores are filled by coarse saddle dolomite cement (Fig. 6d) or planar euhedral dolomite cement exhibiting a concentric zonation (Fig. 6e, f). The saddle dolomite is a common type of late diagenetic dolomite cement, characterized by large, crystal-size, curving or saddle-shaped crystal faces and undulose extinction.

The lower-middle part of the Hámor Dolomite cca. 50 m above the stratigraphic base was studied and sampled in the Nyavalyás quarry (Figs. 1b, 3,), where the succession is made up of thick-bedded, medium to dark grey dolomite with a few decametres-thick intercalation of dark grey laminated dolomite (Fig. 7a). The 1–1.5 m thick beds (Fig. 7b) usually exhibit well- to moderately-preserved depositional texture, although partially destructed fabric was also encountered. The rocks contain mm to cm-sized micritic nodules or clasts with a micrite coating in a very fine to fine crystalline peloidal matrix (Fig. 7c). Faecal pellets (Fig. 7d), a few foraminifera, and fragments of molluscs also occur. A homogenous, very fine crystalline dolomite texture was found in one of the studied samples. Dark grey, laminated dolomite intercalations also occur in the succession (Fig. 7e). In one of them, 1–3 mm thick laminae of very fine and fine crystalline matrix alternate. It contains a large amount of tiny peloids, micritic remnants of ostracods, and a few thin-shelled bivalves (Fig. 7f).

The fabrics of the samples taken from scattered small outcrops of the Nyavalyás Member near the upper yard of the Nyavalyás quarry (Figs. 1b, 3) display very similar features to those reported by Velledits (2004) from core Miskolc-10, and they correspond with the three microfacies types defined by her. These types are as follows: (A) Limestone rich in mm-sized fragments of dasycladalean algae (*Physoporella pauciforata undulata, Physoporella dissita, Physoporella intusannulata*; Fig. 8a, b), which can be correlated with the dasycladalean limestone lithofacies found in the lower part of the Nyavalyás Member; (B) Limestone containing specimens of foraminifera *Pilammina densa* in a rock-forming quantity (Fig. 8c, d), which may correspond with the foraminifera packstone lithofacies type found in the middle part of the Nyavalyás Member in well Miskolc-10. Partial dolomitization of the very fine crystalline limestone leading to obliteration of the original texture was observed in one of our samples (Fig. 8d); (C) Completely dolomitized peloidal micrite–microsparite fabric with medium crystalline fenestral and mouldic pore-filling dolomite cement (Fig. 8e, f). It may correspond with the dolomite mudstone lithofacies prevailing in the upper part of the Nyavalyás Member in core Miskolc-10 (Velledits 2004).

Isotope geochemistry

The carbon and oxygen isotope data are plotted in Fig. 9 and tabulated in Supplementary Table S1. The samples taken from the Várhegy quarry yielded $\delta^{18}O$ values for the matrix from −3.83 ‰ to −1.92 ‰, whereas their $\delta^{13}C$ values fall in a narrower range from 1.87 ‰ to 2.53 ‰. Two separated coarse crystalline cement samples were measured from this locality, which yielded $\delta^{18}O$: −11.98 ‰; −7.15 ‰ and $\delta^{13}C$: 1.89 ‰; 2.24 ‰, respectively. The samples from the Nyavalyás quarry yielded $\delta^{18}O$ values for the matrix from −3.51 ‰ to −2.56 ‰ and their $\delta^{13}C$ values fall in the range of −0.27 ‰ to 1.55 ‰. A completely dolomitized sample taken from the Nyavalyás Member (N1) yielded similar values $\delta^{18}O$: −3.14 ‰ to −2.82 ‰ and $\delta^{13}C$: 0.54 ‰ to 0.61 ‰. The values for dolomitized mottles of a partially dolomitized sample (N2) are as follows: $\delta^{18}O$ −3.95 ‰ and $\delta^{13}C$ from −0.02 ‰ to 0.42 ‰. With regards to the Lillafüred exposure, we measured bulk samples from the cracked, brecciated matrix which yielded $\delta^{18}O$ values from −3.4 ‰ to −3.17 ‰ and $\delta^{13}C$ values from 2.87 ‰ to 2.79 ‰. The $\delta^{18}O$ values of coarse crystalline cements fall in the range of −7.58 ‰ to −11.77 ‰ and the $\delta^{13}C$ values from 0.09 ‰ to 2.87 ‰.

On mm-sized dolomite crystals taken from vug filling cement (Supplementary Table S1: sample L3c) of the Lillafüred exposure clumped isotope, measurements were carried out which yielded a Δ_{47} value of 0.3367±0.084 ‰; from this value, 169±8 °C apparent temperature was calculated.

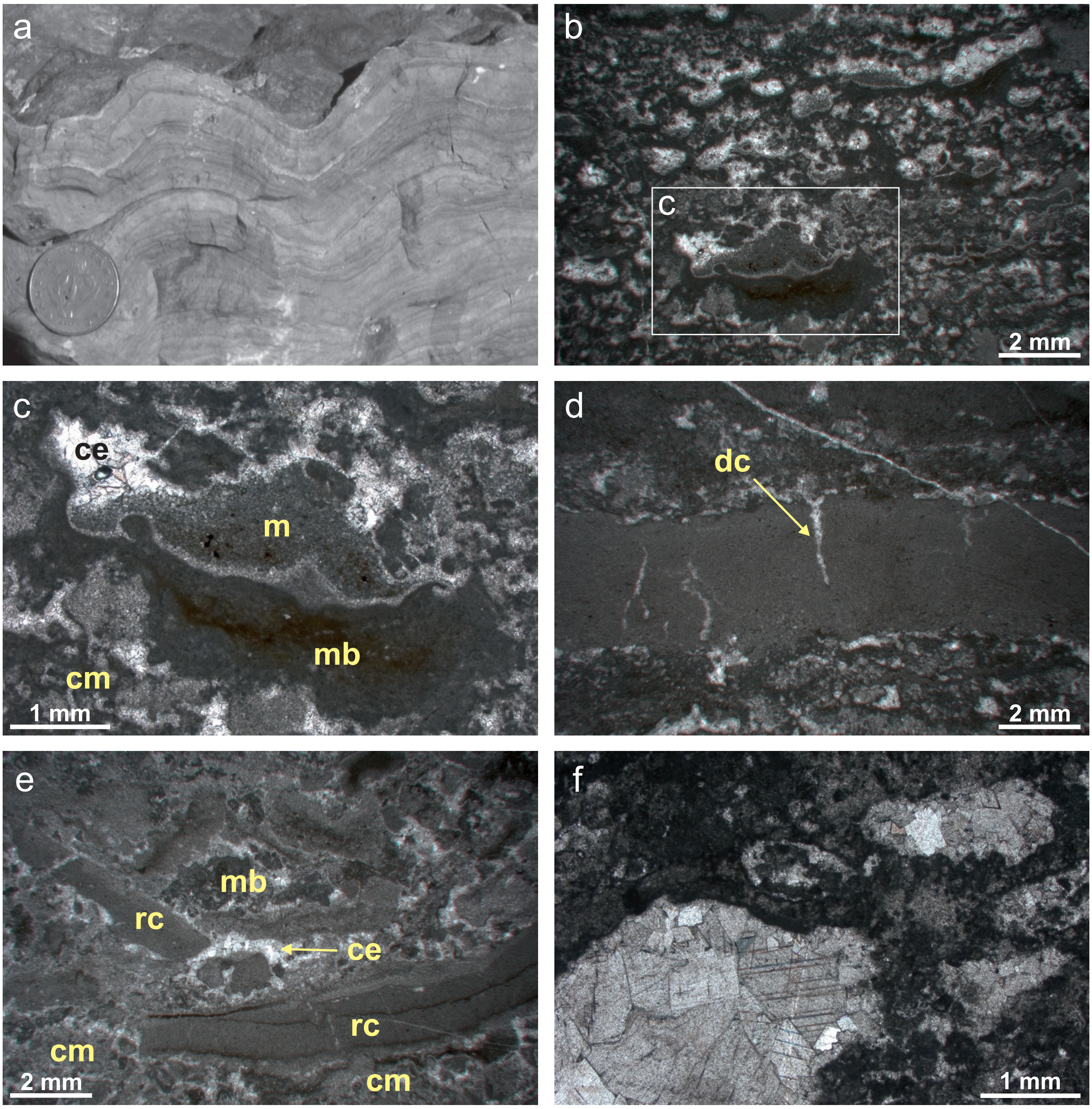

Fig. 5. Macroscopic features and microfacies characteristics of stromatolitic layers in the middle part of the Hámor Dolomite in the Várhegy quarry, Felsőtárkány. **a** — Wavy laminated stromatolite bed. **b** — Stromatolite of excellently preserved fenestral laminated fabric (sample VK8a). **c** — Details of the fenestral fabric (framed on **b**): clotted micritic matrix (cm); finely laminated microbial micrite (mb); the lower part of the fenestral pore is filled by dense micrite (m); the topmost part of the pore is occluded by medium-crystalline cement (ce; sample VK8a). **d** — A homogenous micrite lamina occurs between two fenestra-bearing clotted micrite laminae. Initiated from its uneven upper surface desiccation cracks (dc) intersect the upper part of the micrite lamina (sample VK8b). **e** — A breccia horizon was encountered in the stromatolite layer. It is made up of rip-up clasts (rc). Clotted micritic matrix (mb) and medium-crystalline cement (ce) occur among the clasts (sample VK8b). **f** — Coarse-crystalline dolomite cement in mm- to cm-sized vugs (sample VA2).

Interpretation and discussion

Dolomitization of the Hámor Formation

Near- near surface/shallow burial pervasive dolomitization

The typically moderately or well-preserved depositional fabric and the predominance of very fine or fine crystal size of dolomites in the Hámor Formation suggest early diagenetic, near-surface/shallow burial replacive dolomitization (Gregg & Sibley 1984; Sibley & Gregg 1987). Common occurrence of pebble-size dolomite clasts, derived from the Hámor Formation, enclosed in the red claystone of the directly overlying Late Anisian terrestrial Sebesvíz Formation provides additional evidence for the early diagenetic near-surface dolomitization. In this context, it is worth mentioning that along

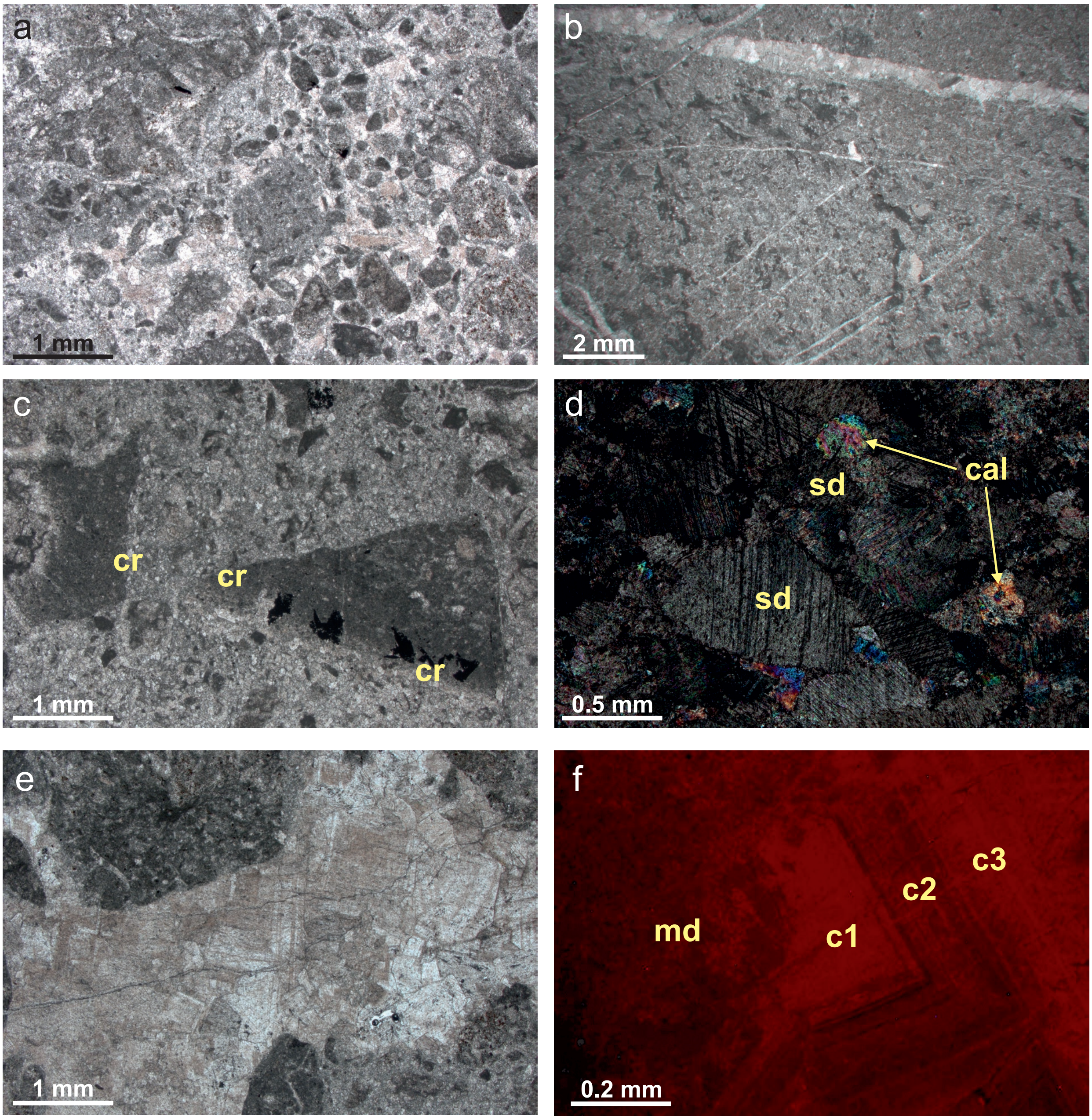

Fig. 6. Photomicrographs of the samples taken from the strongly fractured lower part of the Hámor Dolomite in exposures at Lillafüred. **a** — Brecciated, fine- to medium-crystalline fabric destructive dolomite (sample L2). **b** — Fine-crystalline fabric destructive dolomite. It is dissected by cracks and fractures filled by dolomite cement (sample L2). **c** — Brecciated, fine- to medium- crystalline fabric destructive dolomite. Some breccia clasts are bounded by cracks (cr; sample L2). **d** — cm-sized dissolution pore filled by coarse saddle dolomite (sd) cement; the small dissolutions pores are occluded by calcite cement (cal). Cross-polarized light (sample L1). **e** — Planar euhedral dolomite cement exhibiting a concentric zonation. Plane-polarized light (sample L2). **f** — CL image of a part of a coarse-crystalline pore filling dolomite cement displayed in **e**. The matrix dolomite (md) is overgrown by planar dolomite cement showing concentric zonation. The first cement phase (c1) displays bright orange CL and faint zonation. The second one (c2) exhibits definite concentric zonation with alternation of dull red to non-luminescent zones. In the third phase (c3) the zonation becomes less definite.

with the dominant dolomite clasts, limestone and partially-dolomitized clasts that had most likely been derived from the Nyavalyás Member were also encountered. In cases where the pervasive dolomitization had been younger, the limestone clasts would have been affected as well.

The oxygen isotope data of the fabric retentive dolomite samples from the Várhegy quarry and the Nyavalyás quarry (Fig. 9, Supplementary Table S1) fit into the Anisian marine range (Korte et al. 2005), especially when considering the positive shift of $\delta^{18}O$ values in the dolomite. For estimation of crystallization temperatures of the matrix dolomite samples, the fractionation equation by Land (1983) was applied assuming −3 ‰ $\delta^{13}O_{SMOW}$ values for the parent fluid. These calculations indicate relatively low temperature (30–40 °C)

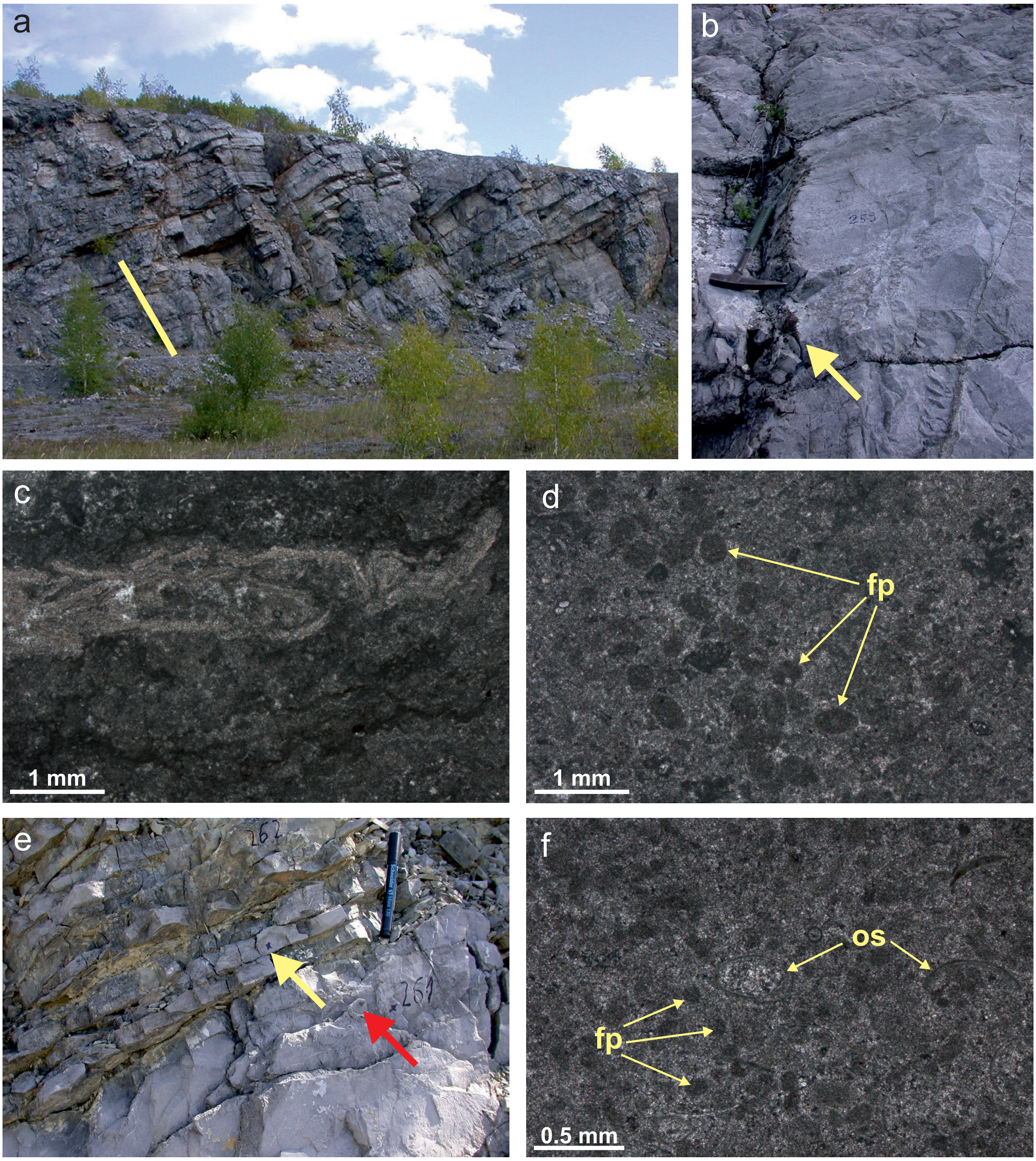

Fig. 7. Macroscopic features and microfacies characteristics of the upper part of the Hámor Dolomite in the Nyavalyás quarry. **a** — Thick-bedded dolomite in the upper yard of the quarry. The yellow line marks the sampled interval. **b** — Beds of medium grey fine-crystalline oncoidal dolomite. Sample Nq3 (its position is marked by the yellow arrow) was taken from this bed. **c** — Microbially encrusted mollusc shell fragments (sample Nq2). **d** — Faecal pellets (fp) in very fine-crystalline clotted matrix (sample Nq2). **e** — A thick bed of light grey fine-crystalline dolomite (position of sample Nq5 is marked by red arrow) is overlain by a bed of dark grey fine-crystalline dolomite punctuating by cm-thick argillaceous horizons (position of sample Nq6 is marked by yellow arrow). **f** — Ostracod shells (os) and faecal pellets (fp) in fine-crystalline matrix (sample Nq6).

dolomitizing fluid of sea-water or mixed fresh and sea-water origin (Fig. 10). Early diagenetic dolomitization via evaporated seawater (e.g., Adams & Rhodes 1960; Hsü & Siegenthaler 1969) is not likely, since more positive $\delta^{18}O$ values would be expected for dolomite precipitated from evaporated seawater (Land 1980). During the late 1970s and 1980s, the “mixing zone” dolomitization model (Folk & Land 1975; Badiozamani 1973) became prominent for explanation

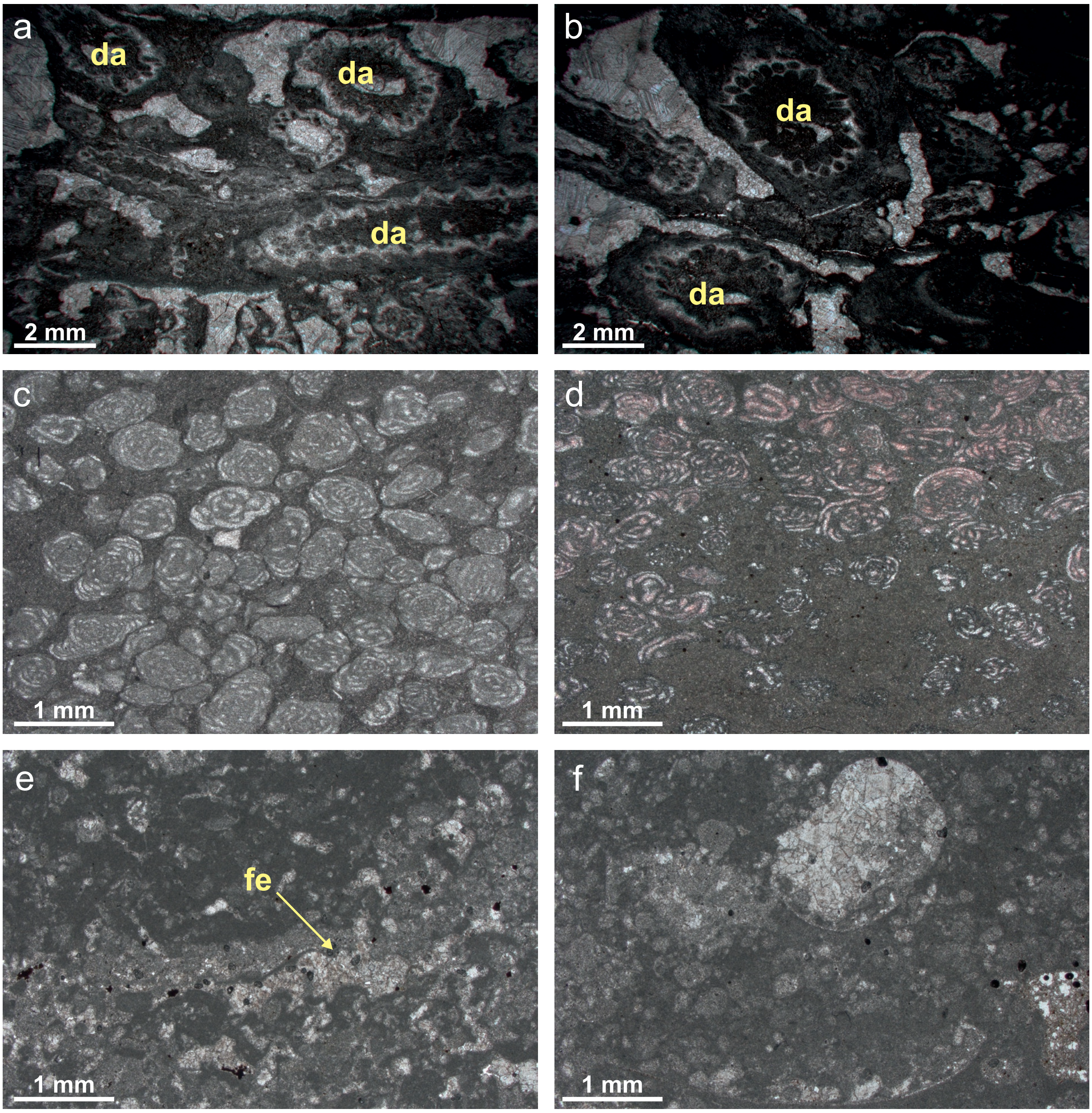

Fig. 8. Photomicrographs of Nyavalyás Limestone Member of the Hámor Formation. The samples were taken from the outcrops west to the upper yard of the Nyavalyás quarry. **a** and **b** — Limestone of bioclastic packstone texture. It contains fragments of dasycladalean algae (da, *Physoporella pauciforata undulata, Physoporella dissita, Physoporella intusannulata*) in rock-forming quantity (sample N3). **c** and **d** — Partially dolomitized limestone of bioclastic packstone texture. It contains foraminifera (*Pilammina densa*) in rock-forming quantity. Photomicrograph **d** was taken from a thin-section stained with alizarin-red; the non-stained patches indicate the dolomitized mottles (sample N3). **e** — Dolomite of moderately preserved clotted peloidal microsparitic fabric with cement-filled fenestral pores (fe). Stained thin-section (sample N1). **f** — Dolomite of moderately preserved clotted peloidal microsparitic fabric with fragments of gastropod and bivalve shells. Microbial crust (mc) is visible on a thin-shelled bivalve. Stained thin-section with alizarin-red (sample N1).

of dolomitization that took place in shallow marine to peritidal settings. However, more recent work has highlighted the kinetic problems involved with nucleating dolomite crystals in mixed water (Smart et al. 1988; Machel 2004) together with the lack of Neogene examples. Accordingly, this model has been abandoned. Contemporaneously, new concepts emerged suggesting that stable isotope compositions of dolomites depleted in $\delta^{18}O$ are consistent with dolomitization in warm normal marine seawater and various hydrodynamic processes were proposed for propelling seawater seepage (Kohout et al. 1977; Saller 1984; Saller & Moore 1986; Land 1991; Whitaker & Smart 1993). Reactive transport models demonstrated that movement of normal seawater by thermal convection through platform carbonates can lead to dolomitization of permeable carbonates (Whitaker et al. 2004; Whitaker & Xiao 2010). Results of numerical modeling suggest that long-term (order of million years) convection of seawater in the temperature range of 20–30 °C may lead to the dolomitization of large carbonate bodies (Whitaker & Xiao 2010).

Based on the petrographic and isotope geochemical constraints, seepage of seawater led to early diagenetic pervasive dolomitization of the shallow marine carbonate deposits in the study area. Geothermal heating may have been the driving force for the long-term circulation of the dolomitizing fluid. A crucial pre-requisite for the application of this geothermal convection dolomitization model (Fig. 11; Kohout et al. 1977; Machel 2004; Hughes et al. 2007; Whitaker at al. 1994) is the existence of a steep slope between the shallow marine carbonate factory and the relatively deep marine basin. Through the thin sheet of slope sediments, cold deep sea-water invades into pores of the previously-accumulated semi-consolidated carbonate deposits, and upwelling of geothermally heated pore water drives the long-term seawater circulation (Sanford et al. 1998; Whitaker & Xiao 2010). Pelsonian onset of the disintegration of the ramps and development of isolated carbonate ramps/platforms and basins is well-constrained in the Dolomites as well as in the Transdanubian Range. As for the Bükk Mts., we have no direct evidence for the presence of pre-Ladinan pelagic deposits. However, small pelagic limestone clasts found in the terrestrial conglomerate beds of the late Anisian Sebesvíz Formation (Velledits 2004) seem to support the possibility of the initiation of development of an articulated sea-floor topography in the Pelsonian.

Late diagenetic hydrothermal dolomite cement

In the samples taken from the tectonically strongly-dissected basal part of the Hámor Dolomite in the Lillafüred exposure, the fractures and vugs are filled by medium to coarse crystalline dolomite cement. The coarse crystals commonly display concentric zonation in CL, thereby indicating changes in the chemical composition of fluids (Richter et al. 2003). Saddle dolomite cement was observed in wider fractures and larger vug pores, thus suggesting relatively high (>60 °C) fluid temperature (Radke & Mathis 1980). Clumped isotope measurements on coarse crystalline dolomite cement (separated crystals from samples collected at Lillafüred) indicate temperature of 165–175 °C for the pore fluid. This temperature and $\delta^{18}O_{V\text{-}PDB}$ value (−10.6 ‰) imply that the cement precipitated from a fluid, which was enriched in ^{18}O ($\delta^{18}O_{V\text{-}SMOW}$ 6.8 ‰, Fig. 10). When comparing this value to that of the other dolomite cements, the latter show slightly higher $\delta^{18}O_{V\text{-}PDB}$ values (−8.72 ‰ to −7.58 ‰), possibly reflecting that we could not perfectly separate the cement from the matrix in these cases. The $\delta^{13}C_{V\text{-}PDB}$ values fall in the range of 0.09 ‰ to 2.87 ‰. The slightly depleted value is explained by the temperature-related fractionation effect. From the Várhegy quarry, we could separate only a few samples from coarse crystalline dolomite cement for stable isotope analysis. These samples yielded very similar values (e.g., $\delta^{18}O_{V\text{-}PDB}$ −11.98 ‰) to those found in the Lillafüred section, thereby suggesting identical pore fluid.

The nappe structure of the Bükk came into being during the Early Cretaceous (130–120 My) and led to folding and low-grade metamorphism (Árkai 1983). This was followed by another tectono-metamorphic event involving large-scale folding and formation of bedding-parallel shear zones in the Late Cretaceous (Árkai et al. 1995). The studied exposure of the Hámor Dolomite at Lillafüred is located near the contact with the Lower Triassic Ablakoskővölgy Formation, which shows strong shearing and is likely related to the Late Cretaceous deformation phase. The competence contrast of the thick-bedded Hámor Dolomite (dipping ~030°/60° here) and the incompetent laminated limestone and marl led to formation of small-scale folding and related cleavage. In contrast, an irregular network of fractures and related vugs came into being and was occluded by dolomite cement in the Hámor Formation. Intensive fracturing and brecciation of the dolomite were also observed in other localities of the same contact (northern boundaries of the outcrops along the northern edge of the Bükk Plateau).

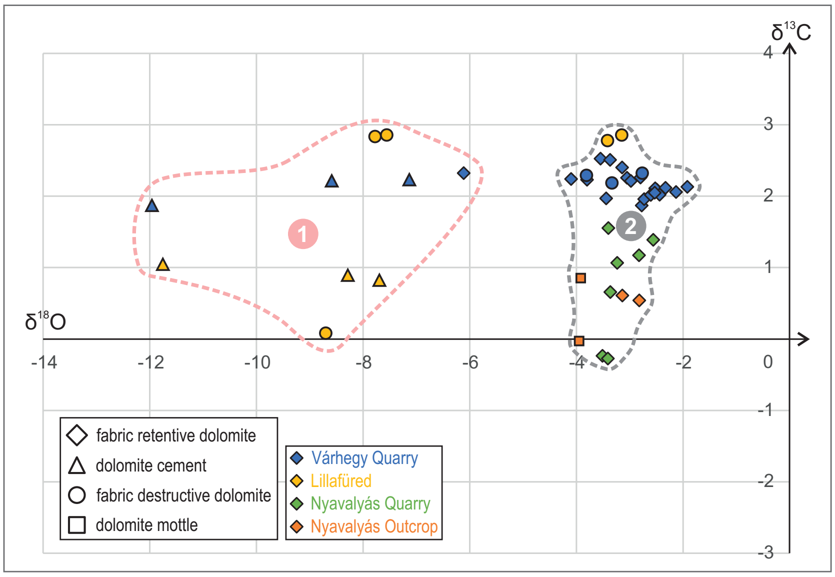

Fig. 9. Carbon and oxygen isotope (‰, V-PDB) plot for dolomite samples of the Hámor Formation. Cluster 1: dolomite (dominantly finely crystalline) formed by near-surface/shallow burial setting via circulation of sea-water derived fluid. Cluster 2: dolomite (dominantly coarse crystalline cement) formed via fault-controlled hydrothermal fluid.

Dolomitized and non-dolomitized Middle Anisian shallow marine carbonate successions near the western termination of the Neotethys Ocean

A definite facies similarity was pointed out between the Triassic formations of

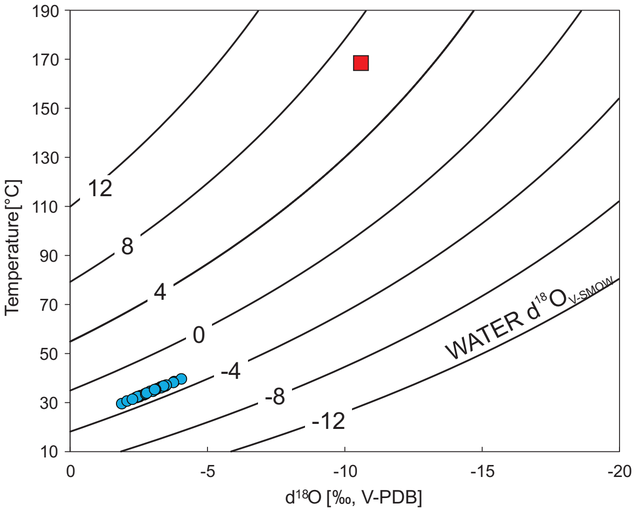

Fig. 10. Estimated crystallization temperatures versus measured oxygen isotope composition (‰, V-PDB) of the matrix dolomite samples from the Hámor Formation. In addition, the temperature converted from Δ_{47} value of clumped isotope measurements and $\delta^{18}O_{V\text{-}PDB}$ of coarse crystalline dolomite cement (red square, sample L2) is also displayed. Contours represent the isotope composition of water in isotopic equilibrium with the dolomite, calculated using the fractionation equation by Land (1983).

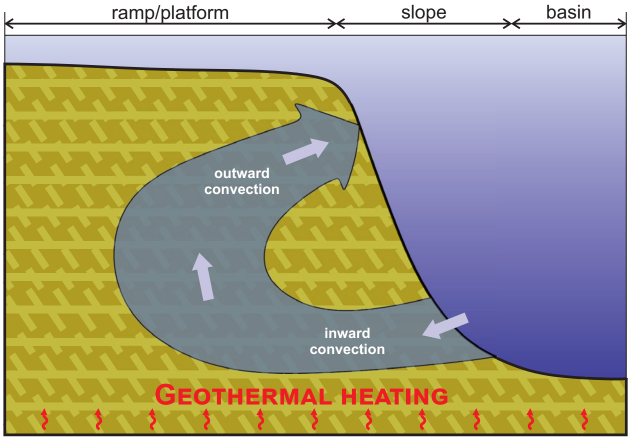

Fig. 11. Conceptual model of dolomitization via convection-driven seawater (geothermal convection or Kohout-convection dolomitization model based on figures from Kohout et al. 1977; Whitaker & Smart 1993; Machel 2004).

the Bükk and Inner Dinaridic Jadar and Sana-Una units (Protić et al. 2000; Filipović et al. 2003). In both of the latter units, the Anisian is represented by dolomitized shallow marine carbonates (Jablanica Fm. and Japra Fm., respectively). In the other parts of the Inner Dinarides as well as in the Outer Dinarides, Steinalm-type ramp carbonates occur in the Pelsonian, which are usually overlain directly by deep-water carbonates (Gawlick et al. 2012; Sudar et al. 2013). These ramp successions were not affected by any noticeable pervasive dolomitization.

The Kuna Gora, Strahinjščica, and Ivanščica Mts. in NW Croatia and the Kamnik–Savinja Alps in NE Slovenia are situated at the junction of the Southern Alps and the Dinarides. They can be considered as the westward continuation of the Mid-Hungarian Megaunit. In the NW Croatian Mts., the Pelsonian is represented by shallow marine carbonates where both limestones and dolomites occur. The dolomites exhibit obliterated or poorly-preserved sedimentary fabric with faint stromatolitic lamination, locally. The limestones are characterised by an oncoidal grainstone texture with benthic foraminifera (Kukoč et al. 2023). In the Kamnik–Savinja Alps, the lower part of the Anisian is represented by massive dolomite (Serla Fm.) overlain by bedded dolomite (Strelovec Fm.) of Pelsonian age (Celarc et al. 2013; Miklavc & Celarc 2022). Drowning of these shallow marine carbonate factories took place in the middle part of the Illyrian (Kukoč et al. 2023).

In the central part of the Southern Alps (Dolomites), fault-related segmentation of the area began during the Pelsonian (Farabegoli & Guasti 1980). On the elevated blocks, prograding isolated carbonate platforms arose where carbonates of the Upper Serla Formation were accumulated. The internal platform successions are made up of bedded limestones and dolomites, consisting of sponge/algae boundstones. The formation is bounded upward by a karstified erosional unconformity surface (Stefani et al. 2004). Isolated carbonate platforms (Camorelli, Dosso dei Morti, Albiga) were formed also in the area of the western part of the Southern Alps (Lombardy), although in these cases, the structural control of their edges is ambiguous. Litho- and biofacies of the shallow marine carbonates (Camorelli Formation) are similar to those of the Steinalm-type ramps (Unland 1975; Gaetani & Gorza 1989). Dolomitization of platform carbonates has only been reported from the western part of this area (Berra et al. 2005).

During the Middle Triassic, the Transdanubian Range unit was situated between the eastern part of the South Alpine and the south-western part of the Upper Austroalpine units (see Fig. 2). In the Transdanubian Range, fault-controlled disintegration of the previously-existing carbonate ramp had begun in the Pelsonian and led to the development of deeper basins, as well as smaller and larger submarine highs between them (Budai & Vörös 1992, 1993). Isolated platforms formed on the highs where 50–100 m thick carbonate successions consisting of metre-scale peritidal–lagoonal cycles (Tagyon Formation) accumulated. In the central platform of the Transdanubian Range Unit (Tagyon Platform), the succession consists predominantly of limestone containing partially and completely dolomitized intervals, whereas the northeastern one (Kádárta Platform) is completely dolomitized (Haas et al. 2014, 2017, 2021). Drowning of the platforms took place in the latest Pelsonian to the early Illyrian interval (Budai & Haas 1997; Budai & Vörös 2006; Karádi et al. 2022).

In the territory of the Northern Calcareous Alps (Upper Austroalpine unit), shallow-marine carbonates (Gutenstein Formation) were deposited in a semi-restricted environment during the early Anisian. An abrupt deepening took place in the late Bithynian, resulting in the deposition of deeper water limestones. After this episode, shallow open ramp conditions were established by the end of the early Pelsonian, where Steinalm-type shallow marine limestones with diverse fauna and flora were deposited. Some of them were affected by dolomitization (e.g., Zill Dolomite – Oberhauser 1980). Drowning and tectonic segmentation of the ramp took place in the late Pelsonian (Velledits et al. 2017; Gawlick et al. 2021).

The Middle Triassic history of structural evolution and sedimentation in the area of the Inner Western Carpathians was similar to that of the Upper Austroalpine units. In the Aggtelek Hills (Silica Nappe), the early Anisian dark grey limestone (lower member of the Gutenstein Formation) was formed in a restricted basin. In the early Pelsonian, this was followed by the deposition of carbonates typified by thick sponge-microbial boundstone beds (the upper member of the Gutenstein Formation) that had formed in a shallow restricted ramp environment (Hips 2022). During the late Pelsonian, after an abrupt change in the environmental conditions, the sediments were deposited in a well-oxygenated, moderately agitated inner ramp environment, as well as on the related tidal flat zone (Piros 2002). A cc. 150 m thick sequence was accumulated, made up of cyclic alternation of subtidal bioclasic limestone and commonly dolomitized stromatolite beds (Steinalm Limestone Formation). The presence of dolomitized oncoidal beds and local occurrence of coarse crystalline dolomite were also reported (Piros 2002). Drowning in the latest Pelsonian led to the secession of the shallow marine carbonate production (Péró et al. 2015).

In the Mecsek and Villány-Bihor units of the Tisza Megaunit, which is located on the wide internal belt of the of the European margin of the Neotethys after deposition of siltstones, dolomites, and evaporites, carbonate ramp sedimentation began in the late early Anisian (Török 1998). During the Pelsonian, thin-bedded limestones were formed in middle and outer ramp environments. As a result of the decreasing sea level in the late Anisian to the Ladinian, peritidal carbonates were deposited in a thickness of 100–350 m (Csukma Formation). The succession was subject to pervasive dolomitization in a near-surface setting (Lukoczki et al. 2020). Anisian to Ladinian dolomite (Szeged Dolomite) similar to the Csukma Formaton was encountered in several cores in the basement of the Szeged Basin, Southeast Hungary, which belongs to the Békés-Codru unit of the Tisza Megaunit (Garaguly et al. 2018).

Comparison of dolomitization of the Hámor Dolomite with dolomite in other Middle Triassic formations of a similar facies setting

The review presented above revealed that although ample literature on Anisian shallow marine carbonate formations of the peri-Pannonian region is available, in the majority of it, only the presence or in some cases, the petrographic features of the dolomitized rocks are mentioned, and specific investigations for determination of the dolomite-forming processes are almost completely absent. Accordingly, we were able to apply only the results of the studies carried out in the Transdanubian Range (Haas et al. 2014, 2017, 2021), Villány Hills (Lukoczki et al. 2020), and Szeged Basin (Garaguly et al. 2018) for the comparative analysis, which included sedimentological observations and detailed petrographic, as well as isotope geochemical data.

In the Transdanubian Range Unit, traces of likely microbially-mediated early dolomitization were preserved in the slightly dolomitized limestone successions of the small Tagyon Platform (Haas et al. 2014, 2017). Results of C and O stable isotope studies suggest that in the case of the larger Kádárta Platform, the semi-consolidated, and locally slightly-dolomitized limestone was subjected to large-scale dolomitization via geothermally-derived circulation of seawater along the basin-ward platform margin, whereas reflux of seawater derived mesohaline fluids led to pervasive dolomitization in the internal parts of the platform (Haas et al. 2021). The C and O isotope values measured on the very fine to fine crystalline matrix of dolomites in platform margin successions of the Kádárta platform show close similarity to those measured on the Hámor Dolomite samples (Fig. 12). As far as the cements are concerned, in the slightly-dolomitized Tagyon Platform, both calcite and dolomite cement phases were found in the selected samples yielding $\delta^{18}O_{V\text{-}PDB}$ −7.3 and −7.4 ‰ values, respectively. These values, which are less negative than those of the pure dolomite cements described from the Hámor Formation, indicate precipitation of calcite and dolomite cement in intermediate (i.e., between the near surface-shallow burial and the deep burial zones) to deep burial diagenetic setting (Haas et al. 2014, 2017). The boundary between the shallow and intermediate settings is generally defined by the change from the mechanical to the chemical compaction, whereas the oxidized mineralogy becomes reduced in the intermediate zone (Machel 2004).

In the Villány Hills, the sedimentary, petrographic, and isotope geochemical characteristics of the Csukma Formation (Fig. 12) indicate early diagenetic pervasive dolomitization via geothermal convection of normal or slightly modified seawater in a near-surface to shallow burial setting. This was followed by partial recrystallization of the previously-formed dolomite in an intermediate burial setting (Lukoczki et al. 2020). The mechanism of early diagenetic dolomitization of the Csukma Formation may have been similar to that of the Hámor Formation, however, it is rather poorly manifested in the stable isotope values due to the subsequent recrystallization.

Petrographic and geochemical investigations of the Szeged Formation led to the conclusion that pervasive dolomitization of the shallow marine succession took place in a near-surface to shallow burial setting via reflux of slightly evaporated seawater. This was followed by formation of nonplanar matrix dolomite and saddle dolomite cement by relatively high temperature fluid, which was likely channelled along Cretaceous overthrust zones in an intermediate to deep burial setting (Garaguly et al. 2018). The $\delta^{18}O$ values of samples representing the first early diagenetic dolomite phase are quite similar to those measured on the corresponding phase of the Hámor Dolomite (Fig. 12). However, the negative values suggest that instead of evaporated seawater, normal salinity seawater may have been the dolomitizing agent. Accordingly, the applicability of the reflux model in these cases is doubtful. As far as the saddle dolomite is concerned, the conditions of precipitation of this cement phase may have been similar to those in the Hámor Dolomite.

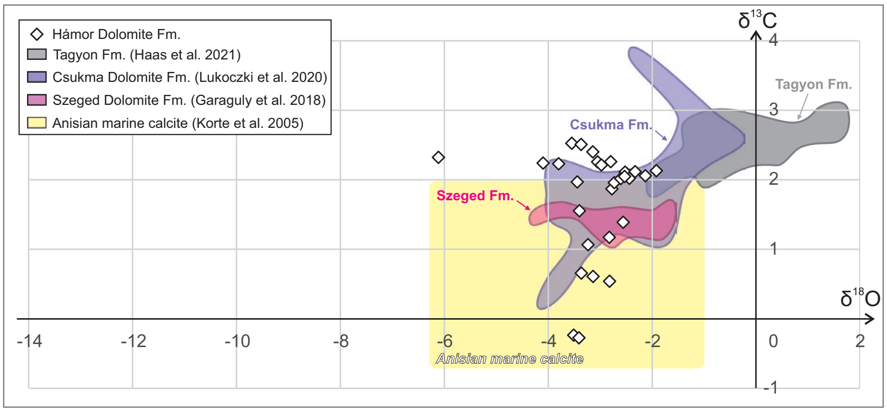

Fig. 12. Comparision of carbon and oxygen isotope values (‰, V-PDB) measured on fine-crystalline matrix dolomites (fabric retentive samples) from the Hámor Formation with fine-crystalline matrix dolomites of the Tagyon, Csukma, and Szeged Formations, respectively. The Anisian marine values are based on unaltered brachiopod shells. The comparison of the distribution clusters reveals that the cluster of the Hámor Formation shows a significant overlap with that of the Szeged Formation. There is a partial overlap with the cluster of the Csukma Formation, but here we have to take into consideration that the time range of this formation is much longer. As for the Tagyon Formation, the cluster extends from the negative $\delta^{18}O_{V\text{-}PDB}$ field (−2 ‰) to the positive one (+1.8 ‰) suggesting that the marginal part of the large Kádárta Platform was affected by geothermal dolomitization (a field between −2 ‰ and +0.5 ‰) whereas reflux of sea-water derived mesohaline fluids (a field between +0.5 ‰ and +1.8 ‰) led to pervasive dolomitization in the internal parts of the platform.

Conclusions

- Moderately or well-preserved depositional fabric and the predominance of very fine and fine crystal size of dolomites in the Hámor Formation indicate early diagenetic, near-surface-/shallow burial dolomitization. The carbon and oxygen stable isotope data fit into the Anisian marine range and constrain dolomitizing fluid of normal salinity seawater.
- The petrographic features and stable isotope properties suggest that the predominantly fabric retentive pervasive dolomitization of the shallow subtidal–peritidal carbonate succession took place in a near-surface/shallow burial diagenetic setting as a result of long-term circulation of relatively low-temperature (cc. 30–40 °C) fluid of seawater origin.
- Geothermal convection may have been the driving force of the long-term circulation of the seawater derived dolomitizing fluid. This model implies the inflow of cool and deep seawater into an isolated ramp or carbonate platform through its foreslope. In the Bükk Mts., we have only indirect evidence for the initiation of the segmentation of the previously-existing, widely-extended shallow ramp, and whereby development of isolated ramps/platforms and fault-bounded basin between them as early as the Pelsonian. However, inferences on the structural evolution of the excellently-exposed Dolomites in the Southern Alps and the results of detailed studies of coeval formations in the Transdanubian Range seem to support this interpretation.
- The structural evolution and the related paleogeographic setting (i.e., the development of an isolated ramp/platform–basin pattern) was likely the basic controlling factor of the pervasive early diagenetic shallow burial dolomitization of the Hámor Formation. In the Transdanubian Range, when applying similar analytical and evaluation methods, we came to similar conclusions for pervasive dolomitization of the Pelsonian Tagyon Formation in the marginal belt of a large, isolated platform. However, in this area, the isotope characteristics indicated climate-controlled reflux dolomitization in the internal part of the same platform.
- The coarse crystalline dolomite cement in the fractures and pores of the Hámor Formation was precipitated from relatively high temperature (cc. 165–175 °C) water and led to recrystallization of the dolomite along the fracture zones. The fractures were opened and occluded by cement, most likely in the Late Cretaceous deformation phase.

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Electronic supplementary material is available online:
Supplementary Table S1 at http://geologicacarpathica.com/data/files/supplements/GC-75-2-Haas_TableS1.xlsx