

Article

Persisting Rock-Buffered Conditions in the Upper Triassic and Lower Jurassic Dolomites of the Central Apennines (Italy) During Diagenesis, Burial, and Thrusting

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Abstract: Basin-scale dolomitization of carbonate sequences occurs over long time spans and results from diagenesis, burial, and tectonically driven fluid fluxes. Depicting the different geological processes producing dolomitized carbonate sequences requires combining accurate field, petrographic, and geochemical analyses. Here, we investigate the dolomitization processes in carbonates of the Norian to Toarcian age exposed in the Gran Sasso Massif, Central Apennines of Italy, by integrating field observations, standard and CL petrography, carbon, oxygen, strontium and clumped isotopes, minor elements, and X-ray diffractometry. The carbonates show pervasive replacive dolomitization, and dolomite cements are observed in bed-parallel and thrust-related veins. Replacive dolomites show incomplete replacement from modified seawater in oxidizing conditions, with minimum temperatures of 40–65 °C and a ⁸⁷Sr/⁸⁶Sr lower than coeval seawater. The first dolomitization event started at shallow burial in the Late Triassic–Early Jurassic and was later affected by replacement at intermediate burial depths. Bedding-parallel dolomite veins crystallized due to fluid overpressures at deep burial depths in a rock-buffered system without variations in geochemistry. Fault-related dolomites cemented thrust-related fractures during compressional deformation in the Messinian–Early Pliocene from seawater modified by mixing with external fluids. Precipitation temperatures of replacive, bedding-parallel, and fault-related dolomite veins are similar. Despite the dolomite types being characterized by different textures and petrographic features, rock-buffered conditions resulted in insignificant variations of their geochemical properties.

Keywords: dolomitization; clumped isotopes; rock-buffered conditions; seawater dolomitization; periadriatic platform



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1. Introduction

Dolostones host 80% of hydrocarbon resources in carbonate rocks worldwide and are excellent exploration targets because of their higher fracture permeability compared to limestones [1–4]. The porosity distribution in dolomitized carbonates is related to the host rock's

genetic mechanism that promoted dolomitization, which can be understood by detailed field-work coupled with geochemical analyses. For this reason, many studies in the last half century focused on the study of the conditions and mechanisms of dolomitization by integrating stratigraphic and structural analysis, petrography, mineralogy, fluid inclusion, minor and trace elements, carbon, oxygen, strontium stable isotopes, and other geochemical analytical methods to document the spatial distribution, textures, paragenetic sequence of dolomites, the dolomitizing fluid composition, and their temperature with the aim of understanding the dolomitizing fluids' origin and the dolomitization mechanism ([5–17] and many others).

However, dolostones are frequently the result of multiple and complex dolomitization processes. The geochemical signature of early diagenetic dolomites, which often represent the most volumetrically abundant dolomite type, are obliterated by the replacement of low-temperature, metastable dolomites into stable, higher-temperature dolomites during increasing burial [3,18–20]. Dolomite replacement does not change the overall mineralogy, but produces modification of crystallographic, physical, and geochemical properties. Each of these properties can be significantly altered during the process, or they can retain the geochemical signature of the previous dolomitization event [21]. Quantifying which and how much of these properties has been altered is of utmost importance for the interpretation of the dolomitizing fluid and dolomitization mechanism [22–25].

Fluid inclusion microthermometry remains the only methodology to directly measure the dolomitizing fluid precipitation temperature and salinity. Moreover, it allows for a detailed sequence of the thermal conditions and, in cases, to infer the pressure during precipitation [16,26,27]. Nevertheless, microthermometry is not always the best solution in the study of the dolomitizing fluid's properties. In particular, the analysis of highly fractured rocks characterized by small, necked, and decrepitated inclusions with precipitation temperatures below $\sim 50\text{ }^{\circ}\text{C}$ is tedious, time-consuming, and can lead to erroneous interpretations. A viable alternative consists of clumped isotope thermometry, which has been applied in recent decades to carbonates precipitated at low temperatures (less than $\sim 300\text{ }^{\circ}\text{C}$ for dolomites [28]), where solid-state reordering of C–O bonds should be negligible. Despite dolostones being prone to replacement processes, clumped isotope thermometry represents a promising analytical tool to quantify the precipitation temperature, the $\delta^{18}\text{O}$ of dolomites, and the $\delta^{18}\text{O}$ of the dolomitizing fluids. Moreover, clumped isotope thermometry can be useful in assessing dolomite replacement. Specifically, geochemical modelling proves that replacement at increasing temperatures results in a higher apparent $\delta^{18}\text{O}$ fluid at low water to rock ratios. The apparent $\delta^{18}\text{O}$ fluid is increasingly different from the real $\delta^{18}\text{O}$ of the fluid at increasingly lower water to rock ratios [23,24,29].

Here, we document (i) the dolomitizing fluid properties, and we aim to define the (ii) timing and (iii) genetic mechanisms of dolomitized carbonates outcropping in the Central Apennines thrust and fold belt that underwent a tectonic evolution from passive margin deposition, burial, and uplift during compressional deformation and thrusting. Moreover, we aim to answer to the following questions: (a) Which carbonates preserve the geochemical signature of early dolomitization and which have been modified by replacement? (b) In recrystallized dolomites, which geochemical properties have been significantly modified and which have not? For this purpose, we selected the Upper Triassic to Lower Jurassic succession of the Gran Sasso Massif, in the Central Apennines of Italy, where dolostones show unequivocal evidence of early and late dolomitization events. Dolomitization processes have been studied in other Mesozoic carbonates in the Central and Southern Apennines without integrating clumped isotope thermometry [11–14,30]. By integrating field observations with petrographic and geochemical analyses, we study different dolomite textures, which are characterized by similar geochemical properties, specifically insignificant changes in the clumped isotope thermometry and stable isotope geochemistry of the studied dolomite types,

which are invariably characterized by precipitation temperatures from 40 °C to 65 °C and $\delta^{18}\text{O}$ of the dolomitizing fluids from +3‰ to +5‰ V-SMOW. The dolomite types include replacive (R), bedding-parallel vein (Z), and fault-related vein and breccia (F) dolomites. Replacive dolomites were formed at shallow depth in the Late Triassic–Early Jurassic and were affected by replacement from Sinemurian–Pliensbachian seawater during increasing burial in the Jurassic. Bedding-parallel dolomite veins formed at deep burial depths in rock-buffered conditions. Fault-related dolomites precipitated in thrust-related fractures and breccias during Late Miocene contractional deformation in persisting rock-buffered conditions; however, some fault-related dolomites document the contribution of higher-temperature, external fluids.

In this contribution, we document how rock-buffered conditions impact the potential of geochemical analyses in the characterization of dolomitizing fluid geochemistry and the precipitation temperature of dolomite. On the other hand, rock-buffered conditions allowed for the preservation of the geochemical signatures of dolomite replacement and, locally, of early diagenetic dolomitization. Despite the increasing availability of analytical tools with higher resolution, we observe the necessity of detailed fieldwork and petrographic characterization of dolomite types beyond the knowledge of the regional stratigraphic architecture and structures. These are the fundamentals for constraining the age, depth, and timing of dolomitization and for correctly interpreting the genetic mechanisms.

2. Geologic Setting

2.1. Central Apennines

The Apennines fold and thrust belt formed in response to the westward subduction and related slab rollback of the Adria microplate below the European plate since the Miocene [31–34]. Progressive eastward migration of deformation resulted in the thrusting and folding of the Adria passive margin, whose sedimentary cover consists of Upper Triassic dolostones and Jurassic to Miocene shelf to pelagic limestones (Figure 1a,b). On top of the Adria passive margin succession, synorogenic siliciclastic sediments were deposited in eastward-younging foredeep systems that constrain contractional deformation to the Messinian in the Gran Sasso Massif (Figure 1b,c) [35–39].

The oldest sedimentary units exposed in the Gran Sasso Massif are in the Carnian–Norian Dolomie Bituminose Fm., which were deposited in pull-apart basins characterized by hyperhaline, eutrophic fault-bounded basinal environments, associated with left-lateral strike-slip fault systems. The overlying Dolomia Principale Fm. was deposited in the extensive peritidal shelf environment occurring over Adria in Norian and Rhaetian (Figure 1d) [40–42]. Extensional tectonics eventually resulted in the rifting of the Ligurian–Piedmont Neotethys that induced subsidence of the northern part of Adria and the break-up of the peritidal platform into fault-bounded subtidal platforms (e.g., Lazio–Abruzzi platform in the Gran Sasso area indicated with G.S. in Figure 1e) and basins throughout the Jurassic (Figure 1e) [43–45]. The Calcare Massiccio Fm. represents the Lower Jurassic platform deposits, and the Corniola Fm. was later deposited over the drowning platform carbonates of the Calcare Massiccio Fm. Deposition was later characterized by a passive margin sequence, which lasted until the onset of Neogene compression.

Based on vitrinite reflectance data, it has been estimated that the Dolomie Bituminose Fm. has been buried up to ca. 4 km under a low geothermal gradient of about 20 °C/km, therefore reaching maximum temperatures of around 100 °C [46,47]. Upper Triassic and Lower Jurassic carbonates in the Central and Southern Apennines underwent dolomitization at the regional scale, and locally, multiple dolomitization events are documented. Early diagenetic dolomitization occurred from seawater evaporation, seepage reflux and/or convection, while tectonically induced pore water migration and hydrothermal fluids caused late dolomitization during burial [11–14,30].

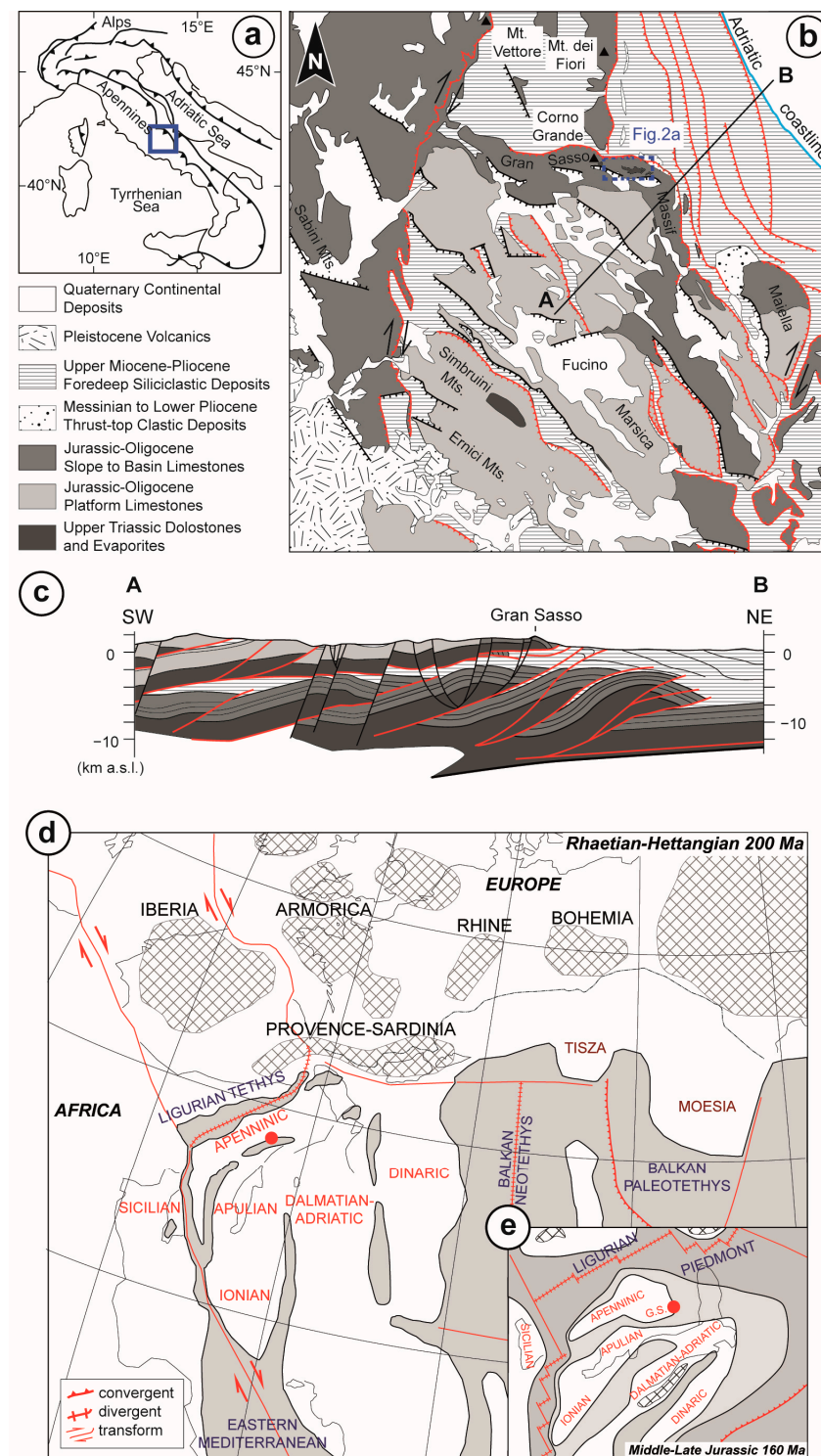


Figure 1. (a) Schematic map of Italy indicating the Central Apennines with blue rectangle. (b) Simplified map illustrating the major structures (extensional faults in black and thrust faults in red) and lithostratigraphic domains of the Central Apennines; blue rectangle corresponds to the area shown in Figure 2. (c) Geologic cross-section AB from the inner thrust and fold belt in the SW to the outer foredeep in the NE of the Central Apennines; the solid black line on the right of the section at the bottom of the sedimentary cover represents the top basement of Adria. (d) Paleogeography of the Mediterranean area at the Triassic–Jurassic boundary highlighting the regions composing the epicontinental platform of Adria (written in red) red lines represent plate margins explained in the inset in the lower left corner; ocean basins are written in blue and emerged massifs are shown by hatched areas. (e) Detail of (d) over Adria in the Late Jurassic (modified after [48]).

2.2. Structure of the Gran Sasso Massif

Miocene compression in the Gran Sasso Massif resulted in an open wedge-shaped thrust stack composed of a N105°- and a N170°-directed segment. Thrusting and folding occurred during Messinian–Early Pliocene times in the study area [35,49], which is located along a 13 km stretch between Vado di Corno to the west and Mt. Camicia to the east, belonging to the N105°-striking segment (Figure 2a). Dolostones are juxtaposed in three tectonic units in the middle of the thrust stack, specifically in the hanging wall of the Vado di Corno, Mt. Prena, and Vado di Ferruccio thrust faults (Figure 2b) [38,39]. These tectonic units are composed of the following, from the top to the bottom: (1) dolomitized Calcare Massiccio Fm.; (2) Dolomia Principale Fm.; and (3) Dolomie Bituminose Fm. and Dolomia Principale Fm. On the westernmost part of the transect, another thrust (top left corner of Figure 2b,c) juxtaposes the dolomitized Corniola Fm. with the dolomitized Calcare Massiccio Fm. The simplified geologic section illustrated in Figure 2d runs along the water divide and shows the projected locations of the samples. This section highlights the lateral relationships between the tectonic units hosting the investigated dolostones. The following three sections have been studied: Mt. Camicia, Mt. Prena, and Vado di Corno (Figure 2e,f).

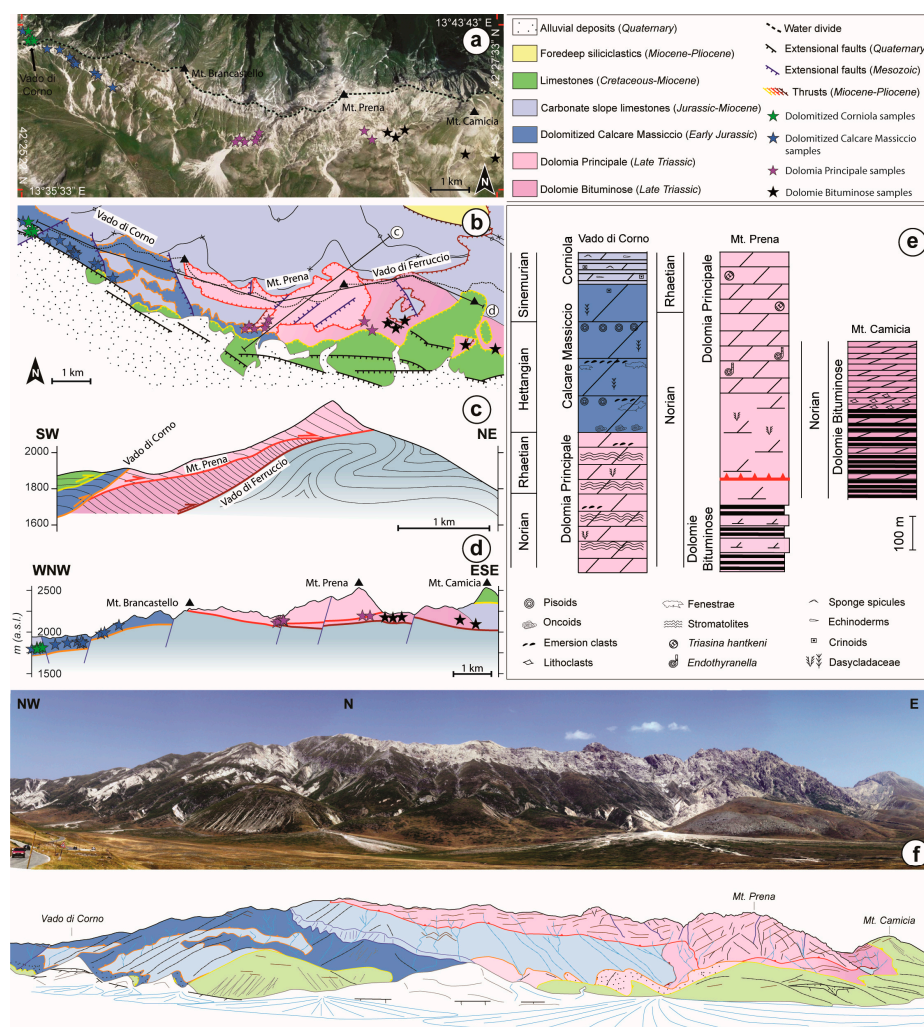


Figure 2. (a) Google Earth image and (b) simplified geologic map of the study area from Vado di Corno pass in the W to Mt. Camicia in the E (simplified from [50]). Stratigraphy, structure, and samples are explained in the legend on the top right of the figure. (c–d) Geologic cross-sections illustrating the thrust-bounded tectonic slices. (e) Simplified logs of the Corno Grande, Mt. Prena, and Mt. Camicia. Synthesis of the stratigraphic and facies analyses from [51–53]. (f) Panoramic view and linedrawing of the study area roughly parallel to the section shown in (d).

2.3. Stratigraphy of the Studied Sections

The Upper Triassic stratigraphy of the study area includes the Dolomie Bituminose Fm. (Carnian–Norian) mudstones rich in organic matter, deposited in a proximal anoxic basin and the Dolomia Principale Fm. (Norian–Rhaetian) intertidal dolostones that were deposited in a shelf lagoon environment. Lateral facies transitions between the Dolomia Principale Fm. and Dolomie Bituminose Fm. have been documented to the south of Mt. Prena and have been interpreted as evidence of a fault-controlled transition between a shelf environment, in the western part, and a slope to a proximal basin (Mt. Camicia) to the east (indicated with shading in the tectonic unit to the south and east of Mt. Prena in Figure 2b–f) [51,52]. The Lower Jurassic stratigraphy includes the Calcare Massiccio Fm. (Hettangian–Sinemurian) shallow water carbonates deposited in a fault-bounded, shelf interior tidal flat environment and the Corniola Fm. (Sinemurian–Toarcian) thin-bedded carbonates recording the transgression and progressive drowning of the shelf [54,55]. The Calcare Massiccio Fm. and Corniola Fm. outcropping in the study area are completely dolomitized (Figure 2e,f).

In the Mt. Camicia section, 500–600 m of Dolomie Bituminose is exposed. The lower part of the stratigraphic succession is composed of mudstones with abundant bituminous layers with fluid escape and slump structures. Moving upwards, dolostones are characterized by dolomite lithoclasts and blocks in finely laminated mudstones. The Mt. Prena section includes 100–200 m of Dolomie Bituminose Fm., tectonically overlaid by the Dolomia Principale Fm. The latter has a thickness of 800 m in this section, of which the lower part is massive and the upper part is stratified. The Vado di Corno section is characterized by 600 m of well-stratified peritidal cycles of Dolomia Principale Fm. The depositional environment is interpreted as a tidal flat. The succession is then formed by 600 m of dolomitized Calcare Massiccio Fm.

3. Methods

Dolomites were sampled in 31 sites across the study area, and 85 thin sections were obtained. Petrographic optical analysis was performed using a Zeiss® Axioplan 2 microscope (Jena, Germany). Cold cathodoluminescence microscopy was performed using a Technosyn® 8200 Mark II cold CL stage (Barbara, CA, USA), mounted on a LEICA® DM2700P optical microscope (Wetzlar, Germany), at a 10 kV and 256 kV gun current at the University of Parma.

3.1. X-Ray Diffraction Analyses

The stoichiometry and crystal order of 36 dolomite samples were investigated using a Bruker® D2 Phaser X-Ray Diffractometer (Billerica, MA, USA). Operating conditions are 45 kV and 40 mA, angular range from 15° to 70°, step size of 0.018 °2 θ , and a counting time of 1 s for a total of 46 min acquisition time. A graphite secondary monochromator was used to minimize background noise. XRD scans were analyzed with the software DIFFRAC.SUITE EVA (2018) and fitted by pseudo-Voigt functions. K α 2 background contributions were removed and resulting peak profiles were corrected with the internal standard of silica, with the main peak (111) at 28.44 °2 θ . The Ca content of the crystal lattice was determined by the position of the main dolomite peak $d_{(104)}$. The degree of order R was derived by the intensity ratio of the dolomite peaks $d_{(015)}$ and $d_{(110)}$ [56,57].

3.2. Minor Elements Analyses

Twenty-seven samples of specific dolomite types were hand drilled from polished rock slabs and were analyzed for Mg, Fe, Sr, Mn, and Ba using an inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer® Optima 4200 DV, Thane, India) at the Department of Chemical and Geological Sciences of the University of Modena and Reggio Emilia. Ten milligrams of powder was repeatedly washed with MilliQ® water (Darmstadt, Germany), dried, and dissolved in 1N HNO₃. After centrifugation, the supernatant was transferred and diluted with MilliQ® by a factor of 10 to a 4% nitric acid solution for Fe, Sr, and Ba analyses. An aliquot of this solution was further diluted by a factor of 100 to measure Mg. All diluted acids were prepared from ultrapure 16N HNO₃ SEASTAR® (Sidney, BC, Canada). The ICP-OES system was externally calibrated with multi-elemental calibration standard solutions. It was operated with an RF power of 1.4 kW, a plasma gas flow of 15 L min⁻¹, an auxiliary gas flow of 0.2 L min⁻¹, and a nebulizer gas flow of 0.6 L min⁻¹. Detection limits are 1 ppb for Sr, Mn, and Ba, and 5 ppb for Fe and Mg. Each of the twenty-seven samples and the standard solutions as unknowns were analyzed in three replicates and precision was better than 5% RSD (relative standard deviation) for Mg, Sr, and Fe, and better than 20% for Mn and Ba.

3.3. Carbon and Oxygen Isotopes Analyses

Stable isotope ratios are expressed in δ -notation relative to the V-PDB (Vienna Pee Dee Belemnite). Two hundred and sixty-six sub-samples of selected dolomite types were drilled directly from thin sections with an ESI® New Wave Research Micromill (Omaha, NE, USA). Approximately 150–200 μ g of carbonate powder for each sample was loaded into a GasBenchII autosampler interspaced with standard reference materials (NBS18, NBS19, and MAB99). After helium flushing, 100% orthophosphoric acid was added at 25 °C and reacted at a constant temperature of 72 °C. Oxygen isotope compositions were corrected according to the acid fractionation factors given by [58]. Resulting gasses were analyzed automatically using a Thermo Finnigan® Delta V+ mass spectrometer (Somerset, NJ, USA) at the Department of Life Sciences of the University of Parma. Each sample was analyzed twice, and data uncertainty is $\pm 0.10\%$ for $\delta^{13}\text{C}$ and $\pm 0.15\%$ for $\delta^{18}\text{O}$.

3.4. Carbonate Clumped Isotope Thermometry

Nine hand-drilled dolomite samples from polished rock slabs were prepared for clumped isotope analysis. The clumped isotope compositions of the carbonates were determined at ETH Zürich using a Thermo Fisher Scientific® MAT253 mass spectrometer (Waltham, MA, USA) coupled to a Thermo Fisher Scientific® Kiel IV carbonate preparation device, following the method described by [59–61]. A PoraPakQ trap kept at $-40\text{ }^{\circ}\text{C}$ to eliminate potential organic contaminants is included in the device. Prior to each sample run, the pressure-dependent backgrounds were determined on all beams to correct for non-linearity effects in the mass spectrometer according to [62]. During each run, three 95–110 μ g aliquots of different samples, five aliquots of the carbonate standards ETH-1 and ETH-2, and ten aliquots of the standard ETH-3 were analyzed using the LIDI method [61]. Ten replicates for each sample were measured over a period of 3 weeks to avoid biases owing to short-term variations in the performance of the instruments. Data processing was conducted with the software Easotope (2021) [63]. The results are reported in the I-CDES scale [64]. Temperatures were calculated using the [65] calibration. The uncertainty in temperature is reported at the 95% confidence level. The $\delta^{18}\text{O}$ of the fluid and precipitation temperature were calculated from the Δ_{47} using the equations proposed by [66].

3.5. Strontium Isotope Analyses

The whole procedure was conducted in a clean laboratory under a laminar flow hood, with a typical Sr blank < 100 pg. Strontium isotope ratios were measured by MC-ICP-MS (Thermo Scientific® Neptune, Waltham, MA, USA) at the Department of Chemical and Geological Sciences of the University of Modena and Reggio Emilia. Twenty samples of dolomite (10–50 mg) were prepared by drilling rock slabs. The samples were rinsed three times with MilliQ® water. After drying, each sample was leached two times using a solution of 0.3% *w/w* acetic acid to sequentially dissolve about 30% and 40% of the powdered material, following the procedure described by [67,68]. The Sr isotope composition of a sample is considered to be that of the second leaching step. To also evaluate the Sr isotope composition of the loosely bonded Sr fraction, in two samples, the solutions from three leaching steps were analyzed (30%, 40%, and 30% of the powdered material). Solutions were then dried and dissolved in 3M HNO₃. Sr was separated from the matrix by ion exchange chromatography following procedures reported by [69]. Solutions were diluted to ~50 ppb and introduced into the Neptune using a Elemental Scientific® (Omaha, NE, USA) desolvating system (ESI-APEX IR) and a 100 µL min^{−1} nebulizer. Samples and standards were analyzed in a static multicollection mode in a single block of 100 cycles with an integration time of 8.4 s per cycle. Mass bias normalization was performed using the exponential law and a ⁸⁷Sr/⁸⁶Sr ratio of 8.37520. Isobaric interferences of ⁸⁶Kr and ⁸⁷Rb on ⁸⁶Sr and ⁸⁷Sr species were corrected. The ⁸⁷Sr/⁸⁶Sr ratio was corrected for instrumental bias to an NBS-987 value of 0.710248 [70]. Repeated measurements of the NBS-987 standard yielded a mean ⁸⁷Sr/⁸⁶Sr value of 0.710233 ± 0.000014 (2SD, n = 19).

4. Results

4.1. Field Observations

The dolostones far from thrust faults preserve most of their depositional structures, despite being locally affected by intense fracturing (Figure 3). The dolomitized Corniola Fm. (Co Fm.) is composed of thin-bedded, dark-coloured mudstones and subordinate wackestones, locally hosting abundant chert nodules (Figure 3a). The dolomitized Calcare Massiccio Fm. (CM Fm.) consists mostly of fenestral, oncoidal, and foraminiferal packstones and grainstones, including subordinate wackestones (Figure 3b). The Dolomia Principale Fm. (DP Fm.) consists of massive, thick beds, although in the upper part of the exposed succession thin-laminated packstones and wackestones occur (Figure 3c). The Dolomie Bituminose Fm. (DB Fm.) appears as a well-stratified sequence of laminated, organic matter-rich, fine-grained dark grey dolostones (Figure 3d). All the formations in the study area are crosscut by bedding-parallel dolomite veins (Figure 3e,f), especially in the upper part of the DP Fm. and in the dolomitized CM Fm. Bedding-parallel dolomite veins are scattered throughout the study area and are generally parallel to sedimentary lamination. They locally occur in closely spaced clusters alternating with bedding-parallel stylolites (Figure 3f). Thrust faults are composed of brittle cataclastic fault rocks in the DP Fm. and CM Fm. and foliated gouges with S–C structures in the DB Fm. and Corniola Fm. (Figure 3g). Younger dolomite veins occur in thrust fault damage zones, forming metre-thick crackle to mosaic breccias that crosscut or re-open and cement both bedding-parallel dolomite veins and stylolites (Figure 3h).

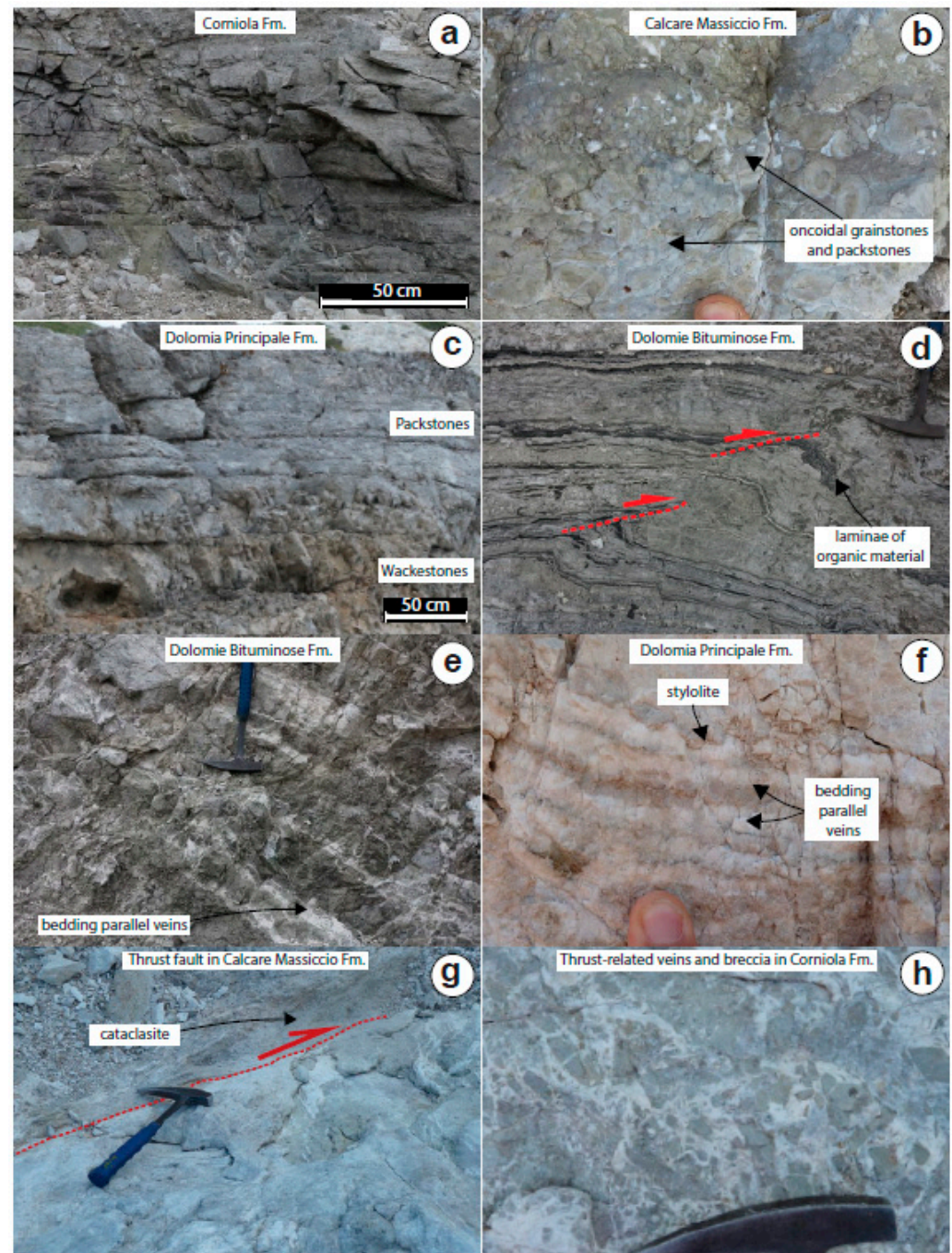


Figure 3. (a) Field image of thin-bedded mudstones of the dolomitized Corniola Fm. (b) Detail of low-porosity oncoidal grainstone/packstone showing interparticle dolomite cement; finger for scale. (c) Relatively undeformed wackestones and thin-bedded packstones of Dolomia Principale Fm. (d) Field image of finely laminated, organic matter-rich Dolomie Bituminose Fm. (e) Outcrop picture of bedding-parallel dolomite veins and crackle breccia pockets in well-laminated organic-rich Dolomie Bituminose Fm. (f) Detail of bedding-parallel dolomite vein cluster overprinted by stylolites in the Dolomia Principale Fm. (g) Field photographs of thrust fault in the Calcare Massiccio Fm. and (h) related dolomite veins and crackle to mosaic breccias adjacent to the thrust fault in the Corniola Fm; dotted red lines represent fault surfaces and the red arrows indicate kinematics.

4.2. Microfacies Classification

Host rock samples have been classified into standard microfacies types [71] to infer their depositional environments (Table 1). The DB Fm. is composed of finely laminated mudstones and wackestones, rich in organic material in the lower part of the succession

and in chert nodules in the upper part (Figure 4a; SMF1 and SMF3). These facies types are composed of dolomicrosparites and have no fossil content in the analyzed thin sections. The DB Fm. includes microbioclastic peloidal wackestones, lithoclastic wackestones, and breccias in the middle part of the succession to the west of Mt. Camicia (Figure 4b,c; SMF2 and SMF4). Breccias are composed of lithoclasts showing different dolomite crystal sizes derived by the erosion of finely laminated facies types. The DP Fm. is composed of massive dolostones with mostly fabric-destructive dolomite with planar-s to non-planar crystals; nonetheless, massive dolostones include whole assemblages of dasycladacean algae. Massive dolostones also include packstones with coated grains. The DP Fm. in the samples to the west of Mt. Prena is composed of foraminiferal packstones/grainstones with *Triasina hantkeni* and *Griphoporella curvata* (Figure 4d–f; SMF8, SMF11, and SMF18). The CM Fm. consists of laminated packstones and wackestones with fenestrae, stromatolitic laminations, and clotted peloid micrite textures such as *Cayeuxia* in the western Vado di Corno area, including oncoidal dolomicrosparites with planar-e to planar-s texture (Figure 4g,h; SMF8). The CM Fm. is also composed of fenestral packstones with textularidae, other foraminifera, and oxidized lithoclasts (Figure 4i; SMF19; SMF20; SMF21; SMF22; SMF23; and SMF24). The Co Fm. is mostly represented by dolomicritic, peloidal, bioturbated wackestones with sponge spicules, echinoderms, crinoids, and ostracods (Figure 4j,k). The Co Fm. is locally affected by fabric-destructive dolomitization, microcrystalline quartz, and oxide cementation (Figure 4l).

Table 1. Summary of the microfacies and interpreted depositional environments in the analyzed samples.

Facies Code	Facies Association	Facies Type	Formation	Depositional and Diagenetic Features	Depositional Environment
SMF1	Marine	Spiculite wackestone	Corniola	Co: dolomicrite, late calcite, quartz, oxides; sponge spicules, crinoids.	Intra-shelf basin
SMF2	Marine	Microbioclastic peloidal calcisiltite	Corniola Dolomie Bituminose	Co: dolomicrite, local bioturbation, peloids, late calcite, quartz, oxides; sponge spicules, echinoderms, crinoids. DB: dolomicrite with peloids, late quartz.	Intra-shelf basin
SMF3	Marine	Pelagic wackestone	Dolomie Bituminose	DB: non-fossiliferous, organic matter-rich, finely laminated dolomite.	Intra-shelf basin
SMF4	Slope	Microbreccia, clastic packstone	Corniola Dolomie Bituminose	Co and DB: Sedimentary breccias composed of dolomite lithoclasts and dolomicrite cement.	Slope
SMF5	Slope	Allochthonous bioclastic packstone	Corniola	Co: dolomicrite; echinoderms, crinoids, bivalves, ostracods.	Slope
SMF8	Subtidal	Whole fossil wackestone	Dolomia Principale	CM: dolomicritized algae thallii. DP: dolomicrite; cortoids, foraminifera.	Lagoon
SMF11	Subtidal-intertidal	Coated bioclastic grainstone	Dolomia Principale	Fabric destructive dolomite with preserved dasycladacean algae	Lagoon-tidal flat
SMF18	Subtidal	Packstone with abundant algae and foraminifera	Dolomia Principale	Fabric destructive dolomites; <i>Triasina Hantkeni</i> , Endothyridae, peloids, other foraminifera.	Lagoon
SMF19	Subtidal-intertidal	Densely laminated bindstone	Calacare Massiccio	Laminated dolomicrite; cyanobacteria; crinoids	Lagoon-tidal flat
SMF20	Subtidal-Intertidal	Laminated stromatolitic bindstone	Calacare Massiccio	Laminated dolomicrite; cyanobacteria; thrombolithic structures.	Tidal flat
SMF21	Supratidal-Intertidal	Fenestral bindstone/packstone	Calacare Massiccio	Laminated dolomicrite; cyanobacteria; thrombolithes; fenestrae; peloids.	Tidal flat
SMF22	Intertidal	Oncoid packstone	Calacare Massiccio	Laminated dolomicrite; oncoids, fenestrae.	Tidal flat
SMF23	Supratidal-Intertidal	Non-fossiliferous micrite	Calacare Massiccio	Homogeneous dolomicrite; peloids.	Tidal flat
SMF24	Intertidal	Lithoclastic packstone	Calacare Massiccio	Laminated dolomicrite; fenestrae, oncoids, oxidized pelletoids, cortoids, algae fragments, siphonvalvulinae, other foraminifera.	Tidal flat

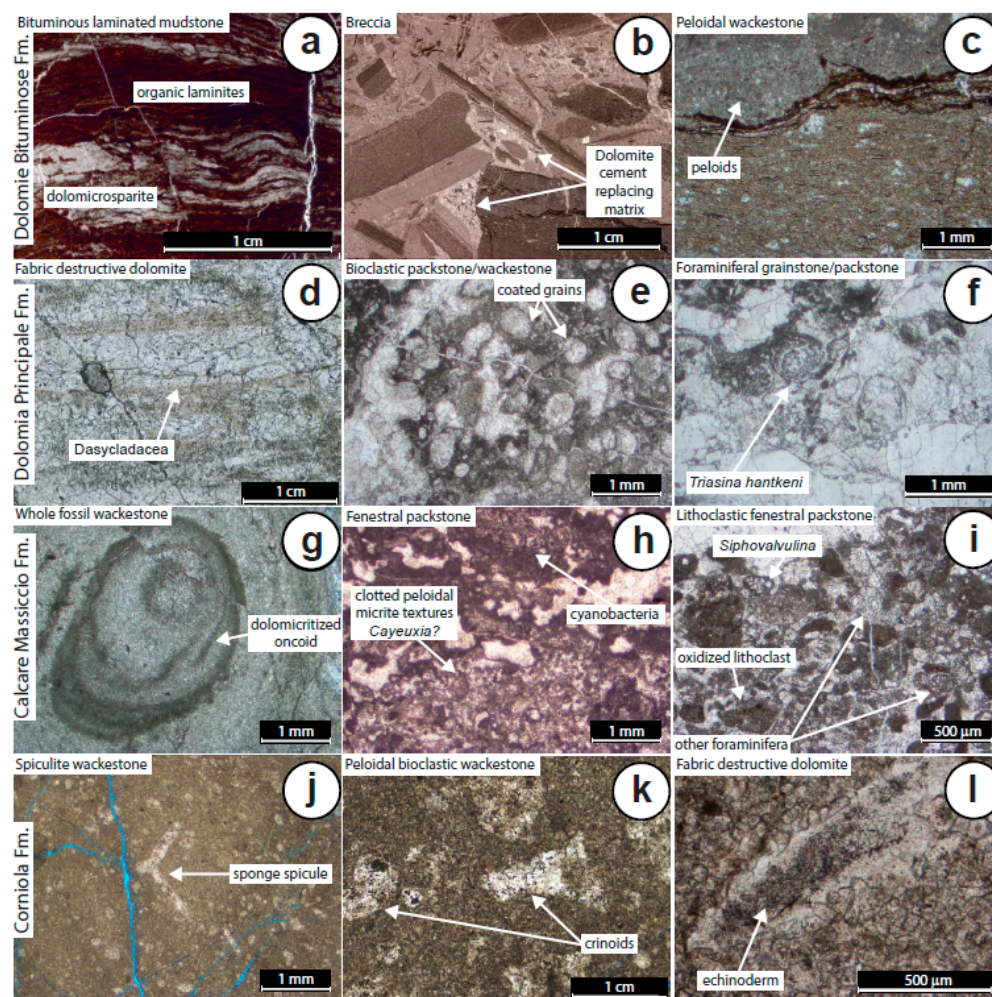


Figure 4. Microphotographs in transmitted light of the analyzed samples showing selected microfacies and microfossils. (a) Organic matter-rich, finely laminated dolomite mudstone in DB Fm.; SMF3. (b) Sedimentary breccia with finely laminated dolomicritic lithoclasts in DB Fm.; SMF4. (c) Finely laminated peloidal and cherty wackestone with organic material-rich wavy lamina in DB Fm.; SMF2. (d) Fabric-destructive planar-s dolomite with preserved habit of dasyclads in DP Fm.; SMF11. (e) Coated grains in packstone/wackestone in DP Fm.; SMF8. (f) Foraminiferal packstone/grainstone replaced by planar-s dolomites including abundant foraminifera in DP Fm.; SMF18. (g) Micritized oncolite in wackestone in CM Fm.; SMF8. (h) Fenestral packstone with clotted peloidal fabric in CM Fm.; SMF21. (i) Lithoclastic fenestral packstone lamina including textulariidae, dasycladads, oxidized clasts, and other foraminifera in CM Fm.; SMF24. (j) Wackestone with sponge spicules in Co Fm.; SMF1. (k) Peloidal bioclastic wackestone with fragments of crinoids in Co Fm.; SMF1. (l) Preserved echinoderm fragment in planar-s fabric-destructive dolomite in Co Fm.; SMF2.

4.3. Petrography of Dolomite Types

Below, we describe in detail the petrography of dolomites, in the wall rock, in bed-parallel veins, and in the thrust-fault-related veins. We then sum up the main petrographic characteristics of the three main dolomite types identified.

The DB Fm. is composed of replacive planar-s and planar-e dolomicrosparticles, reaching locally 150–200 μm with intercrystalline clays and organic matter, and showing non-dull to dull purple luminescence with rare dull orange dolomite crystal nuclei, dolomite textures of [72]. Bed-parallel stylolites crosscut this type of replacive dolomite. The cement of bedding-parallel veins in the DB Fm. is composed of coarse planar-s dolomites, non-luminescent to dull purple, with a blotchy pattern (Figure 5a,b). Fault-related dolomite cements are planar-s to non-planar, and have dull purple to dull red luminescence.

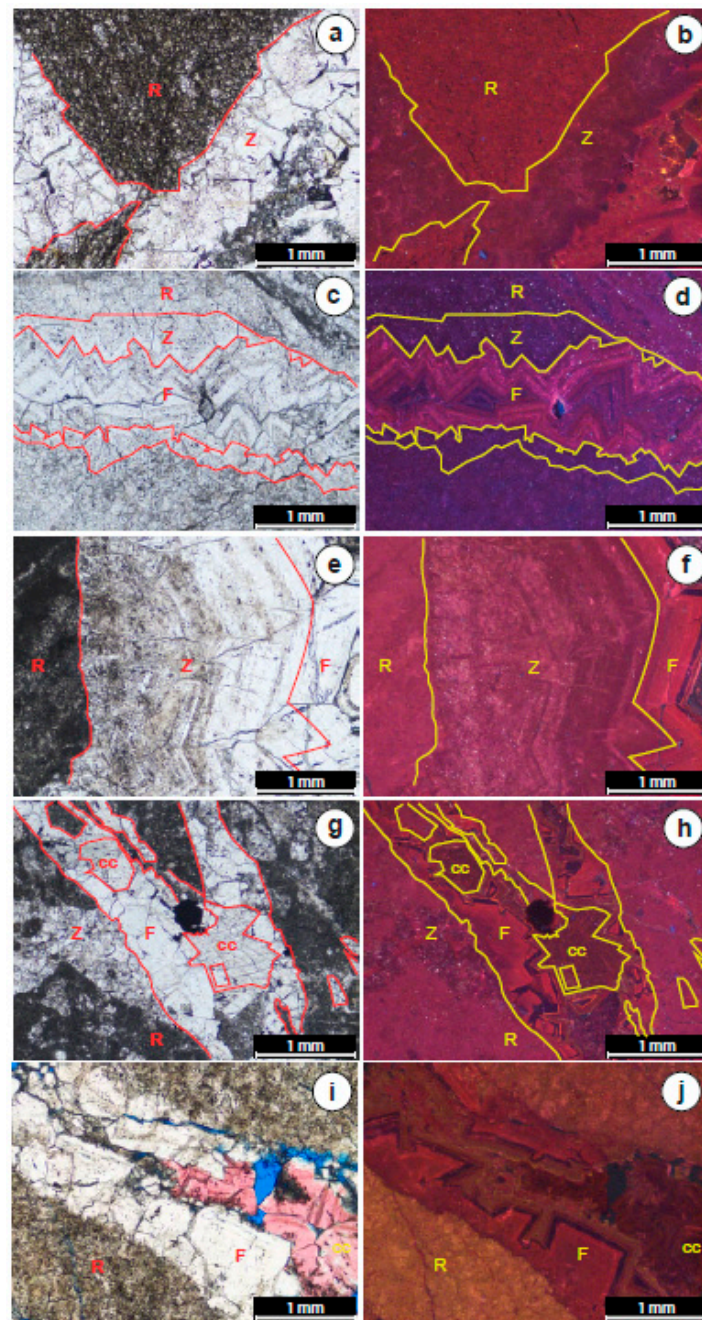


Figure 5. Selected microphotographs in PPL and CL. CL images are shown with over-exposed luminescence to highlight the paragenetic phases. (a,b) Bedding-parallel dolomite veins in Bituminous Dolostones Fm. showing fine planar-e replacive dolomites (R) in the host rock and a cement composed of coarse dolomite crystals (Z), locally saddle. Both are non-luminescent in CL. (c,d) Bedding-parallel dolomite veins in the Dolomia Principale Fm. showing optical continuity of coarse dolomite cement crystals (Z) with replacive, planar-s, fine to medium dolomite (R) of the host rock. Both are non-luminescent. Outer growth, fluid inclusion-rich zones are dull purple luminescent in CL (F). (e,f) Dolomite vein in the Calcare Massiccio Fm. The host rock shows a fine replacive dolomicrite (R). The dolomite vein cement has a fine crystal size and is solid inclusion-rich at the vein margin and becomes progressively solid inclusion-poor and characterized by larger crystal size (Z), both are dull to non-luminescent. The outer growth zones are saddle-shaped and red luminescent in CL (F). (g,h) Thrust-related vein in the Calcare Massiccio Fm. Replacive dolomites are dolomicrites and planar-s, fine-grained, dolomite crystals (R) and are non-luminescent in CL. The vein is cemented by saddle-shaped dolomite crystals with red and thin green-to-yellow growth zone luminescence (F), which is followed by iron sulphides/oxides and late non-luminescent calcite cement (cc). (i,j) Thrust-related vein in the Corniola Fm. The host rock is

characterized by fabric-destructive dolomites with slight green to yellow luminescence in CL (R). The vein cement is composed of dolomite crystals with red luminescence in CL and outer greenish growth zones (F), followed by late non-luminescent calcite cement (cc).

The DP Fm. is characterized by replacive, planar-s to non-planar, fine to coarse (50 to 500 μm), non-luminescent dolomite crystals. Fine, planar-s, replacive dolomites are crosscut by stylolites in the DP Fm., while non-planar, coarse, replacive dolomites crosscut bed-parallel stylolites (Figure 6a). The vein cement is composed of non-planar to planar-s coarse dolomites, with syntaxial growth showing alternating fluid inclusion-rich and -poor growth zones, optical continuity, and aggradational crystallization over replacive dolomites (Figure 5c,d). Both replacive dolomites and dolomite vein cements are non-luminescent. The younger dolomite cement in bedding-parallel veins is composed of planar-s to saddle-shaped dolomites with alternating non-luminescent and dull purple growth zones (Figure 5c,d).

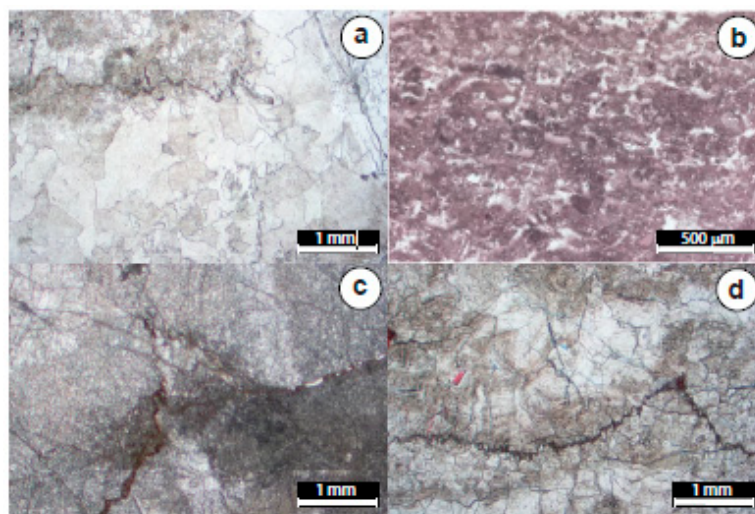


Figure 6. (a) Transmitted light (TL) microphotograph showing stylolite in Dolomia Principale Fm. crosscutting fine replacive dolomites, whereas stylolite is overprinted by coarse dolomite crystals. (b) Thin section scan of fenestral-laminated lithoclastic peloidal wackestone with fenestrae cemented by dolomite with increasing crystal size towards the top of the section. (c) Stylolite-crosscutting replacive dolomicrosparites in the Calcare Massiccio Fm. (d) Stylolite associated with and parallel to bedding-parallel veins in the Corniola Fm.

The CM Fm. is mostly composed of mimetic dolomicrosparites. Replacive, planar-s dolomites rarely exceed 300 μm crystal size, mostly as intergranular cements and in fenestral cavities. Fenestral packstones are characterized by dolomite cemented fenestrae, showing decreasing crystal size towards the bottom, followed by larger equant to blocky dolomite crystals (Figure 6b). Replacive dolomites are non-luminescent to dull purple. Stylolites crosscut dolomicrosparites and replacive dolomites (Figure 6c). Bedding-parallel vein dolomites are planar-s to saddle-shaped, showing increasing crystal size along with decreasing fluid inclusion concentration moving away from vein walls, and are characterized by the same luminescence of replacive dolomites (Figure 5e,f). Dolomite cements in thrust-fault-related veins are characterized by planar-e to planar-s, locally saddle-shaped dolomites with the following luminescence sequence: red, yellow, non-luminescent, dull purple, and green. The latter are locally followed by iron sulphides/oxides and non-luminescent calcite (Figure 5g,h).

The Co Fm. is mostly characterized by replacive mimetic dolosparites and dolomicrites but fabric-destructive, planar-s dolomite crystals of up to 300–400 μm also occur. Dolomicrites are dull yellow and fabric-destructive dolomites are dull purple. Both are crosscut by stylolites (Figure 6d). Bedding-parallel veins are composed of planar-s, locally

non-planar coarse dolomite crystals with syntaxial growth and luminescence comparable to the replacive dolomites. Thrust-related veins in the Co Fm. are composed of planar-e to planar-s, locally saddle-shaped dolomite crystals with red, yellow, non-luminescent, green dull luminescent and late calcite cement, similarly to the CM Fm. (Figure 5i,j).

The petrographic observations are summarized below and reported in the paragenetic sequences shown in Figure 7:

1. Host rocks are characterized by dolomicrosparites and replacive dolomites (R), planar-e to planar-s, up to 300 μm in size, and locally up to 500 μm , non-luminescent to dull purple under CL. Group 1 replacive dolomites are crosscut by stylolites, while group 2 dolomites overprint stylolites. Stylolites crosscut dolomicrosparites, planar-e and planar-s replacive dolomites, indicating that these dolomites crystallized before significant burial-related compaction (Figure 6c,d). In medium to coarse-grained non-planar and planar-s dolomites, stylolites have a faint appearance, and some dolomite crystals are in optical continuity on both sides of the stylolite, indicating dolomitization or dolomite replacement after stylolite formation (Figure 6a).
2. Bedding-parallel veins are cemented by syntaxial dolomite crystals with a coarser size than the replacive dolomite in the host rock, but with very similar luminescence (Z), and are locally associated with and mutually crosscut bedding-parallel stylolites (Figure 6d).
3. Fault-related dolomites (F) have locally saddle habit and display red luminescence with outer growth zones characterized by different luminescence patterns. Type F dolomites mostly occur in thrust-related breccias in the CM Fm. and in the Co Fm. (Figure 5g–j) and overgrow type Z dolomites in bedding-parallel veins (Figure 5e,f).

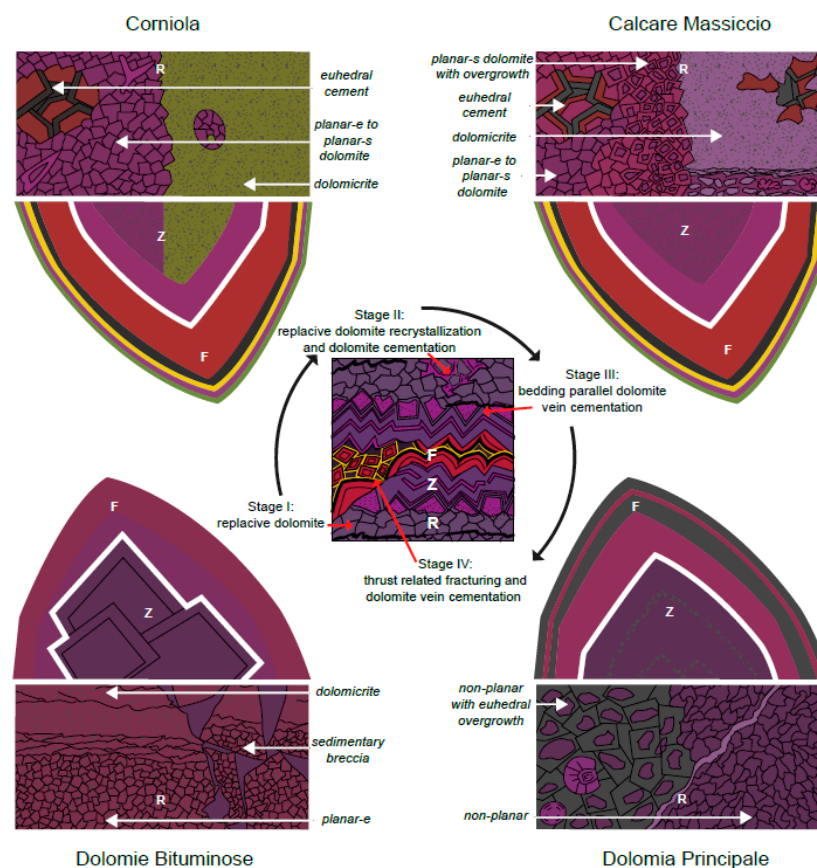


Figure 7. Paragenetic sequences showing the dolomite textures and CL patterns in the studied Upper Triassic and Early Jurassic carbonates. The drawing in the centre of the image shows the simplified dolomitization sequence including replacive (R), bedding-parallel veins (Z), and fault-related (F) dolomites.

4.4. Mineralogical, Geochemical, and Isotopical Analyses

The results of the XRD diffractometry, minor element concentration, carbon, oxygen and strontium isotopes, and carbonate clumped isotope thermometry are reported in the following chapters and summarized in Table 2.

Table 2. Summary of XRD diffractometry, minor elements, and stable and clumped isotopes analyses results.

	Dolomie Bituminose	Dolomia Principale	Calcare Massiccio	Corniola	Replacive	Bedding Parallel	Thrust Related
Ca (mol%) min	51.1	50.2	50.9	50.3	50.3	50.5	50.2
Ca (mol%) average	53.5	51.5	53.1	52.6	53	53	51.7
Ca (mol%) max	55.9	56.1	55.5	55.7	56.3	55	54.3
Ordering min	0.31	0.61	0.37	0.32	0.31	0.32	0.51
Ordering average	0.59	0.7	0.57	0.6	0.59	0.59	0.67
Ordering max	1	0.86	0.9	0.88	0.9	1	0.79
Fe (µg/g) min	40.7	19	40	-	45	30	95
Fe (µg/g) average	1038	52.3	802	-	838	724.1	368.3
Fe (µg/g) max	5874	115	4479	-	4479	5874	642
Sr (µg/g) min	8.3	13.8	0.9	-	0.9	8.3	35.5
Sr (µg/g) average	51.9	29.0	42	-	44.4	41.7	42.2
Sr (µg/g) max	117.7	35	89.6	-	89.6	117.7	48.9
Mn (µg/g) min	14.8	10.1	20.9	-	10.1	14.8	27.4
Mn (µg/g) average	31.1	15	34	-	30.9	29.6	29.2
Mn (µg/g) max	79.7	18.6	81.5	-	81.5	79.7	31
Ba (µg/g) min	9.2	8.8	8.9	-	9.9	8.8	8.9
Ba (µg/g) average	13.1	9.4	11	-	13.2	9.9	9.1
Ba (µg/g) max	16.8	9.9	27.6	-	27.60	12.8	9.4
$\delta^{18}\text{O}_{\text{‰}}$ min	-2.65	-1.91	-6.69	-2.14	-2.02	-1.91	-6.69
$\delta^{18}\text{O}_{\text{‰}}$ average	0.09	-0.51	-0.66	-0.79	-0.25	-0.47	-1.17
$\delta^{18}\text{O}_{\text{‰}}$ max	2.60	2.63	1.00	0.61	2.60	2.63	0.25
$\delta^{13}\text{C}_{\text{‰}}$ min	-1.60	1.91	0.27	1.97	1.40	1.69	-1.60
$\delta^{13}\text{C}_{\text{‰}}$ average	0.57	0.25	0.31	0.25	2.32	2.33	2.17
$\delta^{13}\text{C}_{\text{‰}}$ max	2.69	3.22	2.83	3.07	3.22	3.12	2.94
$T\Delta_{47}$ (°C) min	42.5	51.3	49.9	-	42.5	49.5	49.9
$T\Delta_{47}$ (°C) average	48.0	56.2	51.9	-	49.1	51.7	54.5
$T\Delta_{47}$ (°C) max	52.0	62.3	55.7	-	55.7	55.0	62.3
$^{87}\text{Sr}/^{86}\text{Sr}$ min	0.707510	0.707350	0.707390	-	0.707350	0.707400	-
$^{87}\text{Sr}/^{86}\text{Sr}$ average	0.707511	0.707464	0.707530	-	0.707517	0.707475	-
$^{87}\text{Sr}/^{86}\text{Sr}$ max	0.707540	0.707730	0.707610	-	0.707730	0.707610	-

4.4.1. Ca/Mg Ratio and Degree of Order

The analyzed dolomites can be subdivided into two groups based on cation ordering and Ca/Mg ratios. One group (Group 1) of dolomites has a high Ca content and low cations ordering, with 53.7 to 56.3 mol% of Ca and cation ordering between 0.3 and 0.8; the second group (Group 2) has a low Ca content and high cation ordering, with 50.2 to 52.3 mol% of Ca and cation ordering ranging from 0.4 to 1 (Figure 8). Calcium excess and cation ordering of the analyzed dolomites are independent of the hosting lithology. Most replacive dolomites display Ca excess and low cation ordering, type Z dolomites are equally partitioned into the two clusters and most F-type dolomites have high cation ordering and a low Ca content.

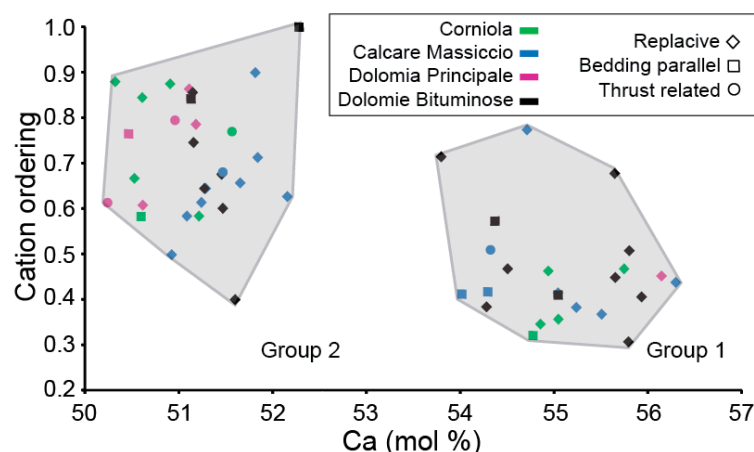


Figure 8. XRD analyses results; plots of calcium excess vs. cation ordering. Samples are plotted according to different hosting Formation and dolomite types, as indicated in the legend. Dolomites are clustered in two groups.

4.4.2. Minor Elements

The analyzed dolomites generally have low contents in trace elements, and there are no systematic variations based on host rock lithology or cement type. Strontium concentration is below 120 ppm. Mg and Sr concentration show a weak inverse correlation (Figure 9a). Iron and manganese concentration are lower than 2000 ppm and 50 ppm, respectively, for most of the samples. Mn concentration increases at increasing Fe concentration, although they are scarcely correlated (Figure 9b). Two samples show higher Fe and Mn. Barium concentrations are 10–15 ppm for most of the samples and never exceed 30 ppm (Table 2). Cation ordering is negatively correlated with strontium concentration (Figure 9c).

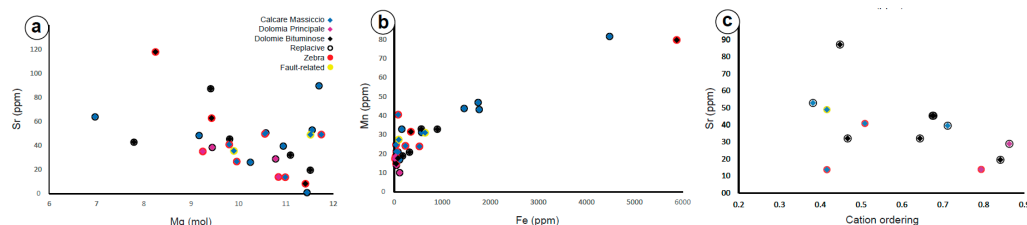


Figure 9. Major and trace element analyses results. Plots of (a) magnesium vs. strontium concentration. (b) Iron vs. manganese concentration. (c) Cation ordering vs. strontium concentration. Legend shows hosting lithology and dolomite type.

4.4.3. Carbon and Oxygen Isotopes

Stable isotope ratios of most dolomite samples fall in a wide cluster, with $\delta^{18}\text{O}$ ranging from -2‰ to 1‰ (V-PDB) and $\delta^{13}\text{C}$ from 1.5‰ to 3.2‰ (V-PDB), except for 7 samples out of 266 (Figure 10). The outliers are represented by four samples belonging to the lowermost parts of the DP Fm. and to the proximal basin facies of the DB Fm. that show enriched $\delta^{18}\text{O}$ values. Another two outliers are fault-related dolomites sampled from the CM Fm. in the thrust fault damage zone juxtaposing CM Fm. and Co Fm., which show lower $\delta^{18}\text{O}$ of -4.6‰ and -6.7‰ and slightly lower $\delta^{13}\text{C}$ of 1.0‰ and 0.3‰ . The last outlier is a fault-related dolomite vein in a layer rich in organic matter within the DB Fm., showing $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of -2.7‰ and -1.6‰ , respectively. The cluster is mostly in the range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of Late Triassic and Early Jurassic seawater [73], with some samples characterized by slightly higher $\delta^{18}\text{O}$. Carbon isotopes vary slightly depending on the hosting lithology. Dolomites of the DP Fm. are characterized by the highest $\delta^{13}\text{C}$, with an average value of $2.6 \pm 0.3\text{‰}$. Dolomites in the Co Fm. have a mean $\delta^{13}\text{C}$ of $2.6 \pm 0.3\text{‰}$.

Dolomites in the CM Fm. have an average $\delta^{13}\text{C}$ of $2.1 \pm 0.31\text{‰}$ and similarly $2.0 \pm 0.6\text{‰}$ for the DB Fm. Replacive dolomites are characterized by the highest $\delta^{18}\text{O}$ average value ($-0.2 \pm 0.8\text{‰}$), followed by bedding-parallel ($-0.5 \pm 0.7\text{‰}$) and fault-related dolomites ($-1.2 \pm 1.0\text{‰}$).

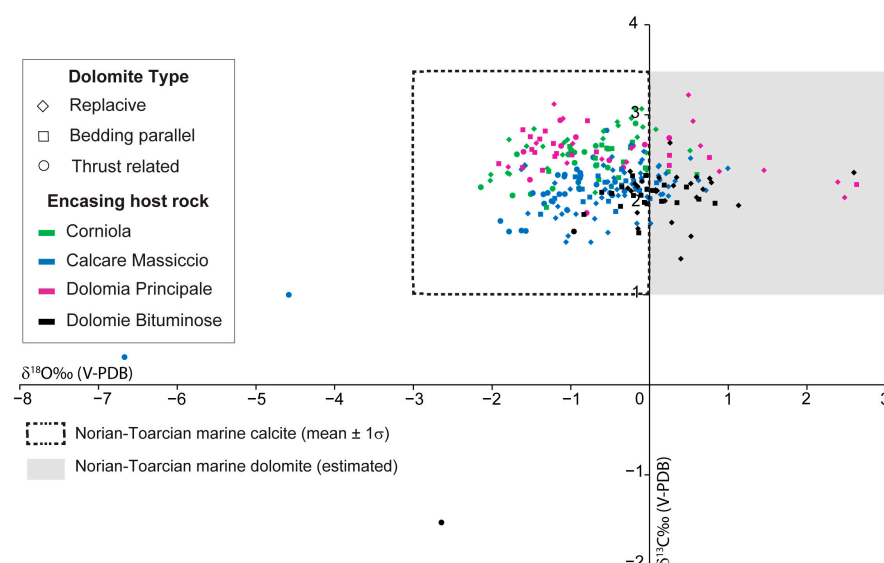


Figure 10. Carbon and oxygen stable isotope analyses results. The $\delta^{18}\text{O}\text{‰}$ (V-PDB) vs. $\delta^{13}\text{C}\text{‰}$ (V-PDB) plot with dashed areas representing stable isotope ranges of Triassic and Jurassic marine calcite precipitated in equilibrium with seawater from [73]. The grey area represents dolomites precipitated in equilibrium with Triassic and Jurassic seawater, calculated using the relation reported in [14]. The samples are plotted according to the different host rock and dolomite types, as indicated in the legend.

4.4.4. Clumped Isotope Thermometry

The $\Delta_{47}\text{dol}$ values range from 0.501‰ to 0.547‰ , which corresponds to temperatures between 42.5 and 62.3 °C , with mean and standard deviation values of $52 \pm 1.8\text{ °C}$ after [65]. Temperature is inversely correlated with the $\delta^{18}\text{O}$ of dolomite cements. Samples characterized by higher temperatures have lower $\delta^{18}\text{O}$ values (Figure 11). The measured temperatures are indistinguishable within errors.

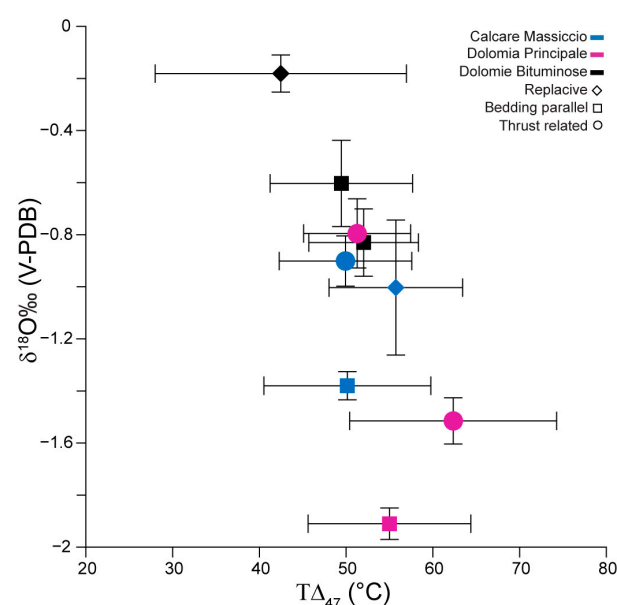


Figure 11. Clumped isotope thermometry results. Temperature after [65], from $\Delta_{47}\text{dol}$ (I-CDES) vs. $\delta^{18}\text{O}\text{‰}$ (V-PDB) plots. Legend indicates the host rock and dolomite types.

4.4.5. Strontium Isotopes

The $^{87}\text{Sr}/^{86}\text{Sr}$ values range between 0.707350 and 0.707730. Host rocks and fracture filling cements show no systematic differences in strontium isotope ratios (Figure 12a). Four dolomitized CM Fm. samples fit the range of strontium isotope ratios of the Early Jurassic seawater, and one sample of DP Fm. matches the strontium ratios of the Late Triassic seawater. The other replacive and bedding-parallel vein dolomite cements are characterized by lower strontium isotope ratios [74]. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the analyzed dolomites is poorly positively correlated with $\delta^{18}\text{O}$ (Figure 12b).

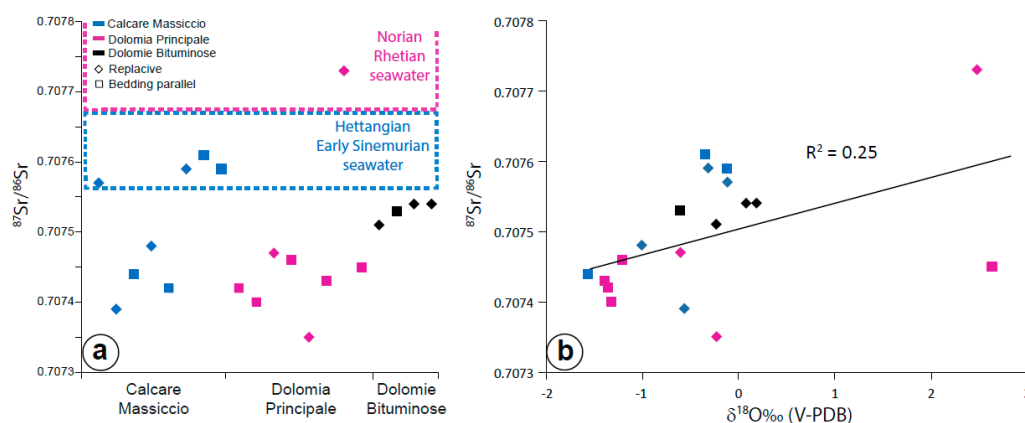


Figure 12. (a) Strontium isotope analyses results. $^{87}\text{Sr}/^{86}\text{Sr}$ of Late Triassic and Early Jurassic seawater from [74]. The samples are plotted according to the host rock and dolomite types, as indicated in the legend. (b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\delta^{18}\text{O}$ ‰ (V-PDB).

5. Discussion

5.1. Interpretation of Dolomite Textures

The microfacies in the host rocks of the DP and CM Fms. indicate that these carbonates were deposited in the platform interior, specifically in tidal flats and lagoon environments. On the other hand, the microfacies in the DB and Co Fms. are ascribed to slope and intrashelf basin environments (see Table 1). Replacive dolomites (R) in the study area can be differentiated into Group 1 and 2 according to textures and their relationships with burial stylolites (see Figure 6). Group 1 is represented by micritic, mimetic, fabric-retentive dolomites, and spar-sized, planar-e dolomites and a second group by larger, mostly fabric-destructive, planar-s to non-planar dolomites. Dolomites of the first group occur in mudstones, wackestones, and thin-bedded fenestral, oncoidal, and foraminiferal packstones, and are overprinted by bed-parallel stylolites. Planar-s to non-planar dolomites of Group 2 partially obliterate stylolites, and were mostly observed in the massive dolomites of the DP Fm. Non-planar and coarse dolomite crystals have been documented to recrystallize from early diagenetic precursors at shallow to intermediate burial depths [3,8,21,75,76].

The dolomite bedding-parallel vein (Z) dolomites in the Gran Sasso Massif are bedding parallel, and are not characterized by a systematic rhythmicity, i.e., their distribution has no characteristic thickness repetition (see Figure 3e,f). These dolomite veins are particularly well developed in fenestral and laminated dolostones, i.e., in tidal flats and intrashelf basin deposits. This indicates a strong sedimentological control on bedding-parallel vein formation. The cathodoluminescence of (Z) dolomites corresponds to that of adjacent (R) dolomites, suggesting similar geochemical properties between them, i.e., rock-buffered crystallization. Their orientation is compatible with a compressional stress field. However, mutual crosscutting with bedding-parallel stylolites can be considered evidence of the superposition of compressional and extensional stress fields during their formation (Figure 6d), which could be generated by episodic fluid pressure increases. Pore fluids

would have to exceed hydrostatic pressure conditions, at least transiently, to migrate to bedding-parallel discontinuities. Suprahydrostatic fluid pressures are generated in deep burial conditions (>2–3 km), and even at shallower depths at fast sedimentation rates [77]. (Z) dolomites in the Gran Sasso Massif are locally characterized by symmetric cement-filling sequences, described as “ABBA” or “ABCBA”, which have been attributed in the literature to diagenetic crystallization rhythmites (DCRs) and zebra rock patterns. The latter are characterized by a rhythmicity of the pattern, which is not documented in the (Z) dolomites of the Gran Sasso Massif. Many mechanical processes have been invoked to explain the formation of zebra rock patterns: (a) fluid overpressures allowing for the opening of fault-related fractures [78]; (b) dissolution–reprecipitation in open cavities [79]; (c) mineral replacement [80]; (d) displacive crystallization forces [81]; and (e) the interaction of mineral replacement, dissolution, and fracturing [82]. Zebra rocks are characterized by an inherent rhythmicity, which has been interpreted as controlled by the following factors: (I) tectonic structures, such as faults, cleavage, fractures, or stylolites [10]; and (II) self-organization processes of natural systems [81]. DCRs, on the other hand, have erratic spacing and spatial distribution, and are controlled by the primary facies and depositional structures [83,84]. There is no agreement on the environmental conditions of the formation of these patterns. Generally, DCRs have been interpreted as syn-sedimentary to early diagenetic [83,84], while zebra rocks form at deep burial depths [10,79,82,85]. However, despite terminological issues, the study of these dolomite patterns has been recently interpreted as a continuum of textures from stratabound bedding-parallel dolomite veins, dolomite breccias, and boxworks, to zebra textures, as a function of decreasing dolomitization intensity at the basin scale [86]. Therefore, zebra textures with intense replacement and abundant dolomite cements are characterized by a strong metasomatic control of the dolomitizing fluid, whereas facies-related dolomites, with limited amounts of cements and replacement, have a strong sedimentological control. In this framework, the bedding-parallel vein (Z) dolomites in the Gran Sasso Massif can be interpreted as stratabound, sedimentologically controlled, bedding-parallel zebra textures.

Dolomite breccia and vein cements precipitated in thrust-fault-related fractures during Messinian–Early Pliocene compressional deformation [35,39]. Fault-related dolomites (F) precipitated as syntaxial cements into thrust-related fractures or overgrew bedding-parallel vein dolomite cements (compare Figure 5f,h). Mosaic breccia textures in fault damage zones could be caused by hydrofracturing due to fluid overpressure or, conversely, due to fluid decompression [87,88]. These processes can be triggered by repeated fluid pulses ascending along thrust faults, such as those described by the fault-valve model [89]. Along-fault fluid migration conveys a different fluid into the thrust-related fractures, or a similar fluid with different temperature, pressure, and redox conditions. (F) dolomites are mostly red luminescent, with late yellow and green growth zones supporting the hypothesis that they precipitated from a different fluid source and/or at different conditions compared to (Z) and (R) dolomites. (F) dolomites are locally composed of saddle-shaped crystals. Saddle dolomite habit is favoured above the critical roughening temperature, which is around 60–80 °C, according to [90,91]. The crystallization temperatures of (F) dolomites obtained from clumped isotope thermometry (50–60 °C) are slightly below the reported minimum temperature for saddle dolomite crystallization. If (F) saddle dolomites crystallized at higher temperatures, the discrepancy could indicate that the analyzed samples include dolomites precipitated at different temperatures. This issue is discussed in Section 5.4.

5.2. Dolomitizing Fluid Constraints from Geochemical Data

The $^{87}\text{Sr}/^{86}\text{Sr}$ of replacive and bedding-parallel vein dolomites in the DB and DP Fm. is lower than Norian–Rhaetian (coeval to deposition) seawater in most of the analyzed

samples [74]. Similarly, half of the analyzed samples of replacive and bedding-parallel vein dolomites in the CM Fm. are also lower than the $^{87}\text{Sr}/^{86}\text{Sr}$ of Hettangian–Sinemurian seawater. The $^{87}\text{Sr}/^{86}\text{Sr}$ lower than seawater can be the result of ascending magmatic fluids and/or mixing with younger seawater. A similar $^{87}\text{Sr}/^{86}\text{Sr}$ in the DB Fm. has been reported by [39], in which noble gases isotopes analyses was also carried out, which allowed for the exclusion of crustal or magmatic fluids in replacive and bedding-parallel vein dolomites of the BD Fm. Fabric-retentive dolomicrosparites in the CM Fm. are characterized by a $^{87}\text{Sr}/^{86}\text{Sr}$ fitting the range of Hettangian–Sinemurian seawater, and could have formed during early dolomitization from seawater. Conversely, fabric-destructive dolomites in the CM Fm. have lower $^{87}\text{Sr}/^{86}\text{Sr}$ values that could have been modified during increasing diagenetic alteration, i.e., a later dolomitization process or by replacement. If we consider that the interaction of magmatic fluids in the DB Fm. can be excluded, the diagenetic fluid producing this $^{87}\text{Sr}/^{86}\text{Sr}$ could be Sinemurian–Pliensbachian seawater [74].

Strontium concentration in all dolomite types does not exceed 120 ppm. Dolomites with a strontium concentration lower than 200 ppm can be the result of seawater, modified seawater, or burial dolomitization [5,6]. Dolomites produced by sabkha and microbially induced dolomitization have 250–600 and 2800–6200 ppm Sr [92]. However, the latter cannot be excluded, because dolomites with a low Sr concentration can also be the product of the replacement of sabkha and microbially induced dolomites. Fe and Mn concentrations of replacive dolomites are below 2000 ppm and 50 ppm, respectively, indicating that dolomitization occurred by oxidizing fluids [7,93]. Locally, we document higher values of Mn and Fe, possibly due to more reducing conditions locally because of high contents of organic material [17]. No significant differences in Sr, Fe, and Mn concentrations occur in (Z) dolomites compared to (R) dolomites.

We have to take into account that the $\delta^{18}\text{O}$ values of (R) and possibly (Z) dolomites can be influenced by replacement processes, especially in closed-system conditions, and by fractionation, which can variate depending on the salinity of the dolomitizing fluid [2–4]. The $\delta^{18}\text{O}$ of dolomites directly precipitating from seawater at ambient surface temperature is characterized by an increase from about +2.7‰ to +4‰ (V-PDB) with respect to marine calcite in a system which has attained equilibrium [17]. Most of the DP and DB Fm. samples are characterized by $\delta^{18}\text{O}$ values that overlap both the range of calcite and dolomite precipitated from Norian–Rhaetian seawater at equilibrium. Also, the $\delta^{18}\text{O}$ values of dolomites in the CM and Co Fms. overlap the range of calcite and dolomite precipitated from Hettangian–Toarcian seawater at equilibrium. The $\delta^{18}\text{O}$ values of (R) dolomites in the DB Fm. are +1‰ higher compared to coeval seawater, and up to +4‰ in an outlier (Figure 10) and other samples of the DB Fm. in the same section—see [39]. Similar $\delta^{18}\text{O}$ values are measured in the DP Fm., showing values +4‰ higher compared to coeval seawater. The $\delta^{18}\text{O}$ values increase with respect to seawater in the DP Fm. and DB Fm. is comparable to the fractionation factor of dolomite precipitating from seawater at equilibrium [14,15]. However, most dolomites are characterized by the $\delta^{18}\text{O}$ of the fluid comprised between +3‰ and +5‰ (V-SMOW), indicating modified seawater as the diagenetic fluid, which $\delta^{18}\text{O}$ could have increased by evaporation, as has been extensively documented in the Neotethys, where the DP Fm. was affected by early diagenetic fabric-retentive dolomitization in evaporative conditions in the Norian (Figure 13) [12,15,19].

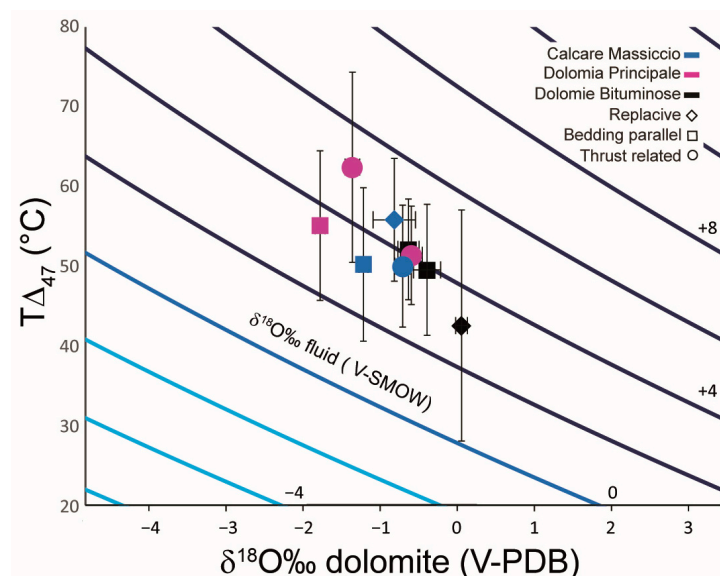


Figure 13. Plot of $\delta^{18}\text{O}$ (‰ V-PDB) vs. clumped isotope temperatures of dolomites; $\delta^{18}\text{O}$ (‰ V-SMOW) of the dolomitizing fluid calculated using the fractionation factor of [66]. Legend shows hosting lithology and dolomite type.

The $\delta^{13}\text{C}$ values of replacive dolomites in the DB, DP, CM, and Co Fms. show overlapping ranges. The $\delta^{13}\text{C}$ values are in the range of coeval seawater and vary according to the host rock [73]. The $\delta^{13}\text{C}$ values have no covariation with $\delta^{18}\text{O}$ values, therefore pointing out that $\delta^{13}\text{C}$ is rock-buffered and invariant. It is to be expected, since the primary carbon isotope ratio is generally retained in carbonates during diagenesis, except at extremely high water to rock ratios [4,94].

(Z) dolomites have $\delta^{18}\text{O}$ similar to (R) dolomites. Similar $\delta^{18}\text{O}$, along with relations with stylolites, similar cathodoluminescence patterns and $^{87}\text{Sr}/^{86}\text{Sr}$ and minor element concentrations, support the hypothesis that (Z) dolomites originated from dissolution/precipitation of (R) dolomites in rock-buffered conditions [21,95].

The $\delta^{18}\text{O}$ of fault-related (F) dolomite cements are slightly lower compared to (Z) dolomites, still widely overlapping. Changes in the fluid composition likely occurred during Messinian–Early Pliocene compression and are highlighted by different cathodoluminescence patterns in (F) dolomites compared to homogeneous non-dull to dull purple luminescence of (R) and (Z) dolomites. Similarly to (R) and (Z) dolomites, the $\delta^{18}\text{O}$ of the fluid of (F) dolomites ranges between +3‰ and +5‰ (V-SMOW), which can be ascribed to seawater modified during burial (Figure 13) [2,3]. Two outliers have lower $\delta^{18}\text{O}$, suggesting mixing with an external fluid. This variation could be the signature of a higher degree of opening of the system to the upward migration of deeper, higher-temperature fluids, or the downward percolation of meteoric/groundwater fluids. Since (F) dolomites cement breccias and veins along thrust faults, the upward ascent of fluids with higher temperatures is more reasonable.

The interpretations of dolomitizing fluid and environmental conditions are summarized below and reported in the conceptual model of Figure 14:

1. (R) dolomitization initially occurred in a near-surface, early diagenetic environment through the influx of modified, locally evaporated seawater, and was followed by dolomite replacement from Sinemurian–Pliensbachian seawater during the Jurassic (Figure 14a).
2. (Z) dolomites formed by dissolution–precipitation of (R) dolomites, which occurred at a >2 km burial depth at suprahydrostatic pore fluid pressures. (Z) dolomites have cathodoluminescence and geochemical characteristics indistinguishable from

the replacive dolomite in the wall rock, suggesting that they precipitated from similar fluids in rock-buffered conditions (Figure 14b).

3. (F) dolomites precipitated along thrust faults during Messinian–Early Pliocene compression and documented local opening of the system to higher-temperature fluids that migrated through tectonic fractures (Figure 14c).

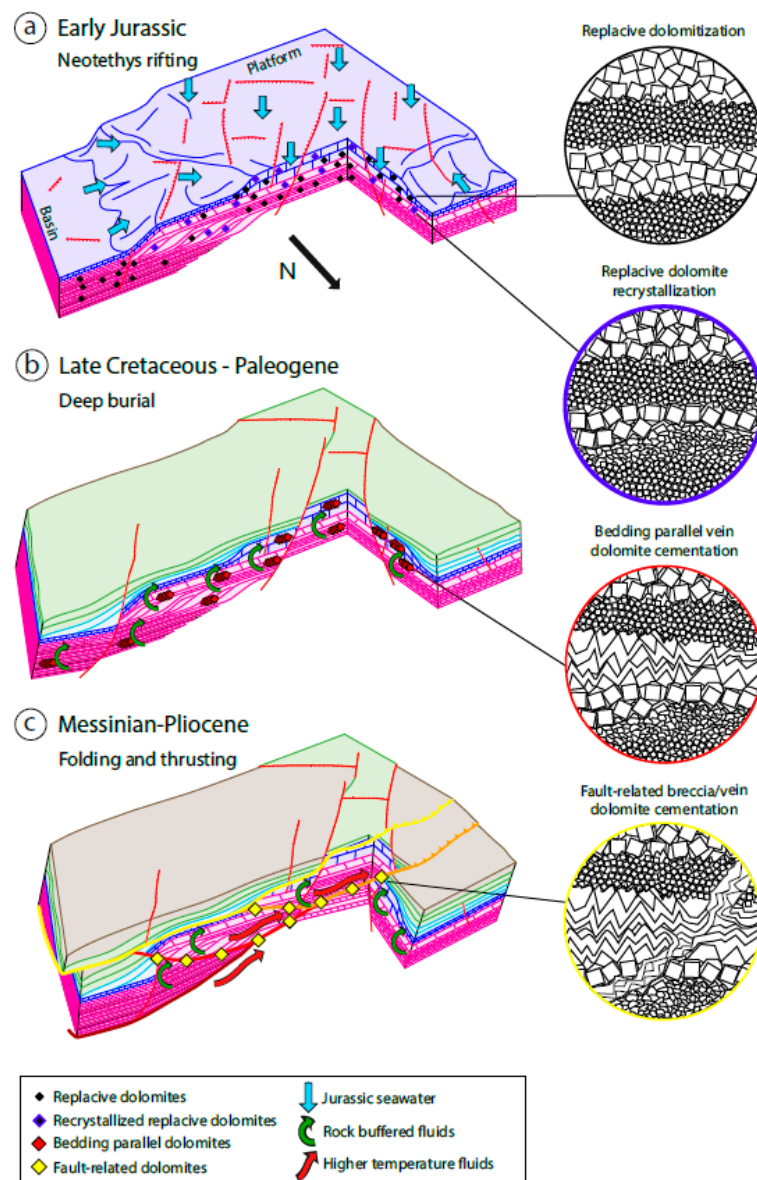


Figure 14. Simplified 3D block model illustrating the dolomitization stages in the Gran Sasso Massif. (a) Early replacive dolomitization in the Upper Triassic and lower Jurassic carbonates at the northern margin of the Lazio–Abruzzi platform. (b) A closed fluid system persisted in the dolomitized rocks during the passive margin stage, resulting in fluid overpressure at deep burial that led to dolomite cementation in bed-parallel veins. (c) Fault-related dolomite cementation in breccias and veins occurred along thrust fault zones during Messinian–Pliocene compression, with minor contribution of other fluids. Extensional faults are in red; thrust faults are drawn with the same colours in the legend of Figure 2; Triassic units are in pink; Jurassic in blue; Cretaceous in green; and Cenozoic in pale brown.

5.3. Dolomitization Timing in the Gran Sasso Massif

Here, we constrain the timing of dolomitization based on field and petrographic observations, clumped isotope thermometry, and the burial history of the study area

(Figure 15). We compare these data with the calculated burial curve of DB, DP, CM, and Co Fms. using the stratigraphy reported in [54,96] and the isotherms of Mesozoic and Cenozoic in the Central Apennines from [97]. (R) dolomites crystallized during early diagenetic dolomitization after deposition. In the Early Jurassic, (R) dolomites reached burial depths corresponding to the minimum replacement temperatures obtained from clumped isotope thermometry (40–45 °C at 300–400 m depth). However, based on our results, we cannot constrain the exact duration of replacive dolomite replacement.

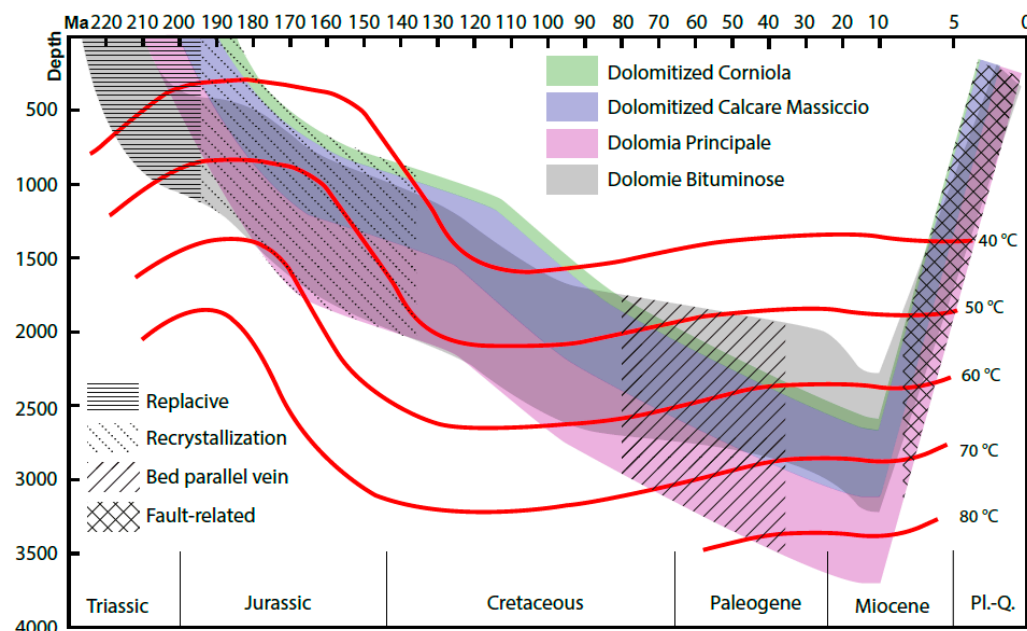


Figure 15. Burial history calculated using the stratigraphic thicknesses reported in [54,96]. Thick red lines represent the isotherms of the Central Apennines region, modified from [97]. The proposed timing of dolomitization stages is represented by the striped and hatched areas.

(Z) dolomites crystallized from the same dolomitizing fluid in rock-buffered conditions at deep burial depths (>2 km). At these depths, fluid overpressures are generated in sedimentary basins. Fluid overpressures are preferentially produced in rocks overlaid by thick impermeable successions. This was achieved after the deposition of the Tithonian to Aptian Maiolica Fm., a 300 m-thick sequence of micritic pelagic carbonates. Moreover, the dolomitized carbonates reached the minimum burial depths for fluid overpressure formation by the Late Cretaceous. (Z) dolomite formation can be therefore assumed to have occurred from the Late Cretaceous to Eocene times.

Eventually, fault-related (F) dolomites in the Gran Sasso Massif formed after the onset of compressional deformation in the Late Miocene, as testified by their distribution in breccias and veins along thrust faults. They precipitated at temperatures of 50–65 °C, which occurred in the Messinian during the uplift stage [35,39]. Fault-related dolomites in the Gran Sasso Massif cannot be considered of hydrothermal origin (e.g., [98]) because their crystallization temperatures are similar to host rock temperatures during precipitation. The geochemical dataset also demonstrates the similarity between (F), (Z), and (R) dolomites supporting local and external fluid mixing rather than a completely different dolomitizing fluid. However, U-Pb dating of (F) dolomites could reveal a younger age of these cements, since further compressional deformation was accommodated along the described thrust faults during the Pliocene and Pleistocene (Tavani, S., personal communication). In this case, (F) dolomites would have to be considered hydrothermal, because the host rocks would be significantly cooler than the fault-related cements (Figure 15).

5.4. Strengths and Pitfalls of Clumped Isotope Thermometry in a Rock-Buffered Environment

Clumped isotope thermometry provides the same crystallization temperatures and $\delta^{18}\text{O}$ ranges (40–65 °C; −2‰ to 0‰ V-PDB) for replacive, bedding-parallel vein (Z), and fault-related (F) dolomites in the Gran Sasso Massif. The $\delta^{18}\text{O}$ of the fluid of all dolomites (R, Z, and F) is in the range from +3‰ to +5‰ V-SMOW (Figure 13) [66]. Replacive (R) dolomites with medium to coarse fabric-destructive textures obliterating stylolites were affected by replacement. Moreover, bedding-parallel vein (Z) dolomites are associated with bedding-parallel stylolites and are characterized by syntaxial dolomite crystals, suggesting that their precipitation is associated with the dissolution of adjacent (R) dolomites. Additionally, (Z) dolomites are characterized by the same stable isotope geochemistry of (R) because of the persistence of rock-buffered conditions. We therefore assume that Z dolomites precipitated from the same dolomitizing fluid that precipitated R dolomites, since they precipitated in a rock-buffered environment and in the same temperature range. However, what are we documenting with clumped isotope thermometry? Are clumped isotopes yielding precipitation or replacement temperatures of (R) and (Z) dolomites?

Firstly, dolomites did not reach the temperature range where solid-state reordering of C–O bonds occurs (~300 °C), meaning that, if replacement occurred, it was the result of dissolution–precipitation processes [28]. Here, we document some patterns in the (R) and (Z) dolomites of the Gran Sasso Massif, which have been related to replacement in the literature: (a) no distinct $T\Delta_{47}$ ranges in different dolomite cements; (b) no systematic difference in $T\Delta_{47}$ depending on dolomite petrographic textures and sizes; and (c) correlation between the $T\Delta_{47}$ and $\delta^{18}\text{O}$ of the dolomitizing fluid. Moreover, replacement occurred in rock-buffered conditions, and in these cases, we can only assess the apparent $\delta^{18}\text{O}$ of the fluid. This $\delta^{18}\text{O}$ of the fluid provides an estimate of the dolomitizing fluid during replacement, which increasingly overestimates the real $\delta^{18}\text{O}$ of the fluid for increasing temperatures and decreasing water to rock ratios [23,24,29]. We also face this issue if the replacement process is incomplete. Similarly, the $T\Delta_{47}$ values do not indicate true replacement temperatures, but only minimum estimates, due to the physical mixing of recrystallized and pristine dolomites. The resulting $\delta^{18}\text{O}$ of the dolomitizing fluid could be related to incomplete replacement in low water to rock ratio conditions or the mixing of different dolomites. $T\Delta_{47}$ is fairly correlated with strontium isotope ratios and mineralogy. The $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca excesses decrease with increasing $T\Delta_{47}$ in replacive (R) and bedding-parallel vein (Z) dolomites in the Gran Sasso Massif (Figure 16a,b). This could imply that dolomites characterized by a lower Ca excess could have been recrystallized during increasing burial or, alternatively, could represent mixing of low- and high-temperature dolomites. Low-temperature dolomites are characterized by a Ca excess of up to 6–7 mol% and crystallize in low salinity and low Mg/Ca ratio conditions, while dolomites forming at higher temperatures and in hypersaline environments are stoichiometric [20,57,99,100]. Given the complexity of dolomitization and dolomite replacement processes, we are not able to discern between replacement and the physical mixing of dolomites.

Lastly, dolomite replacement and dolomite cement precipitation occur from shallow to deep burial conditions, and the real replacement or precipitation temperatures can be drastically higher and/or lower than what we measure with clumped isotope thermometry. Clumped isotope analyses are limited in resolution and provide an average temperature of the measured sample powder, whereas fluid inclusions yield a detailed sequence of precipitation temperatures beyond salinity and salt types. Differences in clumped isotope temperatures and fluid inclusion trapping temperatures were documented by [16,26,27] and a few others. They showed no relation between the range of temperatures measured with clumped isotope measurements and with fluid inclusion microthermometry. Nevertheless, carbonate clumped isotope thermometry is the best analytical tool to characterize a volume-

averaged crystallization temperature, and when fluid inclusion measurements cannot be performed, e.g., really small, necked, and decrepitated inclusions in highly deformed rocks (this case study and [23]). Fluid inclusion measurements were, in fact, attempted on 20 100 μm -thick sections. We found only three measurable aqueous fluid inclusions that homogenized at 70–75 $^{\circ}\text{C}$. We were not able to measure first melting and last melting temperatures, as these inclusions leaked during freezing.

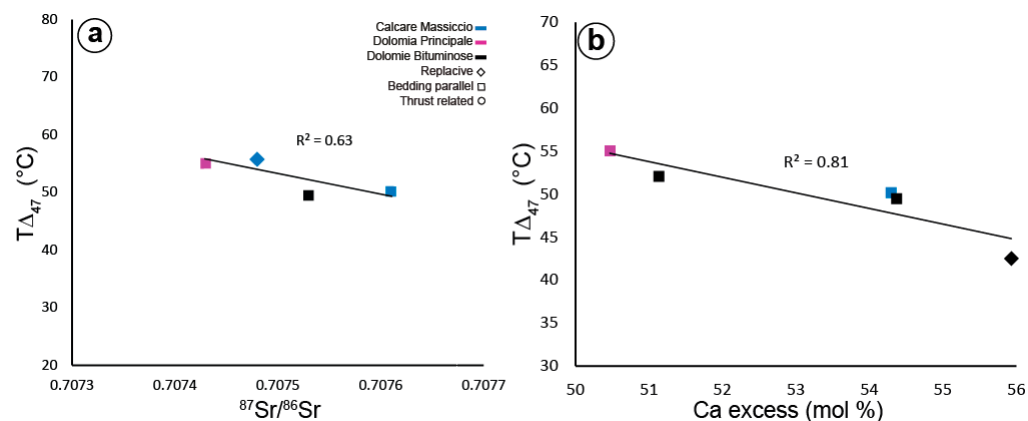


Figure 16. (a) Plot of strontium isotope ratios vs. clumped isotope temperatures. (b) Plot of Ca excess (mol%) vs. clumped isotope temperatures.

5.5. Dolomitization Mechanisms and Dolomitizing Fluids in the Adriatic Region

The replacive, early dolomitization processes are fairly homogeneous in the peri-Adriatic region, and common aspects between the case studies published in the literature and our original results are described here. The $\delta^{18}\text{O}$ of the dolomitizing fluids, the precipitation temperatures, and the $\delta^{18}\text{O}$ of dolomites documented in the Adriatic region are reported in Figure 17a, while the paleogeography of the area at the Triassic–Jurassic boundary is illustrated in Figure 17b, where the locations of the case studies are included.

The Norian Dolomia Principale (DP) Fm. is characterized by fabric-retentive dolomites formed in peritidal environments from the evaporation of seawater at 25–40 $^{\circ}\text{C}$, with a high Fe concentration and structural order. Dolomitizing fluids have a $\delta^{18}\text{O}$ from +1‰ to +5‰ V-SMOW in the western Southern Alps and Transdanubian Range, and +1‰ to +3‰ V-SMOW in the Apennine platform [12,15]. Where the DP Fm. attained maximum temperatures of 60 $^{\circ}\text{C}$, replacement was incomplete. In these cases, Ca excess decreases linearly at increasing burial dolomitization temperatures [19]. Seepage reflux of seawater is the dolomitization mechanism that promoted early dolomitization in subtidal, slope, and proximal basin carbonates in the Rhaetian, producing fabric-destructive, Ca-rich, and depleted $\delta^{18}\text{O}$ compared to the Norian DP Fm. [12,101]. Seepage reflux of seawater resulted in dolomites characterized by dolomitizing fluids, with $\delta^{18}\text{O}$ from −1‰ to 0‰ V-SMOW in the Apennines platform and from −2‰ to +1‰ V-SMOW in the Lagonegro proximal basin (Southern Apennines; [13]). The Calcare Massiccio (CM) Fm. in the Central Apennines and other Early Jurassic limestones in the Southern Alps (Albenza Fm. and Sedrina Fm. in the Lombardy basin and Mt. Zugna Fm. in the Trento Plateau) are characterized by dolomites that formed in response to different dolomitization mechanisms related to the local and regional morpho-structural setting. In the Central Apennines, replacive dolomitization occurred at less than 50 $^{\circ}\text{C}$ from fluids with $\delta^{18}\text{O}$ values between +2‰ to +7‰ V-SMOW, while in the Southern Alps at higher temperatures from fluids with $\delta^{18}\text{O}$ between −3‰ to +1‰ V-SMOW. Seepage reflux of seawater promoted early dolomitization, while compaction-driven fluid expulsion occurred during burial dolomitization. Both mechanisms were focused along fracture zones and fault-bounded platform escarpments. The

main driving factor of Lower Jurassic limestone dolomitization in the whole Adriatic area is the high heat flux and geothermal gradient related to the Neotethys rifting [11,14,102,103].

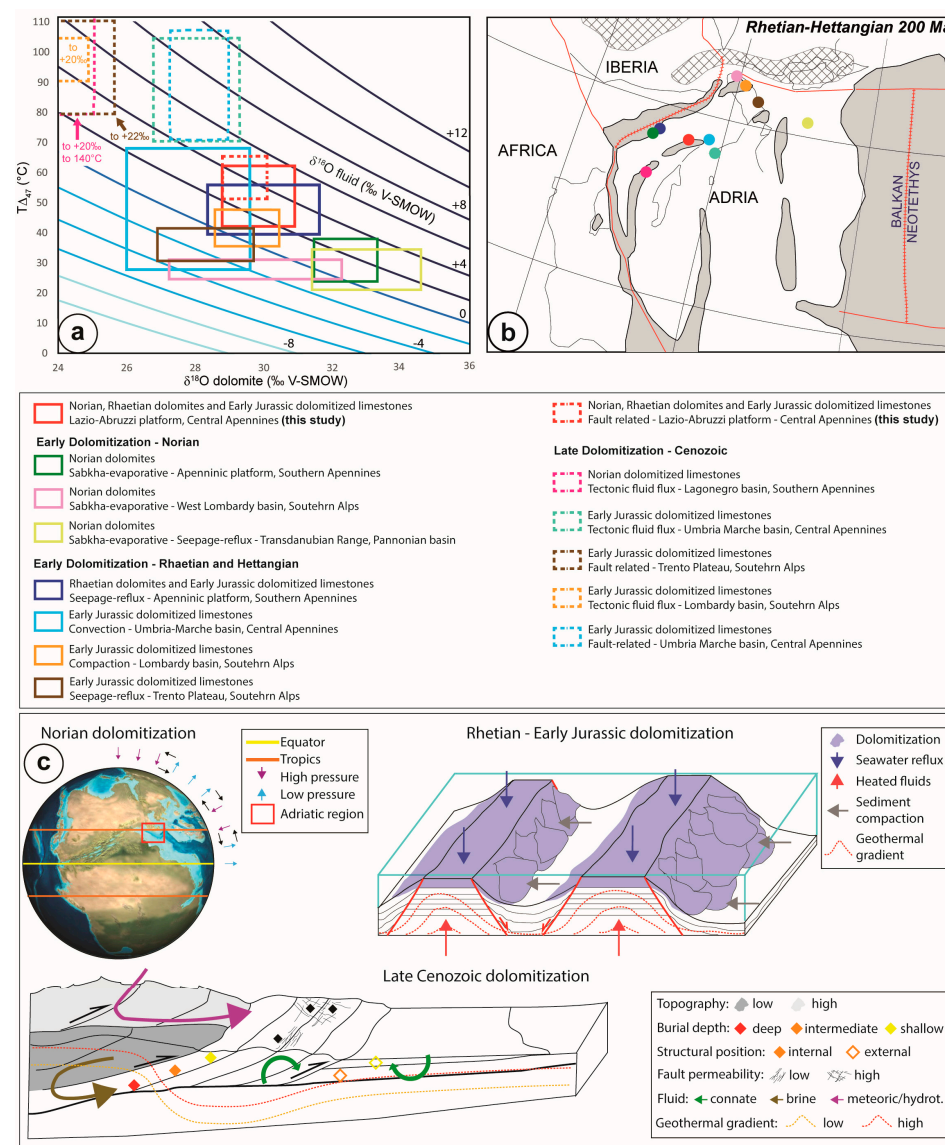


Figure 17. (a) Comparison of dolomitizing fluid geochemistry in the Adriatic region from published data and from this study (red); plot of $\delta^{18}\text{O}$ of dolomites vs. precipitation temperatures; precipitation temperatures of the literature data are measured using fluid inclusion microthermometry when >50 °C, or estimated from the regional context and burial history in the other cases. (b) Paleogeographic reconstruction at the Triassic–Jurassic, indicating with coloured dots the locations of the study area and of the dolomitized rocks from the literature reported in the legend; the legend describes the age of the dolostones, the dolomitization mechanisms, and the paleogeographic context; data from [11–15,19,30,101,103–105]. (c) Conceptual model illustrating the main controls over early and late dolomitization processes in Upper Triassic and Lower Jurassic carbonates in the Adriatic region; Late Triassic paleogeography from Blakey R. <https://deeptimemaps.com>, accessed on 16 January 2025.

Replacive dolomites in the DP Fm. exposed in the Gran Sasso Massif are characterized by stoichiometric dolomites with $\delta^{18}\text{O}$ values of the dolomitizing fluid that are comparable to the Norian dolomites in the Adriatic region, which formed during early dolomitization from evaporated seawater in sabkha environments. Nevertheless, minor element concentrations and the $\delta^{18}\text{O}$ of the dolomites correspond to those of dolomites produced by seepage reflux of seawater. Also, taking into account that the $^{87}\text{Sr}/^{86}\text{Sr}$ is

lower than that expected from seawater coeval to deposition (Norian–Rhaetian), replacive dolomites in the DP Fm. of the Gran Sasso Massif should have been affected by replacement during shallow to intermediate burial from Jurassic seawater. However, some dolomites retain their original signature, pointing to early dolomitization from evaporated seawater. Replacive dolomites in the CM Fm. of the Gran Sasso Massif are characterized by dolomitizing fluids with a $\delta^{18}\text{O}$ similar to other dolomitized Early Jurassic limestones in the Central Apennines. The $^{87}\text{Sr}/^{86}\text{Sr}$ corresponds to the Hettangian–Sinemurian seawater in fabric-retentive dolomites, while it is lower in fabric-destructive dolomites. Moreover, the former are characterized by iron concentrations over 200 ppm and the latter below 200 ppm. This is evidence that the CM Fm. was also affected by replacement from younger Sinemurian–Pliensbachian seawater. Differently from the DP Fm., the fabric-retentive dolomites are characterized by a lower $\delta^{18}\text{O}$, showing that, if they preserve their early diagenetic signature, they are dolomitized by a seepage reflux of seawater.

Late diagenetic dolomitization processes differ in fluid properties, although are roughly similar in temperatures of crystallization (80–120 °C) in both Upper Triassic and Lower Jurassic carbonates, depending on the timing of compressional deformation during the Neogene and on regional and local structural setting [11]. Fracture-related saddle dolomite cements in the Central Apennines, with temperatures up to 110–120 °C, were attributed to precipitation from the same dolomitizing fluid source, characterized by $\delta^{18}\text{O}$ from +3‰ to +7‰ V-SMOW, which resulted in Mesozoic dolomitization. The dolomitizing fluids were later remobilized during Miocene compression around peak burial conditions and have been explained as tectonically driven fluid flux [14]. The same mechanism has been invoked for hydrothermal dolomites formed at 80–100 °C in the Lombardy basin and Trento plateau in the Southern Alps, in which dolomitizing fluids range from −1‰ to +1‰ V-SMOW [103,104]. Zebra dolomites in the Lagonegro proximal basin units (Southern Apennines) formed at temperatures of 100–120 °C, by fluids with $\delta^{18}\text{O}$ values of 0‰ to +5‰ V-SMOW and high strontium ratios, which have been interpreted as being due to Miocene seawater during Miocene compression [13,30].

Bedding-parallel vein and fault-related dolomites formed due to late diagenetic dolomitization in the Gran Sasso Massif, and they precipitated from dolomitizing fluids similar to those that promoted early diagenetic dolomitization. However, the lower precipitation temperatures compared to other dolomite cements in the Central Apennines [14] are the result of the limited tectonic burial that affected the Gran Sasso Massif tectonic structure.

We can summarize the following main controls over dolomitization in the regional framework of Adria, which we illustrate in the conceptual model of Figure 17c:

1. The climatic and paleogeographic conditions in the Norian (i.e., hot and arid in the tropical high-pressure belt, stratified water column, and restricted water circulation) promoted the ideal conditions for the evaporation of seawater in extensive tidal flats, which extended over most of the Adriatic region. Therefore, all the carbonates that deposited were dolomitized in surficial sabkha environments by evaporated seawater;
2. The Rhaetian and Hettangian were characterized by wet climatic conditions, not conducive to dolomitization at the surface. The carbonates deposited in these stages were dolomitized by different dolomitization mechanisms depending on the burial history and local tectono-stratigraphic context. However, Neotethys rifting produced extensional deformation, resulting in the dissection of the peri-Adriatic platform in structural highs and basins, along with a high geothermal gradient, promoting ideal conditions for seawater circulation into carbonate platforms. The carbonates that were affected by dolomitization are located over structural highs and along their fault-bounded slopes;

3. The late dolomitization processes are controlled by the type of fluids and their modality of flow during contractional deformation. In turn, these are the result of thrust belt evolution in the Alps and Apennines in terms of topography, pressure and temperature, burial and uplift history, and the petrophysical properties of faults and fractures.

6. Conclusions

The Upper Triassic and Lower Jurassic succession outcropping in the Gran Sasso Massif, Central Apennines of Italy, is composed of platform interior and intrashelf basin carbonates that were affected by replacive dolomitization, replacement, bedding-parallel dolomite veins, fault-related dolomite veins, and breccias precipitation. In this contribution, field observations, petrography, and mineralogical and geochemical analyses were integrated to unravel the dolomitization processes, the dolomitizing fluid properties, and the timing of dolomitization. The main results are summarized as follows:

- (i) Replacive fabric-retentive dolomites formed at low temperatures in a near-surface environment by seawater evaporation and seepage reflux;
- (ii) Replacive fabric-destructive dolomites recrystallized at temperatures of 40–55 °C in a shallow to intermediate burial environment in the Jurassic. Their $^{87}\text{Sr}/^{86}\text{Sr}$ is lower than coeval seawater, testifying for replacement by younger Sinemurian–Pliensbachian seawater;
- (iii) Bedding-parallel dolomite veins crystallized at 50–55 °C due to suprahydrostatic fluid pressures at deep burial depth. Formation in rock-buffered conditions resulted in geochemical signatures equal to the replacive dolomites;
- (iv) Fault-related dolomite cements precipitated in thrust-related fractures at comparable temperatures of 50–65 °C, and from dolomitizing fluids similar to those of bedding-parallel dolomite veins. The dolomitizing fluid documents gradual changes in the chemistry of the system due to higher temperature fluids, despite the fact that rock-buffered conditions persisted.

Long-lasting rock-buffered conditions resulted in the precipitation of dolomites that are geochemically indistinguishable from one another. On the other hand, a closed system could promote the preservation of the geochemical signatures of the early dolomitization mechanism, generally the most significant in terms of volume, although often overprinted by replacement during increasing burial. Clumped isotope thermometry represents a promising alternative analytical tool to fluid inclusion microthermometry to constrain the properties of the dolomitizing fluids and, in particular, to ascertain the occurrence of dolomite replacement.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/geosciences15020035/s1>, Lucca_et_al_GSD_Supplementary_Material_Dataset.xlsx.

Author Contributions: A.L., conceptualization, methodology, formal analysis, investigation, data curation, writing—original draft, writing—review and editing, and visualization; S.M., conceptualization, data curation, writing—original draft, and writing—review and editing; F.B., conceptualization, investigation, writing—original draft, writing—review and editing, visualization, and supervision; A.C. (Anna Cipriani), validation, formal analysis, resources, and data curation; A.C. (Antonino Cilona), validation, investigation, resources, writing—review and editing, and funding acquisition; F.S., resources, writing—review and editing, supervision, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All data generated or analyzed during this study are included in this published article and its Supplementary Materials.

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