Comparative study of the origin of dolomites formed in various tectonic units of Hungary

Introduction

Dolomite is a common sedimentary rock type comprising a significant portion of the uppermost part of the Earth's crust. Dolomite rocks are widespread in Hungary and have great practical importance (hosting hydrocarbons, potable water, and ore deposits, and are widely quarried as building stone).

The aim of the project was to reconstruct the dolomitization history of various carbonate rocks of mostly Triassic age from distinct tectonic units of the Pannonian Basin that have not been studied in detail yet. Case studies included the partially and completely dolomitized ramp successions in the Mecsek Mountains and Villány Hills, the partially and completely dolomitized, shallow and deep marine carbonate successions of the Aggtelek Karst and Bükk Mountains. In addition, we completed studies of Permian and Triassic formations in the Transdanubian Range.

The project was performed in accordance with the modified research plan (04.2023). We published 9 papers on case studies on dolomite rock bodies, which occur in various sites in Hungary. We also published a review paper on the major characteristics of dolomites and processes of dolomitization in Hungarian in the Földtani Közlöny. The first phase of our work included fieldwork with sampling that was accompanied with mapping of carbonate bodies occasionally. The samples have been preserved in the Department of General and Applied Geology of the Eötvös Loránd University, which thus became a unique regional collection of the dolomite rocks.

Workflow of the project

In all case studies the conventional methodology of the diagenesis evaluation was generally applied, that was supplemented by additional methods appropriate to the given formation.

- Petrographic and textural analysis of the dolomites, using standard, cathodoluminescence, fluorescence and scanning electron microscopy in order to characterize and discriminate various dolomite generations
- Bulk mineralogical composition of the samples (X-ray powder)
- Geochemical composition -- major and trace elemental composition of each distinctive dolomite phases, stable carbon and oxygen isotope composition
- Fluid inclusion thermometry was used on suitable samples to estimate the temperature and salinity of the dolomitizing fluids that implies the origin of the fluids

The diagenetic model included the reconstruction of paragenetic sequence and dolomitization processes, evaluation of the burial history. The results of the case studies were placed into a broader regional context via comparison with coeval dolomites of other structural units within the Tethyan realm.

Results

A fault-related dolomite body was documented from the Lower Jurassic limestone at the Kálvária Hill of Tata. The details of its genesis were published in the Földtani Közlöny (Győri et al. 2018). A few metres-sized dolomite body is present in the Lower Jurassic limestone strata of the Kálvária Hill of the Gerecse Mts. The dolomite making up this body is unique, both in the outcrop itself and in the Jurassic

beds of the Gerecse Mts. It is laminated, yellow-red and follows a fracture, thus further invading the host Jurassic limestone along a bedding plane. The dolomite that effectively replaces the host rock is fine to medium crystalline; locally, saddle dolomite crystals have also been observed. The breccia zone is cemented by white-grey-yellow calcite that incorporates dolomite crystal fragments. Calcitized dolomite crystals can be found in the host Jurassic limestone next to the breccia zone. The three different dolomite types are most probably associated with the same dolomitization event. Dolomitizing fluids could have migrated through fractures and occasionally along bedding planes. The stable isotope data of the dolomite suggest that dolomitization probably took place in the burial realm, either from the existing pore water or hydrothermal fluids; the latter would have migrated through fractures in the lithified Lower Jurassic limestone. The post-sedimentary character of the fractures suggests a post-Late Jurassic age for the dolomitization. The meteoric origin of the calcite found in fractures — and as cement in the breccia zone — points to subaerial exposure. This would imply the occurrence of a pre-Late Cretaceous–Palaeogene dolomitization event.

Two Ladinian-Carnian vertebrate localities, hosted by mixed siliciclastic-carbonate strata, were known from the Villány Mountains. Sedimentary environment of the dolomite-dolomarl-claystone-sandstone succession was described in details by Botfalvai et al. (2019). Four main lithofacies were identified and interpreted, consisting of dolomite (deposited in a shallow, restricted lagoon environment), dolomarl (shallow marine sediments with enhanced terrigenous input), reddish silty claystone (paleosoil) and sandstone (terrigenous provenance) indicating that the sediments of the Construction vertebrate site were formed in a subtidal to peritidal zone of the inner ramp environment, where the main controlling factor of the alternating sedimentation was the climate change. However, the recurring paleosol formation in the middle part of the section also indicates a rapid sea-level fall when the marine sediments were repeatedly exposed to subaerial conditions.

The diagenetic history of the Middle Triassic Csukma Formation of the Mecsek Mts. was studied in detail using conventional and novel methods, such as carbonate clumped isotope thermometry. Integration of various petrographic and geochemical techniques revealed that multiple phases of dolomitization and dolomite recrystallization affected the studied formation (Lukoczki et al. 2019). Shallow marine to peritidal carbonates of the Triassic Csukma Formation in the Mecsek Mts. of SW Hungary are made up of dolomites, limestones and dolomitic limestones that show evidence of a complex diagenetic history. Integration of petrographic, conventional stable oxygen and carbon isotope, clumped isotope, and strontium isotope data with the paleogeography, paleoclimate, and burial history of the region revealed four major diagenetic stages. Stage 1: The peritidal carbonates were dolomitized penecontemporaneously during the Middle Triassic by refluxing evaporatively concentrated brines. Stage 2: Increasing burial during the Late Triassic–Jurassic resulted in recrystallization of the Kán Dolomite Member in an intermediate burial setting. Stage 3: During the Early Cretaceous seawater was drawn down and circulated through rift-related faults, causing renewed recrystallization of the Kán Dolomite Member as well as dolomitization of the Kozár Limestone Member and the underlying limestones in a deep burial setting, but only in the vicinity of the faults. Stage 4: During the Late Cretaceous and Cenozoic thrusting resulted in tectonic expulsion of basinal fluids and precipitation of multiple saddle dolomite cement phases near the faults. The results of this study imply that the clumped isotope method integrated with other geochemical data can successfully be applied to identify the nature and potential sources of extra-formational diagenetic fluids responsible for dolomitization and recrystallization. This study provides conclusive evidence for multi-phase dolomitization and dolomite recrystallization over several millions of years (Middle Triassic

through Early Cretaceous) and several thousands of meters of burial in the Csukma Formation in SW Hungary. Furthermore, this study is the first to identify fault-controlled dolomitization by circulating Cretaceous seawater within Triassic carbonates of central Europe, further supporting the viability of the interpretation of dolomitization by seawater initially drawn down and then geothermally circulated through faults in extensional basins.

After publication of the results of our studies on the Mecsek Mts. occurrence of the peritidal Csukma Formation, results of our studies on the Villány Hills occurrence were also came out in the International Journal of Earth Sciences (Lukoczki et al. 2020). Peritidal carbonates of the Csukma Formation (Csukma Dolomite Member) in the Villány Hills, SW Hungary, were investigated to determine the nature of the dolomitization and recrystallization processes that affected these rocks during their complex tectonic evolution, and to evaluate if clumped isotope data preserved signals from the original dolomitization event or are indicative of the later recrystallization processes. Sedimentary and petrographic features, as well as geochemical characteristics integrated with the tectonic evolution of the area indicate that dolomitization likely occurred penecontemporaneously via geothermal convection of normal-to-slightly modified seawater in a near-surface to shallow burial setting. This was followed by partial recrystallization of the dolomites in an intermediate burial setting with low water-to-rock ratios. Results of this study suggest that the clumped isotope temperatures of dolomites, partially recrystallized via dissolution–re-precipitation, may provide a minimum estimate of the temperature of recrystallization. However, caution has to be taken when interpreting the thermal history and fluid evolution of successions that were affected by significant recrystallization, because the clumped isotope temperatures and the calculated fluid compositions might inaccurately represent the diagenetic conditions.

In the area of the Transdanubian Range the publication of a summarising paper (Győri et al. 2020) on the dolomitization of Lower Triassic shallow-water, mixed siliciclastic-carbonate sequences from the Balaton Highland in Sedimentary Geology means a great progress in the understanding of a special type of shallow-water reflux dolomitization. Seven cores were chosen for petrographic and stable isotope investigations aiming to reconstruct the paragenetic sequence with special regard to the dolomitization and hydrothermal events. Five lithotypes were differentiated: (i) dolomite, (ii) sandy, silty, clayey dolomite, and dolomarl, (iii), dolomitic siltstone and sandstone, (iv) dolomitic limestone, and (v) limestone. In these lithotypes, three types of dolomites are present: non-ferroan replacive, ferroan replacive, and ferroan cement. Fabric retentive and fabric destructive non-ferroan replacive dolomitization are interpreted to have occurred by seepage reflux. Supporting evidence includes the presence gypsum and anhydrite in the Lower Triassic beds. Stable isotope values of the ferroan dolomite (δ18O of −10.7 to −4.2‰ and δ13C of −4.8 to 4.7‰) suggest dolomitization by fluids of relatively high temperature. The similar stable isotope values (δ18O of −9.3 to −5.8‰ and δ13C of −1.9 to 2.5‰) of the non-ferroan dolomite phase suggest that the reflux dolomite was overprinted by this second dolomitization event. Traces of exotic minerals, such as barite, chalcopyrite, galena and sulphosalts were found as fillings of vugs and fractures in the dolomite-cemented sandstone. The metals could have been sourced from the underlying Permian red sandstone beds. The heterogeneous sediment composition had profound impact on the diagenesis of these sedimentary successions.

Based on studies of the succession exposed in the Kádárta Quarry, a paper on the stratigraphy and evolution of the Middle Anisian Kádárta Platform and the overlying formations of slope and basin facies was published in the Palaeogeography Palaeoclimatolgy Palaeocology (Karádi et al. 2022). Two tuff samples were taken for isotope geochronology. The in-situ zircon U–Pb dating was performed by laser-ablation single-collector sector-field inductively coupled plasma mass spectrometry. Zircon crystals gave an age of 241.5±2.0 Ma and 237.6±1.7 Ma for the two measured samples. The biostratigraphic and radiometric ages revealed the presence of a gap between the Pelsonian (Middle Anisian) shallow-marine carbonates and the overlying deep-water succession, since the onset of pelagic sedimentation was dated as late Illyrian (latest Anisian). Based on studies of dolomitized platform carbonates in the Kádárta Quarry we re-evaluated our previous concept on the structure evolution and dolomitization of the Middle Triassic platformsin the Transdanubian Range (Haas et al. 2022). In the Middle Anisian, extensional tectonic movements led to the development of isolated carbonate platforms. One of the platform successions (Tagyon Platform) consists predominantly of limestone that contains partially and completely dolomitized intervals, whereas the other one (Kádárta Platform) is completely dolomitized. Drowning of the platforms took place in the latest Pelsonian to the early Illyrian interval when submarine highs came into existence and then condensed pelagic carbonate successions with volcanic tuff interbeds were deposited on the top of the drowned platforms from the late Illyrian up to the late Ladinian. Traces of probably microbially-mediated early dolomitization were preserved in the slightly dolomitized successions of the Tagyon Platform. This might also have been present in the successions of the Kádárta Platform, but was overprinted by geothermal dolomitization along the basinward platform margin and by pervasive reflux dolomitization in the internal parts of the platform. The Carnian evolution of the two submarine highs was different, and this may have significantly influenced the grade of the shallow to deeper burial dolomitization.

A comprehensive paper on the summarization of the study on the Upper Norian Rezi Dolomite (Keszthely Mts.) was published in the International Journal of Earth Sciences (Haas et al. 2022). Petrographic and isotope–geochemical characteristics of the Upper Triassic dolomitized carbonate deposits, formed in a fault-controlled intraplatform basin, and interpretation of the dolomite-forming processes are presented in this paper. From the latest Carnian to Middle Norian under semi-arid climatic conditions density-driven flux of seawater derived mesohaline fluids was the dominant mechanism of the near-surface pervasive dolomitization of the thick platform carbonate succession. In the late Middle Norian incipient rifting of the Alpine Tethys led to establishment of an extensional structural regime and onset of the formation of the Kössen Basin. In the study area, above the dolomitized platform carbonate succession, platform-derived carbonate sediments were accumulated in a fault-bounded, semi-restricted sub-basin of the Kössen Basin, whereas talus breccias and debrites were deposited near a basin-bounding master fault. The basin deposits (lower and upper members of the Rezi Dolomite Formation) were subject of early diagenetic dolomitization in shallow burial setting. Enhanced salinity seawater was the dolomitizing fluid; the synsedimentary fracturing may have promoted the fluid flow and thereby the dolomitization. Thick-bedded carbonates (middle member of the Rezi Dolomite Formation) representing a progradational tongue of the ambient platform are intercalated between the basin deposits. The dolomitization of this unit can be explained by the reflux model.

In the Bükk Mountains, we have completed the investigation of the Middle Triassic (Anisian) Hámor Dolomite that is the most significant dolomite formation in this region, cc. 400 m thick (Haas et al. 2024). 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.

Additionally, we completed the microfacies and dolomite petrographic investigations, geochemical measurements and fluid inclusion studies from the uppermost Anisian–Carnian Wetterstein Formation located in the Aggtelek Karst. The manuscripts on the results are under preparation. 1. *Hips et al. Facies pattern of Triassic Wetterstein carbonate platform controlled by subsurface salt-tectonics, Silica Nappe, Hungary.* This paper focuses on the sedimentary facies of the platform carbonate (Wetterstein Formation) in the Aggtelek facies area, with special regard to the microbial reef and the related lithoclastic grainstone slope facies. The study provides microfacies and stratigraphic data to the reconstruction of a refined facies model of Triassic carbonates; moreover, it intends to reveal the interrelationships among the carbonate platform development, structural geologic evolution and evaporite expulsion. This study aims to provide additional building blocks for a better understanding of the development of the Triassic platform carbonates widely distributed in the Alpine–Carpathian region, which was significantly shaped by tectonic processes. 2. *Hips et al. Diagenesis of Triassic Wetterstein carbonate platform controlled by basinal brine sourced from evaporite series, Silica Nappe, Hungary*. This paper focuses on the diagenetic alterations of the platform carbonate (Wetterstein Formation) in the Aggtelek facies area, with special regard to the dolomitization process and calcite cementation. The study provides petrographic, geochemical and fluid inclusion data from dolomitic limestone and dolomite rock bodies to the reconstruction of burial history of Triassic carbonates; moreover, it intends to reveal the interrelationships among the fluid flow, structural geologic evolution and evaporite expulsion.

We published a review paper on the history of dolomite research and the state of art of this sub-discipline internationally and in our country in the Földtani Közlöny (Haas and Hips 2020). Since the first description of dolomite, over the past two centuries there has been a great deal of progress with respect to knowledge on the genesis of this rock. Based on inferences emerging from the intense research that has taken place, relevant genetic models have been developed. It is now generally accepted that large, dolomite bodies with a wide extent were formed from lime mud or limestone via mineral replacement; furthermore, the dolomite mineral may also have been precipitated as cement in pore spaces. The paper presents the basic lithological, petrographic and geochemical characteristics of the dolomites and the commonly-applied methods for observation and measurement of the rock

properties. According to our current knowledge, it summarizes the general criteria and mechanisms of dolomitization and provides an overview of the most important dolomite-forming processes. The latter take place in various depositional environments: namely, marine and lacustrine, and diagenetic settings (for example, shallow, intermediate, and deep burial). In the second part of the article, the dolomite occurrences in Hungary are considered, along with several case studies from the dolomite-rich Transdanubian Range and Tisza Megaunit. The case studies demonstrate that every dolomite body exhibits remarkably distinct features, formed as the result of multi-stage processes. These processes are mainly determined by host-rock properties, the consecutive dolomitization processes, the evolution of local structures, and the regional geodynamical setting.