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SELECTIVE DOLOMITIZATION BY SYNTAXIAL OVERGROWTH AROUND DETRITAL DOLOMITE NUCLEI: A CASE FROM THE JURASSIC OF THE LIGURIAN BRIANCONNAIS (LIGURIAN ALPS)

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14	AROUND DETRITAL DOLOMITE NUCLEI: A CASE FROM THE
15	JURASSIC OF THE LIGURIAN BRIANÇONNAIS (LIGURIAN ALPS)
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30	

ABSTRACT

32 Dolomite crystals, occurring in Middle Jurassic dolostones and dolomitic limestones of the Ligurian Brianconnais Domain (French-Italian Ligurian Alps), show irregular, complex zoning 33 34 evidenced by cathodoluminescence (CL) and backscattered electron imaging. Comparable zoning patterns from other study areas have been attributed alternatively to recrystallization or dissolution-35 36 precipitation processes. However, none of these mechanisms can account for the range of 37 observations from the Ligurian Brianconnais Domain, which include: 1) the presence of multiple 38 core types, each with different CL characteristics; 2) marked compositional differences between 39 cores and surrounding rims (ferroan vs. nonferroan, Mg/Ca ratio); 3) a marked shape difference 40 between cores, with irregular outlines, and rims which progressively approach a well-developed 41 rhombohedral habit. These features are most reasonably interpreted as dolomitic rims that formed as 42 syntaxial overgrowths around detrital dolomite nuclei, which in turn originated from erosion of 43 underlying Triassic rocks and triggered selective replacement of fine-grained calcareous sediment. 44 Failure to recognize the exact nature of this type of dolomite crystal may lead to overestimating the 45 degree of dolomitization and to overlooking possible detrital inputs in a basin otherwise supplied 46 with pure allochemical sediments, with consequent loss of information on the tectonosedimentary 47 evolution.

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INTRODUCTION

The modes and environments of dolomitization of carbonate sediments are still an open and controversial problem in earth sciences. This ambiguity is due mainly to the fact that an actualistic approach seems to be largely inadequate, as the great abundance of dolomite in the geological past is at odds with its fairly rare occurrence in Holocene sediments (e.g., Hardie, 1987; Machel, 2004; Meister et al., 2013). The study of zoning in dolomite crystals provided important insights into dolomite formation mechanisms, showing that a number of processes, well known in limestone diagenesis, including recrystallization, dissolution, and void-filling cement precipitation, may be 57 common in dolostones too (e.g., Harris and Meyers, 1987; Cander et al., 1988; Gregg and Shelton, 58 1990; Gregg et al., 1993; Machel, 1997; Reinhold, 1998; Jones, 2005, 2007; Ehrenberg et al., 2006; 59 Choquette and Hiatt, 2008). Zoning refers to spatial differences of composition within a crystal 60 (Reeder, 1991) and, leaving aside sectoral zoning, may display a great variety of patterns: crystals 61 may be alternatively homogeneous (i.e., nonzoned), concentrically zoned with zone boundaries 62 parallel to crystal faces, concentrically zoned with irregular zone boundaries, or "chaotically zoned" 63 (i.e., displaying complex patchy distribution of compositionally different portions). Zoning reflects 64 changing conditions during crystal growth, from rapid growth in stable conditions, to steady state 65 growth under slightly changing chemical parameters, to more complex evolution of diagenetic 66 processes involving discontinuous growth, dissolution, and recrystallization. Cathodoluminescence, 67 because of its high sensitivity to minor geochemical changes in the diagenetic environment (e.g., 68 activator and quencher concentration, Eh and pH, ion activity, growth rates; Machel and Burton, 69 1991; Machel, 2000), is a useful technique to highlight zoning. Cathodoluminescence moreover allows identification of the most suitable portions of the crystals for carrying out further analyses 70 71 aimed at characterizing quantitatively the geochemical features of the different zones (e.g., Mg/Ca ratios, Fe and Mn content, δ^{18} O and δ^{13} C). 72

73 Studies on dolomitization, performed with this kind of petrographically controlled approach, 74 led recently to reinterpretations of previously described case histories. For example, Choquette and 75 Hiatt (2008) provided a new possible explanation of common fabrics in sucrosic dolostones such as 76 the so-called CCCR (cloudy-centered clear-rimmed dolomite: Murray, 1964; Sibley, 1982): they 77 showed that the cloudy cores consist of replacive dolomite, whereas clear rims consist of a 78 dolomite cement filling secondary pores generated by limestone dissolution. On the other hand, 79 dissolution of dolomite crystals followed by centripetal dolomite cementation in the resulting 80 hollows (inside-out dolomite: Jones 2007) has been proposed as an alternative hypothesis for 81 explaining complex zoning patterns that other authors related to recrystallization (Harris and 82 Meyers, 1987; Cander et al., 1988; Reinhold, 1998).

83 Complex zoning patterns have been recognized in dolomite contained in Middle Jurassic 84 dolomitic limestones of the Ligurian Brianconnais (Ligurian Alps, NW Italy) (Fig.1). Stratigraphic, 85 sedimentologic, petrographic, and geochemical evidence collectively indicate that none of the 86 above-mentioned processes can account for the observed pattern. This contribution does not discuss 87 all aspects of the dolomitization of the Jurassic limestones of the Ligurian Brianconnais; it is rather 88 focused on the description and interpretation of particular zoning patterns that may be of general 89 interest for researchers working on variably dolomitized strata. The purpose of this study is to 90 explore the possible importance of a different mechanism, a selective limestone replacement as 91 syntaxial overgrowths of dolomite around detrital grains.. The identification of this kind of dolomite 92 in fact documents the presence of terrigenous grains which otherwise could be unrecognized in 93 apparently pure allochemical rocks. This in turn may provide solid evidence of syndepositional 94 faulting that resulted in exhumation and erosion of older dolomitic formations. The diagenetic 95 evolution is also simplified as it changes from a complex sequence of events (dissolution, 96 reprecipitation, or recrystallization) to a single phase of dolomite growth around detrital cores. 97 Because it provides new insights, the syntaxially overgrown detrital dolomite (SODD) hypothesis 98 may be applicable to understanding other dolomites in the geologic record that do not find 99 satisfactory explanations in the existing models.

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GEOLOGICAL SETTING

The Briançonnais Domain is one of the first-order tectonic units of the Alpine orogen (Fig.
1). It crops out from the Swiss Alps to the Ligurian Alps, where it is labelled "Ligurian
Briançonnais." In the frame of Alpine paleogeography, the Briançonnais has been interpreted as a
highstanding block, individuated during Late Triassic-Early Jurassic rifting, along the distal portion
of the European continental margin, bordering the western Tethys basin (Vanossi et al., 1984;
Lemoine et al., 1986; Lemoine and Trümpy, 1987; Lanteaume et al., 1990; Mohn et al., 2010).
Alpine deformation and metamorphism of the Briançonnais Domain generally decrease westward,

i.e., from the internal to the external parts. The study area is located in the exterior part (External
Ligurian Briançonnais)(Fig. 1), where deformation generated pervasive tectonic foliations confined
to marly and clayey intervals of the succession (Piana et al., 2009). Consequently, primary
stratigraphic features, such as depositional geometries, facies, and microfacies, are largely
preserved in carbonate sedimentary units.

The Ligurian Brianconnais consists of Permian volcanic and volcanosedimentary rocks 114 115 overlain by a Mesozoic-Cenozoic sedimentary succession that includes (Vanossi et al., 1984; 116 Lanteaume et al., 1990; Bertok et al., 2011) (Fig. 2): Upper Permian (?)-Lower Triassic 117 conglomerates and littoral cross-bedded quartz arenite (Quarziti di Ponte di Nava, QPN: over 100 118 m) overlain by Lower Triassic lagoonal mudrock 10-15 m thick (Peliti di Case Valmarenca, PCV); 119 Middle Triassic peritidal dolostone and dolomitic limestone (Dolomie di San Pietro dei Monti, 120 DSPM: about 300 m), bounded at the top by a Late Triassic to Middle Jurassic stratigraphic hiatus 121 caused by subaerial exposure; Middle Jurassic inner-shelf limestone and dolomitic limestone 122 (Calcari di Rio di Nava, CRN: 20-90 m); Upper Jurassic pelagic limestone, locally showing a Rosso 123 Ammonitico facies (Calcari di Val Tanarello, CVT: 10-60 m), bounded at the top by an important 124 stratigraphic discontinuity; Upper Cretaceous hemipelagic sediment (Formazione di Upega, FU: 125 about 100 m); Middle Eocene nummulite-rich limestone (Calcari della Madonna dei Cancelli, 126 CMC: about 30 m), overlying another unconformity and followed by hemipelagic and turbiditic 127 sediment (Flysch Noir, FN). Clear evidence of Middle Jurassic to Cretaceous post-rifting, 128 syndepositional tectonic activity, with extensional and transcurrent components, has recently been 129 documented in the study area (Bertok et al., 2011, 2012). 130

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MATERIALS AND METHODS

This study is focused on the dolomite occurring in the Middle Jurassic CRN inner shelf
carbonates that range from almost pure dolostone to slightly dolomitic micritic limestone. Middle
Triassic dolomites have not been studied in detail, but only for purposes of comparison. Several

sections have been studied and sampled, spread over an area of about 10 km² (for location and 135 136 stratigraphy refer to Bertok et al., 2011). Petrographic studies of polished thin sections prepared from about 30 specimens were carried out by plane-light, cross-polarized-light, and 137 138 cathodoluminescence (CL) microscopy, performed with CITL 8200 mk3 equipment (working 139 conditions: approximately 17 kV and 400 µA) to identify zoning in crystals. Backscattered electron 140 imaging (BSE) of polished thin sections was also carried out with a Cambridge Stereoscan 360 141 SEM instrument, which allowed differentiation between calcite and dolomite on a microscopic 142 scale, and, together with microprobe analyses, provided an opportunity to relate CL colors and 143 intensities to intracrystal compositional changes. Twenty seven in situ quantitative microprobe 144 analyses on dolomite crystals were performed with an EDS Energy 200 and a Pentafet detector (Oxford Instruments) associated with the SEM. The operating conditions were: 15 kV accelerating 145 146 voltage, around 1 nA of probe current, and 50 seconds counting time. SEM-EDS quantitative data 147 (spot size = $2 \mu m$) were acquired and processed using the Microanalysis Suite Issue 12, INCA Suite 148 version 4.01; SPI natural mineral standards were used to calibrate the raw data; the RoPhiZeta 149 correction (Pouchou and Pichoir, 1988) was applied. Analytical statistical errors Σ on atomic weight 150 % are 0.08 for Mg and Fe and 0.13 for Ca.

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DOLOMITE: OCCURRENCE AND FEATURES

153 In the Mesozoic succession of the External Ligurian Brianconnais Domain, dolomite occurs 154 in the Middle Triassic DSPM and the Middle Jurassic CRN lithostratigraphic units. The DSPM 155 consists mainly of pure dolostones that exhibit different facies (mainly dolomicrite, massive or 156 thinly laminated, characterized by fenestrae or gypsum pseudomorphs, and subordinate peloidal grainstone with flaser bedding and breccias) all reflective of a peritidal depositional environment. 157 158 These rocks mainly consist of very finely to finely crystalline dolomites (less than 10 µm to tens of 159 μm) resulting from a nondestructive replacement of micritic sediments. Very coarsely crystalline 160 dolomite (up to some millimeters) also occurs as a cement filling shrinkage pores and vugs.

161 Replacive dolomite displays CL colors ranging from nonluminescent (NL), to moderate to dull red 162 and greenish, depending on the beds (Fig. 3); void-filling dolomite cements displays moderate- to 163 bright-red colors. EDS analyses show that replacive dolomite consists of systematically nonferroan 164 and nearly stoichiometric dolomite (Ca:Mg molar ratio ranging from 1.0:1.0 to 1.05:0.95; low-Ca 165 calcian dolomite, LCD, of Jones and Luth, 2002)(N=4). Al₂O₃, SiO₂, and K₂O have also been 166 detected (total percentage around 2-3%) which point to the presence of a minor clay fraction. 167 Middle Jurassic CRN limestones show a variable degree of dolomitization that generally 168 decreases from the stratigraphic bottom to the top and that ranges from complete (at the very base in 169 one section, lowermost 50 cm) to only minor (less than about 5% dolomite in the uppermost part). 170 The most widespread limestone lithofacies consist of mudstone to wackestone with sparse crinoid 171 fragments and benthic foraminifera. Millimeter- to centimeter-size angular to rounded clasts of 172 dolostone occur at the very base as a transgressive lag over the Upper Triassic – Lower Jurassic 173 subaerial discontinuity surface. Single dolomite crystals, up to 200 µm in size, with a pitted, 174 irregular outline locally occur as nuclei of coated grains (ooids, microoncoids) in the matrix of such 175 transgressive conglomerate (Fig. 4). In some sections, angular to rounded, millimeter- to 176 centimeter-size clasts of dolostone also are present in the lower part of the Middle Jurassic 177 limestone, in centimeters- to decimeters-thick beds of matrix- to clast-supported breccia (Fig. 5). 178 The common occurrence of shrinkage pores in dolostone clasts documents their provenance from 179 the underlying Middle Triassic DSPM. Dolomite in pure dolostone at the very base of the CRN 180 occurs mainly as subhedral to euhedral crystals with planar faces (Fig. 3); crystal size is fairly 181 homogeneous, at approximately 100 µm. CL observations reveal that most dolomite crystals contain irregularly shaped cores, mainly NL but also showing dull red and greenish luminescence. 182 183 The cores are surrounded by a thin bright orange rim. Scattered dull-blue-luminescing quartz grains 184 with the same size as dolomite crystals can also be recognized (Fig. 3) 185 Dolomite in CRN dolomitic limestone occurs as euhedral to subhedral crystals of variable

186 size (15 to 150 μ m). They have irregularly shaped cores, 10 to 100 μ m in size. Core edges are

187 generally highly irregular, angular, and with embayments, whereas planar edges and subrounded 188 shapes are uncommon (Figs. 6, 7, 8). Cores show the same CL features as those of the underlying 189 pure dolostone (mainly NL but also dull red and greenish) but are surrounded by more developed 190 and complexly zoned rims. The most common pattern is represented by an inner bright-orange 191 zone, directly surrounding the core, followed outward by a middle moderate-orange zone and by an 192 outer NL zone (Figs. 6, 7, 8). Local deviations from this common pattern include additional 193 discontinuous, bright-orange hairline zones. The markedly different colors enable clear observation 194 of the geometry of the interfaces between the different zones. Whereas cores display highly 195 irregular edges, with smooth to angular to very jagged outlines, outer zones tend to increasingly 196 approach the rhombic habit, so that each zone is thicker where the core edge was farther from the 197 rhomb faces. A quasi-perfect parallelism between zone interfaces and euhedral outer faces of the 198 crystal usually is reached only by the moderate-orange-NL boundary. The small size of the cores 199 and zoned rims commonly hinders accurate EDS analyses. However, where possible, analyses 200 reveal that NL nuclei and orange CL zones are nonferroan, whereas the NL outer zone is commonly 201 slightly ferroan (0.7 – 2.0 mole % FeCO₃). Moreover, the Ca:Mg ratio varies from 1.05:0.95 to 202 1.07:0.93 (average 1.06:0.94) in the cores (low-Ca calcian dolomite, LCD, of Jones and Luth, 2002) 203 (N=2) and from 1.08:0.92 to 1.19:0.81 in the rims (average 1.13:0.87, i.e., mostly high-Ca calcian 204 dolomite, HCD, of Jones and Luth, 2002) (N=11) (Fig. 9). BSE imaging also reveals zoning with 205 crystals exhibiting homogeneous, darker cores and lighter rims. Outer rims also are characterized by 206 brighter micrometer-size irregular spots composed of calcite (Fig. 10).

Polycrystalline dolomite lithoclasts are also present; they are up to some hundred
micrometers in size and consist of decimicrometer-size crystals. They show a homogeneous
cathodoluminescence, which may be greenish, dull red, or NL, and are not surrounded by zoned
rims (Fig. 11). The Ca:Mg ratios (from 1.03:0.97 to 1.04:0.96) (N=2), nonferroan composition, CL
features, and presence of SiO₂ and Al₂O₃ allow comparison of these polycrystalline lithoclasts with
Triassic dolostone.

213	Dolomite also occurs as a coarsely crystalline mosaic, infilling a network of mainly
214	subvertical veins, up to 2 mm wide, which are locally developed. Veins crosscut the Middle Triassic
215	DSPM -Middle Jurassic CRN unit boundary and taper out, within some decimeters higher up in the
216	section, where the Jurassic strata display a gradual transition from fully dolomitized, at the base, to
217	partially dolomitized. A marked zoning of dolomite filling the veins is immediately apparent from
218	CL observation, with the following sequence (from inner to outer parts): I) NL, II) bright orange,
219	III) moderate orange, and IV) NL (Fig. 12). The two NL zones are ferroan $(1.7 - 3\% \text{ FeCO}_3)$ (N=8)
220	whereas the orange luminescing zones are nonferroan as is also well evidenced by BSE images
221	(Fig. 12).
222	
223	DISCUSSION
224	The features of dolomite observed in the Middle Jurassic carbonate rocks of the External
225	Ligurian Briançonnais Domain can be summarized as follows:
226	1) in the lower part of the CRN, lithoclastic breccia or conglomerate with dolostone clasts
227	are interbedded with micritic limestone. These beds have been interpreted as the result of storm-
228	induced currents transporting offshore clasts eroded from rocky coasts locally developed on Middle
229	Triassic, subaerially exposed, dolostone (Bertok et al., 2011);
230	2) monocrystalline dolomite grains occur as nuclei of coated grains in the lower part of the
231	CRN;
232	3) dolomite crystals are present throughout the CRN but are particularly abundant in the
233	lower part, where they are associated with quartz grains of comparable size and polycrystalline
234	dolomite lithoclasts up to some hundreds of micrometers in size;
235	4) dolomite crystals are zoned under CL and display homogeneous cores and zoned rims;
236	cores are irregularly shaped, whereas rims show increasingly better developed rhombohedral crystal
237	faces progressing outwards;

238 5) cores of dolomite crystals, occurring side by side in the same thin section, show a
239 conspicuous variability in CL features (NL, dull red, greenish);

6) independently of the size and CL color of the core, rims show the same succession of CLzones;

242 7) vein-filling sparry dolomite mosaics show four CL zones (NL, bright orange, moderate
243 orange, NL), three of which (bright orange, moderate orange, NL) correlate with rims of rhombs;
244 8) polycrystalline dolomite lithoclasts are not surrounded by zoned rims;

9) compositional features (CL, BSE, Ca:Mg ratios, ferroan vs. nonferroan, presence or
absence of SiO₂ and Al₂O₃) show that cores are different from rims but indistinguishable from
Middle Triassic dolostones and polycrystalline clasts occurring in the lower part of the CRN.

Points 1 and 2 demonstrate that a dismantlement of Middle Triassic dolostone was taking 248 249 place in the Middle Jurassic during deposition of CRN. Finely crystalline dolostone gave rise to 250 polycrystalline lithoclasts of a size ranging from fine sand to pebbles. More coarsely crystalline 251 dolostone or fenestral pore-filling dolomite cements, instead, could weather out to monocrystalline 252 grains that were transported to a shallow marine environment where they acted as nuclei for coated 253 grains. Point 3 confirms that terrigenous grains were shed into the CRN basin and documents that 254 denudation and exposure affected also the Lower Triassic quartzarenites (QPN). Points 4, 5, and 6 255 document that the cores of dolomite crystals are primary elements of the Middle Jurassic sediment 256 whereas rims result from a common diagenetic evolution recorded by all dolomite rhombs. Point 7, 257 together with Point 4, proves that rims and vein-filling dolomite are coeval and cogenetical and that 258 rims grew outwards starting from the outer edges of cores. However, it is important to note that the 259 innermost zone of vein dolomite, which is NL, ferroan, and thus brighter in BSE, has no counterpart 260 in the rhombs and cannot be related to the NL cores (Figs. 9, 12, 13). Point 8 shows that 261 monocrystalline cores were necessary to trigger dolomite precipitation, which, conversely, did not 262 take place around fine-grained, polycrystalline lithoclasts. Point 9, together with Points 1, 2, 3, and

5, indicates that both polycrystalline clasts and dolomite crystal cores could be fragments of Middle
Triassic DSPM dolostone reworked into the Middle Jurassic CRN.

265 Detrital dolomite is not a novelty in the geological literature. It has been reported in a wide 266 array of stratigraphic and paleoenvironmental settings. The most obvious occurrence is in terrigenous sediments whose source areas include carbonate successions (e.g., Ordovician non 267 268 marine sandstones, Texas: Amsbury 1962; Cretaceous coastal plain sandstones, Utah: Taylor et al 269 2000, 2004; Cretaceous glauconitic sandstones, Alberta: Young and Doig, 1986; Miocene 270 turbidites, Italian Apennines: Gandolfi et al., 1983). Dolomite grains found in mixed sediments 271 deposited in cool-water platforms (Plio-Pleistocene, Australia: Bone et al 1992, James and Bone 272 2007; Miocene, Menorca: Freeman et al., 1983) have a comparable origin. Carbonate successions may include limited lithosomes of detrital dolomites interpreted as infillings of karstic cavities (e.g., 273 274 Devonian, Canada: Morrow et al 1986; Ordovician, Virginia: Mussman and Read, 1986). Recent 275 deep-sea sediment also contains detrital-dolomite-rich beds that have been correlated to climatic 276 changes in turn affecting aridity, and thus eolian transport (e.g., Cullen et al 2000), or ice sheet 277 dynamics (Andrews and Tedesco, 1992; Knies et al., 1999; Ji et al 2009). Detrital dolomite was also 278 reported in ancient marine limestones and related to eolian transport of penecontemporaneous 279 dolomite from tidal flats or from the erosion of older carbonate rocks (Devonian, New York: 280 Lindholm, 1969; lower Palaeozoic, Newfoundland: Coniglio and James, 1988). The most 281 impressive report of a sedimentary body consisting almost entirely of terrigenous dolomite is the 282 Pennsylvanian Atoka Dolomite, several hundred meters thick, resulting from deposition in a fan-283 delta environment of sediments eroded from Ordovician dolomites (Lyday, 1985). Many papers, 284 moreover, highlight the important role of detrital dolomite grains as nuclei for growth of authigenic 285 dolomite (Lindholm, 1969; Freeman et al., 1983; Bone et al 1992). 286 On the basis of the data and considerations reported above, it appears that the dolomite in

the Middle Jurassic CRN resulted from a process of replacement of calcareous sediment occurring
as selective overgrowth of authigenic syntaxial dolomite around silt- to sand-size, irregular,

289 monocrystalline grains of detrital dolomite (SODD: syntaxially overgrown detrital dolomite) (Fig. 290 13). These grains consist of clasts of reworked Middle Triassic DSPM dolostone showing non-, red 291 or greenish luminescence, depending on the stratigraphic level from where clasts were sourced. Silt-292 to sand-size dolomitic detritus came from the same areas as the breccia-bed clasts, but it was finer 293 grained, scattered within Middle Jurassic sediment, and progressively decreasing in quantity going 294 up-section. The uppermost part of the Middle Triassic dolostones between the Late Triassic and the 295 Early Jurassic underwent a prolonged emersion that locally generated karstic cavities with terra 296 rossa infillings (e.g., Faure and Megard-Galli, 1988; Decarlis and Lualdi, 2008). The Middle 297 Jurassic sea consequently transgressed over rocky coasts made up of dolostones that had never been 298 deeply buried and thus were likely characterized by a typical intercrystalline porosity, possibly 299 enhanced by emersion-related dissolution. The mechanical action of shallow marine processes 300 (waves, storms etc.) led to the surficial disaggregation of these rocks, producing both coarse 301 polycrystalline clasts and finer-grained debris of single dolomite crystals whose external shape may 302 reflect the original euhedral outline, mechanical breakage, or chemical corrosion. The limited 303 degree of transport, probably mainly due to short-lived storm episodes (cf. Bertok et al., 2011), 304 accounts for the very low roundness of detrital cores.

305 The occurrence of detrital dolomite throughout the whole Middle Jurassic CRN, some tens 306 of meters thick, shows that the reworking of the Middle Triassic dolomites was not limited to the 307 earliest phase of transgression. This in turn implies that the Middle Jurassic transgression did not 308 take place over the top of a flat platform but affected a rugged topography that allowed the survival 309 of coastal or even emergent portions of the former Triassic platform. This is also confirmed by the 310 direct superposition of Upper Jurassic limestones over Middle Triassic dolostones in adjacent areas 311 (Vanossi, 1965) and by independent stratigraphic and sedimentologic evidence pointing to faulting 312 processes before and during CRN deposition (Bertok et al., 2011).

313 Detrital dolomite grains, now corresponding to the cores of zoned dolomite rhombs, acted as 314 nucleation sites for authigenic dolomite overgrowth. The widespread micrometer-size calcite

315 inclusions, very well imaged by BSE (Fig. 10) in the rims but absent in the cores, likely consist of 316 undolomitized portions of the original calcareous sediment, possibly corresponding to very fine-317 grained fragments of skeletal grains.

318 At the base of the CRN succession, where detrital dolomite grains were closely packed, pure 319 dolostone were formed where the entire sequence of authigenic dolomite zones could not be 320 recorded; the latter were thicker and well developed in partially dolomitized mud-supported facies 321 with widely spaced dolomite grains. Each younger zone of authigenic dolomite contributed to 322 improve the outer crystal, habit increasingly approaching the rhombohedron that is almost perfectly 323 developed with the last, NL growth stage (Phases 3 and 4 in Fig. 13). This preferential growth 324 towards the rhombohedron edges, and in particular the acute ones, is reminiscent of the syntaxial 325 cements around echinoderm plates that grow at faster rates perpendicular to the plate edge i.e., 326 along the c axis (e.g., Evamy and Shearman, 1965; Walkden and Berry, 1984).

327 The data also permit some thermodynamic inferences about the chemistry of the diagenetic 328 fluids flowing through these sediments (cf. Machel, 2004). The occurrence of a first NL ferroan 329 dolomite generation only within veins could be explained as the result of an early cementation 330 phase by fluids that were supersaturated with respect to dolomite but not undersaturated with 331 respect to calcite (phase 2 in Fig. 13). They therefore allowed precipitation of dolomite in open 332 fractures, but not replacement of calcareous sediments. Subsequently, fluids became undersaturated 333 with respect to calcite and only slightly supersaturated with respect to dolomite, so that dolomite 334 could precipitate by syntaxial overgrowth around a dolomite substrate. This substrate was provided 335 by detrital grains in sediments and by the first-stage dolomite crystals in veins.

Dolomite crystals with comparable zoning patterns have been commonly reported in the literature. Basically, interpretations call upon recrystallization during burial (e.g., Harris and Meyers, 1987; Cander et al., 1988; Reinhold, 1998), dissolution taking place during crystal growth (e.g., Gregg et al., 1993), or intracrystalline dissolution of the core and precipitation of dolomite cement in the resulting pore (inside-out dolomite: Jones, 2005, 2007).

341 In the case studied here, dolomite nuclei show a variety of CL emissions (NL, dull red, 342 greenish) and are surrounded by rims with the same dolomite CL stratigraphy (bright orange, 343 moderate orange, NL from the core outwards). The NL dolomite of the outer rim is a ferroan HCD 344 whereas that of the NL nuclei is a non ferroan LCD, i.e. , they are compositionally very distinct. 345 Moreover, the variability in CL of the cores indicates that they cannot be interpreted as cements 346 filling intracrystalline voids formed by selective dissolution, unless several phases of very patchy 347 precipitation of dolomite cements with different CL are taken into account. Because such complex 348 process seems very unlikely and no evidence of dissolution is recognizable in the dolomite 349 lithoclasts, the inside-out model (Jones, 2007) cannot be applied to our case. Furthermore, the good 350 correlation of the CL zones bright orange, moderate orange, NL in core-surrounding rims from 351 rhombs to vein-filling dolomite definitely proves that rims grew outwards and confutes the inside-352 out hypothesis that conversely would involve an inward growth of dolomite cement in a dissolution 353 cavity.

354 The absence of dissolution features, both in dolomite lithoclasts and in vein-filling dolomite 355 where CL zones are separated by perfectly planar boundaries (Fig. 10), is a valid argument to 356 exclude the possibility of an interruption in crystal growth, associated with some dissolution, and 357 followed by renewed precipitation over a pitted surface, as proposed by Gregg et al. (1993). The 358 shape of the surfaces separating rim dolomite zones (bright orange, moderate orange, NL), roughly 359 subparallel to core edges and developing increasingly euhedral habits progressing outwards, further 360 supports this conclusion and allows to rule out also the hypothesis of recrystallization (Harris and 361 Meyers, 1987; Cander et al., 1988; Reinhold, 1998). The latter would have produced a more 362 chaotic, patchy, luminescence.

The recognition that zoned dolomite crystals may be due to diagenetic overgrowth around inherited, detrital grains goes beyond the mere petrographic aspect and involves wider geological implications. The most relevant conclusion of general interest of this study is that dolomite crystals showing the features here described are *per se* evidence of the presence of detrital grains of

367 extrabasinal origin. This may be trivial in terrigenous or mixed sediments but is of utmost 368 importance in presumably pure allochemical rocks, such as dolostones or dolomitic limestones, in 369 which the growth of diagenetic dolomite masks the presence of a pristine inherited clastic 370 component. If dolomitic formations occur stratigraphically below the SODD-bearing rocks, as in 371 the present case study, some kind of faulting leading to superficial exposure and erosion of 372 previously buried rocks is documented. If instead there is no dolomitic body in the local 373 stratigraphy, the source of the detrital dolomite cores should be searched in allochthonous terranes. 374 In both cases recognition of SODD may provide an additional or even unique clue to 375 syndepositional tectonics.

The second conclusion refers to the diagenetic evolution. The hypothesis here proposed of syntaxially overgrown detrital dolomite implies only a single phase of dolomite precipitation whereas other models, calling upon dissolution, reprecipitation, or recrystallization, involve a more complex diagenetic evolution with obvious implications over patterns of fluid flow through sedimentary-basin infills.

Moreover, the SODD hypothesis imposes a re-evaluation of the actual degree of dolomitization in dolomitic limestones and dolostones since only the overgrowths could be due to calcite replacement. In principle, some dolostones could consist mostly of detrital dolomite, with authigenic dolomite representing only a minor part of the whole rock volume, as it has indeed been reported already in literature (e.g., Lyday, 1985).

Lastly, this study shows that dolomitization may be very selective and it may take place only around detrital dolomite grains. It is worth highlighting that in the absence of such clasts no dolomitization takes place and the flow of potentially dolomitizing fluids leaves no evidence. On the basis of what is discussed above, the main difference of this paper with respect to the one by Choquette and Hiatt (2008), which treats a similar topic, concerns the implications. The major conclusion by Choquette and Hiatt (2008) is that a significant part of sucrosic dolostones results from free-space cementation and not replacement. The detrital origin of dolomite cores was just

393 hypothesized, as a possible alternative to an authigenic origin, due to their small size, substantially 394 of a few micrometers, making them not easily visible in thin section. In the case described in the 395 present paper, dolomite cores commonly reach a fine-sand grain size, give rise to a complex zoning 396 of dolomite rhombs which is perfectly recognizable in thin section, and represent a significant 397 portion of the whole dolomite volume. Therefore, the focus here lies in the proposal of a further 398 model for explaining irregularly zoned dolomite rhombs that adds to the existing ones involving 399 dissolution during growth, dissolution after full rhomb growth, and recementation, or 400 recrystallization.

- 401
- 402

CONCLUSIONS

403 - Stratigraphic, sedimentologic, petrographic, and geochemical evidence from the Middle
404 Jurassic CRN dolomitic limestone and dolostone of the Ligurian Briançonnais Domain (French405 Italian Ligurian Alps) document that irregularly zoned dolomite crystals consist of two distinct
406 domains: an irregularly shaped core of detrital origin and an authigenic rim related to
407 postdepositional diagenesis.

408 - Dolomite cores originated as the monocrystalline component of a detrital input that
409 included also polycrystalline clasts ranging in size from fine sand to pebbles. They were eroded
410 from exposed portions of Middle Triassic dolostone and delivered to the shallow marine CRN
411 basin.

Dolomitization of Middle Jurassic CRN limestone was very selective and proceeded only
around the irregular fragments of detrital dolomite grains, giving rise to syntaxial overgrowths.
Dolomite overgrowth around detrital cores provides another possible explanation for
irregularly zoned dolomite rhombs in addition to dissolution, reprecipitation, or recrystallization. In
spite of a great deal of research on dolomitization, such a process has not been kept in due
consideration so far. Although more than forty years have passed, a statement by Lindholm (1969)
seems to be still a very living issue: "The role of detrital dolomite in carbonate sedimentation and

419	diagenesis warrants attention in future works." Actually not all dolomite in a dolomite-bearing
420	carbonate rock may be due to dolomitization.
421	- The recognition of SODD documents the presence of terrigenous grains which otherwise
422	could be unrecognized in apparently pure allochemical rocks. It may also provide indirect evidence
423	of syndepositional tectonics resulting in fault-related exhumation of previously buried formations or
424	even the emplacement of allochthonous units.
425	
426	
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433	
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- 575
- 576

577 FIGURE CAPTIONS

Figure 1. Simplified geological map with the main tectonostratigraphic units and domains of the
southwestern portion of the Alps. The black square indicates the study area. (Redrawn after Bigi et
al., 1990).

581 Figure 2. Log of the stratigraphic succession of the study area. QPN Quarziti di Ponte di Nava

582 (quartzarenite); PCV Peliti di Case Valmarenca (mudrock); DSPM Dolomie di S. Pietro dei Monti

583 (dolostone and dolomitic limestone); CRN Calcari di Rio di Nava (limestone and dolomitic

584 limestone); CVT Calcari di Val Tanarello (pelagic limestone); FU Formazione di Upega (marly

585 limestone); CMC Calcari della Madonna dei Cancelli (nummulite-rich limestone); FN Flysch Noir

586 (interbedded mudrock and sandstone).

587 Figure 3. A) Transmitted-light photomicrograph and B) CL image showing the stratigraphic

588 boundary between the Middle Triassic DSPM and the overlying the Middle Jurassic CRN. Note: the

589 greenish luminescence of the very finely to finely crystalline DSPM dolostones (compare with

590 Figure 11); the coarser size of the subhedral to euhedral dolomite crystals in the CRN, composed of

591 irregular cores with different luminescences (NL, dull red) surrounded by a thin bright orange rim;

the occurrence of dull blue luminescing quartz grains.

593

594 Figure 4. Transmitted-light photomicrograph showing a grainstone as the matrix of the

transgressive conglomerate locally occurring at the base of the Middle Jurassic CRN and including

lithoclasts of Middle Triassic DSPM: note a dolomite crystal with a pitted edge at the core of acoated grain.

598

Figure 5: Clast- to matrix-supported breccia bed with angular to rounded clasts made of light
Middle Triassic DSPM interbedded with micritic limestone in the lower part of the Middle Jurassic
CRN. Tip of pencil at the bottom for scale is 7 cm long.

602

Figure 6. A) Transmitted-light photomicrograph of a partly dolomitized Middle Jurassic CRN
micritic limestone. The white square indicates the CL close up of Fig. 6B. B) CL image of the
squared area in Part A. Note: the commonly euhedral habit of dolomite crystals; the internal zoning;
the irregular shape of the nonluminescent cores. For further details see text.

607

Figure 7. A) Transmitted light photomicrograph and B) CL image of a partly dolomitized Middle
Jurassic CRN micritic limestone. Note in the CL image the differently luminescing cores of
dolomite crystals, ranging from NL to dull red to greenish.

611

Figure 8. A) Transmitted light photomicrograph and B) CL image of a partly dolomitized Middle
Jurassic CRN micritic limestone. Note in the CL image the differently luminescing cores of
dolomite crystals, ranging from NL to moderate red.

615

Figure 9. Sketch summarizing the main features of the different zones of dolomite rhombs. Ca:Mg
ratios are average values. Among the three possibilities of CL colors of the cores (NL, red and
greenish), the green one has been chosen not to make confusion with the red or NL color of rim
zones.

621	Figure 10. BSE image of a partly dolomitized Middle Jurassic CRN limestone. Note: the contrast
622	between the homogeneous core and the outer rims spotted with brighter micrometer-size calcite; the
623	lighter color of rims compared to that of the core, related to higher amounts of Ca in dolomite.
624	
625	Figure 11. A) Transmitted-light photomicrograph and B) CL image of a partly dolomitized Middle
626	Jurassic CRN micritic limestone. The CL image shows the greenish luminescence of a finely
627	crystalline lithoclast of Middle Triassic DSPM (compare with Fig. 3).
628	
629	Figure 12. A) Transmitted-light photomicrograph, B) CL image, and C) BSE image of a dolomite-
630	filled vein crosscutting the finely crystalline Middle Triassic DSPM dolostones. The white square in
631	Part B indicates the BSE close-up of Part C. In the CL image, four growth zones (I to IV) of
632	dolomite cement are clearly evidenced by NL, bright orange, moderate orange and NL
633	luminescence. In the BSE image the higher Fe content of zones I and IV is evidenced by lighter
634	colors.
635	
636	Figure 13. Cartoon sketching the main phases (1 to 4) of formation of the dolomite. Detrital
637	fragments of dolomite (in green) are deposited together with carbonate mud in Middle Jurassic
638	limestone (1). A first generation of NL dolomite (in black) precipitates only as cement in fractures
639	(2). The subsequent flow of fluids undersaturated in calcite and slightly supersaturated in dolomite
640	results in formation of the same dolomite zones (in bright red, moderate red and dark grey) both in
641	veins and as syntaxial overgrowths around detrital cores (3-4).
642	









- 651 Fig. 2



- 654 Fig. 3



- 657 Fig. 4



660 Fig. 5



664 Fig. 6







- Fig. 8



- 676 Fig. 9



- 679 Fig. 10



683 Fig. 11





686 Fig. 12



