# Review of "Fault-related dolomitization in the Montagna dei Fiori Anticline (Central Apennines, Italy): Record of a dominantly pre-orogenic fluid migration. Se-2018-136

This manuscript presents field, petrographic and geochemical data from non-stratabound dolomites in a complex tectonic setting, and interprets their geofluid origin (parent fluids, timing) in the context of the tectonostratigraphic history.

It is coherent and logically organised. Aspects of the written English need minor improvement (punctuation, plurals, word order, etc); it will benefit from a final revision by a native English speaker.

The data are generally of good quality, and the interpretations are mostly justified from the results presented. In any study such as this, with limitations imposed by the ability to sample all the phases, there is necessarily some latitude or flexibility in the deductions that can be made. However, the authors do a good job of considering alternative possibilities for the fluid sources and timings.

My only issue with the paper is that the authors have not really considered whether there are wider implications or generic advances that can be made from the research. It presents itself as a case study, albeit one with a good integration of structural and diagenetic data. But what is the wider impact that will attract a non-specialist readership? Within the paper the authors all but admit that their findings are only modestly advanced from those of Ronchi and co-workers fifteen years ago (lines 638-642). I had hoped to see more progression in the science, and maybe the authors need to more thoroughly and critically evaluate the Ronchi model in the light of their new data. They could also work the structural data more – rather than just considering fault orientations and timings, what about the character and extent of the damage zones associated with different fault types / generations, and their relationship to the size and shape of dolomite bodies? What determines the lateral extent of dolomites? Is it other faults / fractures, or a gradual reaction front?

One generic aspect that the authors could address is implications for reservoir potential in analogues for this setting. The preponderance of planar dolomite is significant because planar dolomite is usually very beneficial for porperm (unlike many examples of hydrothermal dolomitization that feature tight nonplanar dolomites). Are there dolomitised plays in the Middle East that this study could be compared to (Zagros Mountains for example?), or maybe in Mexico?

Another factor of interest, largely by-passed in the text, is what drove the fluid circulation necessary to cause massive dolomitization when the low temperatures argue against a hydrothermal syn-rift system. Can the authors attempt a mass balance to estimate the order of magnitude fluid volumes needed? Maybe the dolomitization occurred in the down-flowing (cool) limb of a convection cell established on syn-rift faults that breached contemporary sea bed? Or does the dolomite zoning imply a pulsed fluid flow associated with strain cycling or seismic valving? I recommend the recent papers by Hollis and others on the Hammam Faraun fault and related syn-rift dolomitization. Are the D1-2 dolomites formed in a similar manner to this geologically younger example? Likewise, with the later dolomitization, which structures would have been open during compressional tectonics and able to serve as conduits for substantial fluid volumes?

If the authors address these issues their paper, which is already technically good, it will have much greater impact and interest across the sedimentary and structural geoscience community.

I have some more **specific comments** – these are tagged by line number or Figure number:

Line 43: The paper describes the role of evaporite-sourced fluids in the dolomitization process, but I am not sure that it illustrates a controlling role of evaporitic detachments. These may have influenced the tectonic development, but if it is believed that they directly controlled the dolomitization this needs to be specifically discussed later in the paper. Emphasized more in the text

Note the abstract is quite long-winded. It would be good to make it more succinct and punchier. Addressed

Line 69: The Castel Manfrino Dolostones are not labelled in Fig. 1 or Fig. 2b. Added in Fig.1

Line 73, 76: Did Ronchi (2003) base her study on the mapping of Mattei (1987)? Maybe there needs to be a couple of sentences describing Ronchi's findings so that it can be more clearly shown that the understanding has moved on. Added to text

Line 79-83: This is very long-winded and vague. It either needs to be shortened or to include specific details. The sentence is shortened.

Line 129: Given that the early dolomitization (D1-2) is later ascribed to the syn-rift stage, it would be useful to briefly describe the facies and architectural character of the syn-rift carbonates. For example, were they preferentially developed on footwall highs, in which case there was likely a juxtaposition of permeable high energy facies against faults that later hosted fluid flow? Addressed

Line 135-137: It may be a matter of debate, but the authors need to either provide the conflicting evidence or at least express a view and justify it. The sentence is deleted as further discussion is not the focus of this research

Line 152: Can the Montagna dei Fiori fault be indicated / labelled on Fig. 1d? Addressed

Line 164: Ground truthing implies that the features had previously been mapped out using remote data. If so, this should be included in the methods. Addressed

Line 167: So far as I can see, the Sibley and Gregg (1987) terminology (planar-e, planar-s, nonplanar) is <not> used anywhere in the paper, so either it needs to be incorporated or this sentence should be removed. The sentence and related references are removed

Line 186: Can the reproducibility  $(\pm 0.1\%)$  be smaller than the precision  $(\pm 0.2\%)$ ? The inter-lab reproducability is  $\pm 0.1\%$  means the measurement for the same sample in two different labs has a difference of  $\pm 0.1\%$ 

Line 224: Bugarone Formation is not shown on Fig. 1 or Fig 2. Addressed Line 231: Is the wider distribution of dolomitized intervals related to the topography of the valley and the exposures? If not, what is the relationship? Addressed

Line 238: I suggest not using "overprinted", which implies the original fabric / lithology is lost. Why not just use "cross-cut"? (or even just "cut") Addressed

Line 258 and elsewhere: "Dull" is not a colour! Addressed

Line 261 onwards: There could be a bit more detail on the dolomite distribution and fabric with respect to host rock facies. Is it all texturally destructive, is there any textural or mineralogical selectivity, were grainy or muddy facies preferentially dolomitized (controls by permeability versus reactive surface area......?) Addressed

Line 272: There is an issue because CV1, CV2 etc. are introduced before they have been defined and described. I suggest starting section 4.2 with a paragenetic summary to alleviate this problem. Addressed, paragenesis is presented in Fig. 14.

Line 278: By using "frequently" the text suggests that sometimes (infrequently) D2 post-dates bed-parallel stylolites. Is that the case? Addressed

Line 284-285: This sentence needs a figure citation. Addressed

Line 297: Repetition of "euhedral to anhedral" (cf. line 295) – note this is not Sibley and Gregg terminology. Nor is "tightly packed texture" in line 279. Addressed

Line 305: I do not think one dolomite can "recrystallize" another. Recrystallization is a solid-state process that increased mineral stability. To demonstrate it might need data on the ordering, crystallinity and stoichiometry of D1/2 versus D4 (do the authors have any XRD data?). What is more likely is that D4 has locally replaced D1 and D2 by a dissolution-precipitation mechanism. However, the text lacks a clear description of the evidence for replacement. I recall papers by Mazzullo and by Machel that discuss this – it would be good to list the criteria for this case. Addressed

Line 330: In Fig. 11C, D the dolomite does not appear to be yellow-orange, it looks more like orange-brown. Addressed

Line 332: How wide was the extensional fault master plane? Please supply the range of widths (and lengths where possible) of the different vein generations. It is addressed for vein generations.

Line 335-336: What is meant by "with no evidence of physical disruption"? Does it mean that CV3 always passively overgrows D5 in voids and never cuts it? If so, it is easier to say this. Addessed

Line 336: Translucent is not a colour. Addressed

Line 334: What colours are the zones? Addressed

Line 367-368: Rather than "the presumable Lower Jurassic marine dolomites" — which are hypothetical — it is better to say the values are lower than those expected for Lower Jurassic seawater dolomites. Addressed

Line 391: "While....." indicates there should be a second part to the sentence. Addressed

Line 396: What is the lithology of these samples? Addressed

Line 401: Please add a sentence or two on the fluid inclusion petrography and distribution – do inclusions follow growth zones or are they randomly distributed? Are they all primary or are some pseudosecondary? What are their shapes and what are the liquid:vapour ratios in the 2-phase examples? Also, in reporting the results for different cements please give the number of inclusions the ranges are based on (n=). Addressed

Line 409-410: What is the purpose of nucleating a bubble for measurement of freezing temperatures? Addressed

Line 477-478: This sentence appears out of place or at least needs clarification. More than two values are needed to demonstrate a progression. Addressed

Line 503-507: Yes, this makes sense if the veins are filling tension gashes associated with stylolites – such as system is likely to be buffered by the dissolving carbonate. Maybe make this point more explicitly, and contrast with vein types that were more extensive and would have allowed allochthonous fluids to pass through with minimal host-rock interaction. Addressed

Line 518: Hendry et al. (2015) did not discuss  $^{13}$ C enrichment from  $CO_2$  outgassing due to evaporation. They made the point that negative covariance in C and O isotopes within veins could be due to precipitation during  $CO_2$  outgassing related to pressure changes. Addressed

Line 524-551: This is good but is a very long paragraph. Can it be made more succinct? Addressed

Line 550-551: The final sentence needs rewriting; what was confined, the thrust wedge or the fluids? Addressed

Line 556: In the preceding section there is very little mention of fluid mixing. Could the poorly correlated Th, salinity and stable isotopic data reflect precipitation from allochthonous fluids as they mixed with in situ fluids (and cooled)? Degrees of mixing (and of water-rock interaction) may have different from fault to fault

- is it really likely that the hydrogeological systems was as simple as is being presented here? The obtained

data show no systematic variations from fault to fault. Thus, existance of different local hydrological systems cannot be addressed. The sentence is revised ad completed

Line 575-579: Please rewrite this sentence – it tries to say too many things at the same time. Addressed Line 584: Doesn't the displacement of D1-2 on these faults indicate that the dolomite formed before faulting? What is the critical evidence that it is genuinely syn-rift? The syn-rift deposits (Corniola Formation) is affected by these dolomites. Addressed more in the text

Line 590: if D1-2 were related to basement-cutting faults, why are the Sr isotope values much less elevated than for D3 and D4? There is no other alternative for radiogenic Sr source. This is the case for all of the dolomite types. Maybe less basement deriven fluids were involved in D1.

Line 656-657: Please explain how hydrothermal fluids were able to circulate in the compressional tectonic regime – which structures were able to be in tension and therefore transmissive rather than sealing?

Addressed

Line 1139: The cross-cutting relationship in Fig. 8a, b is not very evident. Addressed Lines 1142-1148: Should this discussion be in the main text rather than in the caption? This has been made to avoid a longer discussion.

Fig. 2b: It would help if the colours and ornaments matched Fig. 8a (e.g. Salinello Fm). The text size needs to be increased for better legibility. Addressed

The stereonet data are good, but very little use is made of them in the text of the paper. Addressed in the figure caption

Fig. 5: Please increase the text size and make 5c larger – it is too small to see clearly. Addressed

Figs 6-9, 11: Some of the CL images could be a bit sharper and maybe with increased contrast to better discriminate the dolomite types. Addressed

Fig. 12: The symbols for D3 vs. CV3 and mixed dolomite vs. CV1 are too similar (especially given the small size). I am also not clear how Fig. 12b relates to Fig. 12a; maybe split the legend between the two plots according to what is in them – that might help. Addressed

Fig. 14: How were the burial temperatures in the burial history determined? What assumptions are they based on? Addressed

Fig. 15: I like this figure but I'm still not sure what the fluid flow pathway is in (b). Maybe a broader tectonic context diagram is needed showing expulsion of fluids from the foreland (if that is where they are coming from?). The fluids were migrated from hinterland (now indicated on the sketch) rather than forland.

I hope these comments are helpful, and I look forward to seeing the paper published in revised form.

Jim Hendry

Tullow Oil Ltd, Dublin

## **Specific comments:**

- 1) Abstract: The abstract can be shortened substantially, yet it is missing key information. It provides too much detail of some aspects of this work but lacks equivalent detail in other cases. For example, why are calcite-filled veins not mentioned here? Weren't they a main focus of this study? A more succinct and balanced abstract is required. Also, the abstract would benefit from a "punchline" or statement of the broader implications of this work at the end. What did you learn about the extent of dolomitization near faults? How is this relevant for porosity/permeability evolution and fluid flow in dolomitized, carbonate-hosted hydrocarbon reservoirs and aquifers? Addressed
- 2) Introduction: You may want to consider adding a short statement about why some fault-zones become dolomitized but others don't. What are the requirements? What can you learn from outcrops that you cannot from core alone? I would say that the main benefit would be the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D. Addition of such a field-relations analysis would greatly improve the impact of this work. Addressed
- 3) Geologic setting: This section is a bit long and could be shortened. Addressed
- 4) Methodology: A few things are missing:
  - o How large of a geographic area did you sample? Addressed
  - How did you decide which areas to sample for isotopic analyses? Did you image them first? How? How confident are you that you didn't mix different cements when sampling? Addressed
  - O How many fluid inclusions in your FIAs? What was your reproducibility and error? How did you make sure you did not measure stretched inclusions? Addressed
  - O Documentation of where hand samples came from is very poor. This can be improved by showing the location of the thin sections on outcrop photos, and their spatial relationship with faults etc. These might need to be included in an appendix due to space restrictions, but it is important. Explained in author response

### 5) Field observations

- o What is the spatial distribution of the dolomitized geobodies? Addressed
- o And of the veined sections?
- o 6 outcrop locations are marked on Figure 2 but distributions of the different types of cements are only shown in one image (figure 5b). These are very important relations to assess fluid pathways and the evolution of dolomitization. Addressed
- What are the orientations of CV1–CV4 cement-bearing fractures? Shown in Storti et al. (2018)

### 6) Petrography

O How much calcite cement is there in the breccias? What are the textures? Why are these not included in your diagenetic evolution analysis? How do cements in breccias relate to those in host rocks? Are cements in the host rocks affected by brecciation? Show examples. Addressed

- How did dolomitization affect porosity in both host rock and fault rocks? How
  does porosity compare between limestones and dolostones? Addressed
- Some of the petrographic relationships mentioned need to be backed by images (see my line-specific comments) Addressed
- The order in which dolomite cements and vein-calcite cements are mentioned needs to be improved.
- o What is the relationship between MC and D1/D2? Where is this documented? Addressed
- What is the distribution of CV cements in the host rock (see Laubach, 2003)? This should be properly documented and reported. I don't think vein cement is an appropriate term for these calcite cements. Also, keep in mind that the occlusion of fracture porosity by postkinematic cements can significantly postdate the timing of the opening of the fracture (see Ukar and Laubach, 2016). In other words: the timing of fracturing and cementation are not the same. Keep that in mind in your descriptions. Addressed
- o The observation of CV3 in breccias is quite interesting. Document and show images. What other cements are there in breccias? How did you establish the relative timing of these cements and others? Breccia cements should not be referred to as vein cements. Explained in author response
- o What are the spatial distributions of the different cement types? Addressed

# 7) Geochemistry

- o What are the isotopic characteristics of MC and fibrous cements? Addressed
- o Interpretations, especially for Sr ratios, should be moved to the discussion.

### 8) Fluid inclusions

- o Show images of the different types of fluid inclusions, especially the FIAs.
- O The graphs used to summarize fluid-inclusion thermometric results are not appropriate because key information is lost. Same for salinity. Please replot the data so that the temperature range for each individual FIA is shown. Did you measure an equal amount of FIAs for each type of cement? Otherwise, frequency would not very meaningful in Fig. 13 because it would be sample and cement availability dependent.
- Why are CV temperatures not shown in these graphs? For a higher focus on dolomitization case study

#### 9) Discussion

- o This section can be significantly shortened by avoiding repetition of results.
- I think parental fluid calculations should be shown in the results section, not in the discussion. To emphasize on the nature of parental fluids, we prefer to keep SMOW values in discussion section
- Use parallel writing style for stable isotopes and Sr discussion.???
- O D3 shows significantly higher Sr/Sr than D4. How can both be related to the same event and derived from similar fault-related fluids? D1 and D2 are also fault-related. Why the differences in isotopic signatures, especially if all are related to basement-rooted faults??? Addressed

- The association of D3 and D4 with bed-parallel and shear fractures is mentioned for the first time in the discussion. This needs to be mentioned in the results. Are the cements themselves sheared? Show evidence. Addressed in petrography
- O Discuss the spatial distribution of the different cement and vein/breccia types. What do they indicate about fluid-flow patterns? The breccia types in MDF are not diverse. More details on bereccia is out of focus of this study.
- o The orientation of CV1–CV4-bearing fractures needs to be taken into account in the structural interpretation. A detailed structural interpretation is discussed in Storti et al. 2018. Its now more emphasized in this manuscript.
- Section 5.3: Without a better documentation of the orientations and field relations of the different cements and fracture types it is difficult to assess the validity of the inferred paragenetic sequence and the association of the different cements and structures with tectonic events. Some of the spatial and cross-cutting relationships between different types of cements are first mentioned in this section. Such descriptions should be moved to the results section.
- O What is the driver for fluid circulation? Why are they Mg-rich fluids? What do fluid-inclusion salinities indicate? Addressed in section 5.2
- O Why do you go from dolomite replacement and cementation to calcit cementation? Addressed
- O How are your findings relevant for porosity/permeability evolution and fluid flow in dolomitized, carbonate-hosted hydrocarbon reservoirs and aquifers associated with similar reservoir-scale structures? Addressed
- O How are your conclusions applicable to dolomitization processes associated with faults in general? How far can dolomitizing fluids travel and to what extent do they alter the mechanics and porosity/permeability of the host rock? What are the consequences for fluid-flow in these rocks? Addressed

#### Conclusions

10)

- o More thought needs to go into the conclusions section.
- o I don't think enough data are presented in this study, especially of cross-cutting relationships and orientations of the different "deformation structures" to support the structural interpretation presented in the conclusions. For example, where is the evidence that the opening-mode fractures (no orientations or relationships within the anticline are reported!) and normal faults mentioned in this study are associated with contractional tectonics of the Apenninic orogeny? All are discussed in details in Storti et al. 2018.

Lines 29-31: This needs to be re-written. Layer-parallel shortening would not give place to layer-parallel stylolites. Extensional faulting by itself either. Involvement in the Apenninic thrust wedge of what? Addressed

<sup>11)</sup> Figures and figure captions need work, especially the model shown in Figure 15 (see comments in figure caption).

Lines 48-54: May I suggest you take a look at the recently published Ferraro et al. (2019) paper for a description of the diagenetic evolution of carbonate fault rocks in the central and southern Apennines? Addressed

Lines 54-58: You may want to consider adding a short statement about why some fault zones become dolomitized but others don't. What are the requirements? Addressed

Lines 58-61: What can you learn from outcrops that you cannot from core alone? I would say that the main benefit would be the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D. Perhaps a missed opportunity in this work?

Line 67: I don't see Bugarone in Figure 1. Addressed

Line 69: I don't see catel Manfrino Dolostones in Figures 1 or 2. All the dolomitized intervals are called

#### Castel Manfrino Dolostones

Lines 72-73: How is your study better than Ronchi (2003)? Addressed

Lines 76-78: In Figure 2 it appears that dolomitized bodies are found quite far away from faults, beyond the typical lateral extent of fault damage zones. What is the explanation? Why are some faults associates with dolomitization while others aren't? Does it have to do with age of faults? Other factors? This would be a good topic for the discussion.

Line: 84: I would have liked to see more "field mapping" of the extent of D1–D5 and CV1–CV4 in this work.

Line 87: This sentence should start with a different word than "therefore". What provides insights? How? Addressed

Lines 88-89. Yes. This needs to be discussed in the discussion. Addressed

Lines 90-92: Yes. This needs to be discussed in the discussion. Addressed

Line 96: evolution of the Apennines has been proposed to be the result of Addressed

Line 98: since the Late Cretaceous Addressed

Line 103: The Central Apennines involve OK

Line 110: lower part of the Burano Formation Addressed

Line 115: Deposition of the Hettangian–Sinemurian Calcare Massiccio Formation, with a total thickness ... Addressed

Line 117: following facies are present Addressed

Line 125: deepening-upward trend Addressed

Line 137: olistolith model This sentence is deleted

Lines 138-145: So, does this evidence favor the fault-related model or does this evidence provide an

alternative model? Why does this sentence start with 'However''? This sentence is deleted

Line 151: at a high angle Addressed

Line 162-163: 60 samples distributed across how big of an area? Addressed

Line 164: What structures? Addressed

Line 187: Vienna Pee Dee Belemnite Addressed

Line 215: In order to perform high resolution Addressed

Lines 220-221: bed-perpendicular stylolites Addressed

Lines 224-230: This belongs in the Geological Setting. Addressed

Line 225: There is no evidence of dolomitization Addressed

Lines 231-234: Location names need to be included in figure captions. Addressed

Lines 235-239: This seems out of place. Start by describing mesoscale relations and distributions

of dolomitized geobodies. Then focus on hand-sample and petrographic details. Addressed

Line 235: in fault cores are typically Addressed

Line 237: is "main slip surface" a better term? Addressed

Line 238: cut by rather than overprinted. Are dolomite-filled veins intra- or intergranular?

Line 239: calcite cement Addressed

Line 241: cross-cutting bedding surfaces Addressed

Line 242: from a few meters to hundreds of meters Addressed

Line 243: and the lower part of Addressed

Line 246: High amplitude (>1 mm), bed-parallel stylolites Addressed

Line 247-248: How does porosity differ between limestones and dolostones?

Line 253: grain-supported intervals Addressed

Lines 259-260: Evidence? Addressed

Line 265: we can't see the displacement mentioned in Figure 2A, site 1

Line 267-268: Are they overprinting or overgrowing? Show evidence. We also cannot see the distribution of the different cements at outcrop scale.

271-272: On what basis did you establish that the replacive dolomite within the host rock (D1) and lining fractures is the same?

Lines 275-276: solid inclusions of what? Insert figure call out for concentric zonation. Addressed

Line 281: sweeping extinction Addressed

Line 282: In some crystals, one... what types of solid and fluid inclusions? Addressed

Lines 286-291: Mark locations on map/figure captions and call out the figure. Addressed

Line 290-291: Scaglia Formation in the hanging wall. Addressed

Lines 293-295: This needs to be moved up Addressed

Line 305: bed-parallel shear fractures Addressed

Lines 308 on: There is a problem with CV introduction. What does it stand for? Must introduce them in chronological order. If the calcite cement is in veins it is most likely in the host rock as well (see Laubach, 2003). I don't think calling it vein cement is appropriate. Addressed

Line 308: What porosity? Addressed

Lines 318-320: Show outcrop photo?

Line 319: bed-perpendicular rather than bedding because that's what you use elsewhere. Make sure term usage is consistent throughout. Addressed

Line 321: bed-parallel stylolites. CV1 usually shows (often means time. Correct elsewhere in the manuscript). Addressed

Lines 324-326: Show image of CV2 in tension gashes Addressed

Line 332: extensional fault's master (main?) plane Addressed

Line 339-340: More evidence that the use of CV to refer to calcite cements that occur in a variety of textures and petrographic relations is not appropriate.

Lines 361-364: Why is this mentioned here and not with the rest of the calcite cements? Its ordered based on relative timig

Line 396: I see 3 values plotted for Scaglia. Addressed

Lines 398-399: Interpretation. Move to discussion. Same comment for previous

paragraphs.Addressed

Lines 401-411: This belongs in the Methods section. Addressed

Lines 409 and 439: all-liquid inclusions Addressed

Lines 439-445: This belongs in the Methods section. Addressed

Lines 469-470: This belongs in the methods/results. Why did you avoid them? Could mottled

D be a different type than those reported? Addressed

Lines 471-474: Move to methods. Report parental fluid calculations in the results section.

Line 478: Progressively higher than what? Fixed

Line 481: siliciclastic rocks,... Correct here and elsewhere. Addressed

Line 493:, or values recorded... Add references. Addressed

Lines 499 and 505: Replace comparable with similar. Here and elsewhere. Addressed

Line 507: stylolitization of the host rock (otherwise we do not know what dissolution etc. you are referring to). Addressed

Lines 527-528: fluids related to Late Messinian... overlying Upper Miocene Laga Formation and their possible...Addressed

Line 543: burial-related temperature Addressed

Line 544: it is unlikely that the.. Addressed

Line 546: located at higher stratigraphic levels Addressed

Line 564: calcite cements (FC) in grain-supported stratigraphic levels of the CMF is interpreted to be... Addressed

Line 570: bed-parallel stylolties Addressed

Line 574 and 575: are cut by Addressed

Line 579: Figure 15A call out. Addressed

Line 585: We cannot see the distribution described in Figure 2A.

Line 587: attributed to post-rift Addressed

Line 588: Although an absolute age cannot be provided, Addressed

Line 603: bed-parallel fractures. This is the first mention of shear veins for D4. Are the

cements sheared? Show evidence. Cements are not sheared. Addressed

Line 604: Contractional deformations? How? Describe relationships better. Bed-perpendicular dilation alone would not cause shear.

Lines 608-610: First mention of this. Move to results.

Lines 618-619: bed-parallel veins Addressed

Line 622: fragments suggests that... late-stage evolution Addressed

Line 624: bed-perpendicular stylolites Addressed

Line 624-629. This is way too long. In any case, there is new information here that needs to be moved to the results section. Addressed

Line 629: low homogenization temperatures of fluid inclusions trapped within these cements Addressed

Lines 638-642: So, how is your study better? How are your conclusions applicable to dolomitization processes associated with faults in general?

Figures: Documentation of where samples came from is poor. Locations of samples need to be shown on outcrop photos and/or detailed maps. Add in appendix if space is limited.

Figure 1: Tiny name in a) is unreadable. Mark location of cross-section (A-A') shown in d).

Figure 2: Add names of each field site to the figure caption. Addressed

Figure 3: The picture in a) is too close up to see the context. Mark distribution of D1 etc. as in Fig 5d. Why isn't there more on these breccias (c) in the manuscript? Explain what arrows point to. Pressure solution seams. You are not showing intensity (it would be a number). Perhaps say showing abundant pressure solution seams. What are the abutting relationships? Which abuts which? Move arrow in b) so that the vein is actually visible. Are the other white pods also considered "veins"?

Figure 4: Show spatial distribution of D1, D3, CV1... etc. at the outcrop scale. The sentence seems to say that CV1 veins are dolomitized. Is that what you really mean? What is the dolomite type in b) and c)? Good opportunity to show cross-cutting relationships summarized in Figure 14.

Figure 5: What field site(s) and formation(s) are these from? In b) the zone shown in c) is marked as only having D1 but as D1 + D2 in c). Which one is correct? Any CV2-CV4 here? Addressed

Figure 6: What field site is this? rimmed by fibrous cements (FC), which are overgrown by mosaic cements (MC). overprinted bed-parallel stylolites. D1cements lining a fracture. What do

arrows point to in f) If it is D1, then what is to the right of it? Line 1123: which is cemented by CV1 in the center. Addressed

Figure 7: What field site(s) and formation(s) are these from? What is beyond D3 in e) and f)? Is D3 only present in breccias in this site? What is the CL signal of D3 in breccias and how did you establish correspondence with D3 in host rocks? What is the context of the sample? in e) and f) Addressed

Figure 8: What field site(s) and formation(s)? D3 and D4 are not cross-cutting but it appears that D4 overgrows D3. What is the D4 arrow in b) exactly pointing to? What cement is in the rhomb on the upper right corner? d) I am having a hard time seeing the microfracture. What CV is this? Or do you have dolomite-filled veins as well? Where are these described? What other cements are in e) and f) and what do arrows point to? Lines 1141-1150 belongs in the discussion.

#### Addressed

Figure 9: What field site(s) and formation(s)? If D4 also occurs in fractures why is it not called vein cement as in your CV scheme? What other cements and/or host rock are in these photographs? Add labels. Addressed

Figure 10: These photographs are too close up to see the context. Outlining obscures fractures in a). c-d) These do not look like tension gashes to me (as mentioned in text?). Mislabeled as CV2 on the picture (?) but CV3 in the figure caption. Addressed

Figure 11: What field site(s) and formation(s)? What is a) a sample of? And the rest? Show field context. Addressed

Figure 12: Why aren't these figures in color? The symbols are too similar and they are hard to distinguish from one another. I would assign a color to each formation and a symbol to each diagenetic feature. Addressed

Figure 13: These plots are not very useful because key information is lost. Plot homogeneization and ice melting T ranges so that variability within individual FIAs is captured. Color would help, Also, where are the data for CV cements?

Figure 15: The fracture in a) would not have that orientation if sigma 1 were vertical. Indicate which fault you are referring to in b). The vein in b) would not develop in that orientation if sigma 1 were horizontal. Also, keep in mind that the timing of cementation of the veins by postkinematic cements (see Ukar and Laubach, 2016) postdates timing of opening of the fracture. Don't mix the two! I had no idea that CV4 is restricted to the MdFF until now, because it is not mentioned anywhere in the text. How do you reconcile D3 to be surrounding breccia clasts within the MdFF in this model and sequence? Addressed

Estibalitz Ukar Research Associate Jackson School of Geosciences The University of Texas at Austin Dear Dr. Hendry and Dr. Ukar,

Thank you for the very constructive comments. They not only helped us to improve the quality of the manuscript but also our knowledge of dolomitizataion process. We have tried our best to address your suggestions in this new version of the manuscript.

Regarding the advancement of our research in comparison with the work previously presented by Ronchi et al. (2003), the current study gives much more details about the dolomite characterization and their relation to the structural evolution of the anticline on the regional and local scale. Furthermore, the obtained geochemical and microthermometry analyses do not confirm the role of marly or shaly basinal successions in providing the Mg-rich fluids during the first event of dolomitization (i.e. syn-rift), as proposed by Ronchi et al. (2003). We have tried to be modest in criticizing the latter authors limited research since the current research was build up on their findings. Another important question about the studied dolomites was the role of Scaglia Formation in providing the Mg-rich fluids during compression, because this formation is juxtaposed with the dolostones by the Montagna dei Fiori Fault. Our results do not support this hypothesis.

During our research, we also performed some other advance analyses such as clumped isotopes and U/Pb dating. However, the consecutive overgrowth pattern of dolomites and difficulties in isolating them to get enough and good quality samples increased the uncertainty in the results. Therefore, we decided not to include those data in the manuscript.

In the Montagna dei Fiori Anticline, the structures and their relative chronology are very complicated. A comprehensive structural study on the evolution of the Montagna dei Fiori Anticline was performed parallel with the current study, and published by Storti et al. (2018) in Tectonics. The target of the current study was to focus on dolomitization, and to use the structural model proposed by Storti et al. (2018) to deduce the most likely timing for dolomitization.

The distribution of dolomitization and sampled locations are way larger than the out crop photo scale. The dolomitized intervals are tens of meters mostly exposed in vertical to subvertical outcrops. To be able to show their 3D distribution properly a photogrammetry or LiDAR imaging is required.

The brecciated zones are mostly clast-support with minor calcite and negligible dolomite cement. Moreover, a detailed classification of breccia is not the focus of this research and does not give relevant information regarding this dolomitization case study.

This new version of the manuscript has been reviewed by a native English speaker.

Best regards,

Mozafari et al.

- 1 Fault-controlled dolomitization in the Montagna dei Fiori Anticline (Central Apennines,
- 2 Italy): Record of a dominantly pre-orogenic fluid migration
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### **Abstract**

The Lower Jurassic platform and basinal deposits exposed in the Montagna dei Fiori Anticline (Central Apennines, Italy) are pervasively affected by dolomitization. Based on the integration of field work, petrography, and geochemistry, two fault-related dolomitization events were recognized and interpreted as having occurred before and during the Apenninic orogeny, respectively. Fluid inclusion analysis indicates moderate to elevated salinity values of 3.5 to 20.5 and 12.8 to 18.6 eq. wt. % NaCl, in the first and the second event, respectively. The estimated salinities, in combination with  $\delta^{18}$ O values and  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios, suggest significant involvement of evaporitic fluids in both events, most likely derived from the underlying Upper Triassic Burano Formation. In addition, the  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios up to 0.70963 suggest the circulation of deepsourced fluids that interacted with siliciclastics siliciclastic rocks and/or the crystalline basement during the dolomitization events. The first dolomitization event which is also considered as the most pervasive one started prior to the significant burial conditions, as reflected in homogenization temperatures of their fluid inclusions being mostly below about 40-50°C.

Two major dolomite types (D1 and D2) were recognized as pertaining to this the first event, both postdated by high amplitude bed-parallel stylolites.—, supporting This relationship supports a syn-burial, pre layer-parallel shortening dolomitization, interpreted as controlled by the extensional fault pattern affecting the carbonate succession before its involvement in the

Apenninic thrust wedge. A possible geodynamic framework for this dolomitization event is Early to Late Jurassic rift-related extensional tectonism. The second dolomitization event (D3, <u>D4 and D5)</u> initiated with a dolomite type (D3) is characterized by a slight-temperature upturn (up to 73°C), followed by a second type (D4) with markedly higher homogenization temperatures (up to 105°C), and interpreted as associated with the inflow of hydrothermal fluids, possibly related to major changes in the permeability architecture of faults during early- to synthrusting and folding activity. Eventually, D4 was overprinted by a late generation of dolomite veins (D5) interpreted as associated with late orogenic extensional faulting in the backlimb of the Montagna dei Fiori Anticline. Based on the timing of deformation in the Montagna dei Fiori Anticline, D3 to D5the second dolomitization event likely occurred in Late Miocene to Pliocene times. The findings regarding characteristics and timing of dolomitization here illustrates the long-term controlling role of the eveporitic evaporitic detachments in dolomitization process. Our data This study shows that the Mg-rich fluids that were most likely derived from these evaporites may prime the tectonically involved successions for repeated dolomitization, and <u>hence</u> formation of potential reservoirs <u>in-during</u> sequential tectonic modifications (extensional vs. compressional).

## 1 Introduction

Fault-controlled dolomitization has been the focus of attention in many studies during the last decades due to its influential role in modifying the petrophysical properties of rocks and, hence, anisotropy in fluid migration pathways, and, ultimately on reservoir quality (e.g. Purser et al., 1994; Montanez, 1994; Zempolich and Hardie, 1997; Vandeginste et al., 2005; Davies and Smith, 2006; Sharp et al. 2010). The mechanical and hydrological behaviour of fault zones are in turn influenced by fluid-rock interactions and diagenetic modifications (e.g. Gale et al., 2004; Laubach et al., 2010; Clemenzi et al., 2015; Ferraro et al., 2019). It follows that the mutual interplay between fault activity and fluid driven-rock-fluid interaction can trigger dolomitization of carbonates when exposing to Mg saturated or oversaturated fluids and, consequently, variations in physico-chemical properties of fluids through time and space.

-Leaking or sealing behaviours of fault zones during deformation are key controls for fault-related fluid circulation. A detailed understanding of such an interplay is thus necessary to improve our capability of making reliable predictions of fault-related dolomitization in carbonate reservoirs. Studying outcrop analogues provides fundamental support to meet this requirement

(e.g. Swennen et al., 2012; Dewit et al., 2014; Bistacchi et al., 2015)., and the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D (e.g. Swennen et al., 2012; Dewit et al., 2014; Bistacchi et al., 2015).

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The Lower Jurassic to Lower Cretaceous Umbria-Marche passive margin carbonate succession, in the Central Apennines (Italy), is intensely affected by localized dolomitization both in the onshore fold-and-thrust belt and in offshore foredeep and foreland areas (e.g. Murgia et al., 2004; Pierantoni et al., 2013). The dolomitized intervals which are the focus of this study are well-exposed in the core of the Montagna dei Fiori Anticline (e.g. Ronchi et al., 2003), where the dolomitized Lower Jurassic intervals (Calcare Massiccio, Bugarone and Corniola Formations) and their relationships with fault zones allow to study the mutual influence between deformation structures and dolomitized intervals (Fig. 1). These intervals, known as the Castel Manfrino Dolostones (Crescenti, 1969; Mattei, 1987; Koopman, 1983), have been previously studied by Ronchi et al. (2003) only at its reference section, exposed at the Castel Manfrino location (Fig. 1b), in the central sector of the Montagna dei Fiori Anticline (Fig. 2). A fault-controlled dolomitization model and the relative timing of dolomitization were proposed by Ronchi (2003)the latter authors. based on the homogenization temperatures obtained from microthermometry of the fluid inclusions, and their relation with the thermal history of the area studied. However, no clear relation between dolomitization and structural evolution of the Montagna dei Fiori Anticline on a local scale was provided to confidently link the occurrence of dolomitization to a particular tectonic event. Moreover, the nature and origin of the dolomitizing fluids were not well constrained. Recent re-evaluation of dolostone distribution in the Montagna dei Fiori Anticline (Storti et al., 2017a), showed that the dimension of the dolomitized geobodies (Fig. 2) is much more significant than what was previously mapped by Mattei (1987). Dolostones are distributed within fault damage zones and in the laterally adjacent carbonate rocks, and in intersection areas between fault sets, for a total area in map view of more than 1.5 km<sup>2</sup> (Storti et al., 2017a).

The structural pattern of the Montagna dei Fiori Anticline documents the overprinting of extensional and contractional deformation along major fault zones. Although challenging, the The preserved structural framework in this anticline provides an opportunity to study the direct but complex regional tectonic controls on dolomitization in carbonate successions undergoing multiple deformation events, from rifting to folding and thrusting. This contribution integrates

field mapping, new petrographic, geochemical, and microthermometric analyses, with structural studies (Storti et al., 2018) to characterize the temporal record of fault-controlled diagenetic phases and, more specifically, dolomitization in the carbonatic succession outcropping in the Montagna dei Fiori Anticline. Therefore provides insights into the structural controls on regional fluid flow and their chemical evolution through time. These findings might be of relevance for exploration and reservoir quality prediction in the region of onshore and offshore the Apennines and Southern Alps, both onshore and offshore. Moreover, this work provides additional evidence of the potential influence of fluids derived from evaporitic detachment levels in modifications of geochemical trends and petrophysical properties of the overlying carbonate rocks.

# 2 Geological setting

The Montagna dei Fiori Anticline is a NNW-SSE striking, thrust-related fold located at the mountain front of the Central Apennines (Fig. 1). The geodynamic evolution of the Apennines is generally knownhas been proposed to be the result of the superposition of NE-SW compression (in present-day geographic coordinates), related to the convergence between Eurasia and Africa plates since the Late Cretaceous times (Elter et al., 1975; Dewey et al., 1989; Patacca et al., 1992), on a rifting-related tectono-sedimentary architecture produced by Early Jurassic extension (e.g., Centamore et al., 1971). In such a framework, the Central Apennines developed during Miocene to Plio-Pleistocene times (e.g. Parotto and Praturlon, 1975; Barchi et al., 1998; Mazzoli et al., 2002; Bollati et al., 2012).

The Central Apennines involves the Umbria-Marche succession, which essentially includes Triassic to Miocene carbonates and marls, covered by Miocene to Pliocene synorogenic clastic sediments (Fig. 1). The pre-orogenic succession, from bottom to top, includes Late Triassic evaporites, dolomites and limestones (of the Burano Formation), which the basal detachment runs within its evaporitic interval (Ghisetti and Vezzani, 2000), Early to Late Jurassic platform and basinal limestones and dolostones (Calcare Massiccio, Corniola, Rosso Ammonitico, Calcari a Posidonia and Calcari ad Aptici Formations), and Cretaceous to Early Miocene basinal carbonates (Maiolica, Marne a Fucoidi, Scaglia and Biscaro Formations). In general, the lower part of the Burano Formation is overlaid by the fluvio-deltaic siliciclastics siliciclastic rocks of the Verrucano Formation (Middle-Late Triassic) (Tongiorgi et al., 1977; Ghisetti and Vezzani, 2000; Tavani et al., 2008). Nevertheless, the existence of these siliciclastic rocks in the Montagna dei Fiori area is not yet provedproven. Syn-

orogenic deposits include Miocene marls and turbiditic sandstones (Marne con Cerrogna and Laga Formations) (Artoni, 2013 and references therein).

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The deposition of the Calcare Massiccio Formation, (dated as Hettangian-Sinemurian) and with a total thickness varying between 300 to 700 m (Pialli, 1971), records an important extension pulse in the evolution of Tethyan rifting. The following facies are observed in the lower part of the Calcare Massiccio Formationthis formation which has been interpreted as having been deposited in a peritidal environment: consists of oncoid-rich-peloidal pack- to grainstones in alternation with peloidal wacke- to packstones including horizons of algal bindstones (Calcare Massiccio A; Brandano et al., 2016). The upper part is made up of beds of skeletal and coated grain wacke- to grainstones including microoncoids, echinoderms, calcareous and siliceous sponges, bivalves, gastropods and ammonites (Calcare Massiccio B; Brandano et al., 2016). It The lower part has been interpreted as having been deposited in a peritidal environment, while the upper part corresponds to lower to middle shelf depositional environments, characterized by a general deepening deepening upward trend associated with extensional faulting and drowning of the platform, coupled with subsidence and deposition of the overlying Corniola Formation in the pelagic areas. Overall, the Early Jurassic rifting led to the growth of the Calcare Massiccio Formation in a carbonate platform setting, followed by faulting and drowning, and development of pelagic intrabasins filled by syn-rift sediments (Fig. 1c; Bernoulli et al. 1979; Santantonio and Carminati, 2011). The syn-rift sediments include pelagic limestones of the Bugarone and Corniola Formations. Condensed pelagic limestones of the Bugarone Formation (Lower Pliensbachian-Lower Tithonian; Bugarone Group in Pierantoni et al., 2013) occur at the top of the Calcare Massiccio Formation where it formed fault-controlled highs marking the regional drowning of the carbonate platform (Santantonio and Carminati, 2011). The pelagic limestones of the Corniola Formation (Sinemurian-Toarcian; Colacicchi et al., 1975; Morettini et al., 2002; Bosence et al., 2009; Marino and Santantonio, 2010; Brandano et al., 2016) occur within the fault-controlled (half)grabens in lateral continuation with the Calcare Massiccio Formation. The Corniola Formation in the lower part consists of turbiditic lobes which originated from tectonic brecciation of the Calcare Massiccio Formation. The upper part consists of a well-bedded pelagic mudstone with chert nodules (Di Francesco et al., 2010). In the Montagna dei Fiori, the geologic framework of the outcropping Calcare Massiccio Formation is still a matter of debate between a

fault-related tectonosedimentary pattern (Mattei, 1987; Storti et al., 2017b), and a gravity-driven, olistolith hypothesis (Di Francesco et al, 2010; Santantonio et al., 2017). However, recent

# 2.1 Structural Framework

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The Montagna dei Fiori Anticline is intersected by two major fault categories (Storti et al., 2018), which based on the chronological order include: detailed work in the Salinello valley (Storti et al., 2017a; 2018) Firstly, ~ E-W and ~ N-S striking fault zones showing extensional kinematics bounding the documented that major outcrops of Calcare Massiccio are bounded by mostly ~ E-W and ~ N-S striking fault zones showing extensional kinematics and dominantly affecting the Jurassic rocks older than the Maiolica Formation (Fig. 2A2a, e.g. sites 1 to 4). Overprinting relations indicate that ~ E-W deformation structures are systematically younger than the ~ N-S ones. Similar trends were observed in syn-rift fault zones in other anticlines of the Central Apennines (e.g. Cooper and Burbi, 1986; Alvarez, 1989; Chilovi et al., 2002). Such a tectonosedimentary inheritance was involved in the growth of the Montagna dei Fiori Anticline, which initiated during the Late Miocene (Mazzoli et al., 2002; Artoni, 2003) and progressively evolved into the upper thrust sheet of a well-developed antiformal stack until Plio-Pleistocene times (e.g. Ghisetti et al., 1993; Calamita et al., 1994; Artoni, 2013). The second set of faults is A a major structural feature trending parallel to the Montagna dei Fiori Anticline and dissecting it is the Montagna dei Fiori Fault, a NNW-SSE striking extensional fault system cutting at a high angle through the folded footwall rocks, typically at the forelimb-crest transition (Figs. 1, 2). This fault consists of two partially overlapping main fault zones with an extensional stratigraphic separation exceeding 900 m, and This fault system juxtaposes intensely deformed Late Miocene sediments in the hanging wall, against dolomitized and undolomitized Lower Jurassic and Cretaceous limestones in the footwall (Figs. 1 and 2). The development of the Montagna dei Fiori Fault has been alternatively interpreted as either a pre- (e.g. Calamita et al., 1994, Mazzoli, 2002; Scisciani et al., 2002) or late-folding (Ghisetti and Vezzani, 2000) feature. More recently, the origin of the Montagna dei Fiori Fault has been ascribed to the mutual interaction between horizontal shortening and uplift, and episodic gravitational re-equilibration during antiformal stacking underneath the anticline during Plio-Pleistocene times (Storti et al., 2018). The dolomitized intervals are exposed in the damage zones of the both aforementioned fault categories.

# 3 Methodology

The fieldwork covered an area of over 4 km<sup>2</sup> to delineate the distribution of dolostones.

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The stratigraphic and deformational features of dolostones were analyzed in more than 60 outcrops. The distribution of dolomitized intervals as well as their cross-cutting relationships with bedding planes, stylolites, veins and structures-faults were ground-trutheddocumented and sampled. For petrographic analyses, 130 polished thin sections were studied with standard petrographic methods (transmitted and UV-fluorescent light microscopy). Dolomite crystal morphology and texture is based on the classification proposed by Sibley and Gregg (1987).

The rock slabs and thin sections were stained using Alizarine Red S and potassium ferricyanide (Dickson, 1966) to discriminate dolomite from calcite and evaluate their iron content. Cold cathodoluminescence microscopy (CL) was carried out on representative thin sections (n = 80) at KU Leuven University (Belgium) using a Technosyn cathodoluminescence device (8-15 kV, 200-400  $\mu$ A gun current, 0.05 Torr vacuum and 5 mm beam width).

 $\delta^{13}$ C and  $\delta^{18}$ O analysis were carried out on 117 samples. To ensure the sampling quality and avoid physical mixing of different diagenetic phases, the thin section images were mapped and the sampling targets were determined. Nevertheless, some diagenetic phases could not be isolated due to their sequential overgrowth and small size. Powder samples (150 - 200 µg) were obtained by applying a New Wave Research micromilling device and a dental drill at KU Leuven University (Belgium). The analysis was conducted at Parma University (Italy) and the Friedrich-Alexander-Universität (Erlangen-Nürnberg, Germany) laboratories using Finnigan DeltaPlus V and ThermoFinnigan 252 mass spectrometers, respectively. The carbonate powders were reacted with 100% phosphoric acid at constant temperature of 75°C. Several additional CO<sub>2</sub> reference gases (NBS18, NBS19, MAB99, and a pure Carrara marble) with known isotopic ratio were analyzed during the measurements to determine the  $\delta^{13}$ C and  $\delta^{18}$ O values of the sample. Reproducibility was checked by replicate analysis of laboratory standards and was better than  $\pm 0.1\%$  for  $\delta^{13}$ C and  $\pm 0.2\%$  for  $\delta^{18}$ O at Parma University and  $\pm 0.04$  for  $\delta^{13}$ C and  $\pm 0.05\%$  for δ<sup>18</sup>O at Friedrich-Alexander-Universität. Oxygen isotope composition of dolomites was corrected using the acid fractionation factors given by Rosenbaum and Sheppard (1986). Duplicate homogeneous samples measured in both labs for inter-laboratory reproducibility-show  $\delta^{13}$ C and  $\delta^{18}$ O values within the acceptable range of error deviation (±0.1%) both for  $\delta^{13}$ C and 8<sup>48</sup>O. All carbon and oxygen values are reported in per mil, relative to the "Vienna Pee Dee Belemnite Vienna PDB scale" (V-PDB).

A total number of 21 samples were analyzed for their <sup>87</sup>Sr/<sup>86</sup>Sr ratios. The analyses were conducted at the Department of Analytical Chemistry, Ghent University (Belgium) and at the Vrije Universiteit Amsterdam (the Netherlands). NIST SRM 987 was used as the international Sr standard in both labs. At Ghent University, 15 sample powders (20 mg) were collected using a dental drill device. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio measurements were performed using a Thermo Scientific Neptune Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) instrument. Within the external precision, repeated analyses of the international Sr standard yielded an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.710271 \pm 0.000023$  (2SD, n = 43), in agreement with the accepted <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.710248 for this reference sample (Thirlwall, 1991). At Vrije Universiteit Amsterdam, 6 sample powders (2 - 3 mg) were collected using a New Wave Research micromilling device. Analyses were performed using a ThermoElectron Triton plus TIMS instrument. In order to monitor and document the system's performance, repeated analyses of the international Sr standard (n = 58) were carried out on load sizes of 10 ng and 100 ng which yielded average <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 0.710245±0.000022 (2SD) and 0.710242±0.000008 (2SD), respectively. In both labs mass discrimination correction was performed via internal normalization using Russell's exponential law and the accepted value (0.1194; Steiger and Jager, 1977) of the invariant <sup>86</sup>Sr/<sup>88</sup>Sr ratio.

Fluid inclusion microthermometry analysis was performed on 11 doubly polished wafers (80-130 μm in thickness). Measurements were carried out at Parma University (Italy) using Linkam THMSG-600 and Linkam MDS-600 heating-cooling stages coupled with a Leica DM 2500 microscope. The final melt (Tm<sub>ice</sub>) and homogenization temperatures (T<sub>h</sub>) were reproducible within 0.5°C and 5°C, respectively. The stages were calibrated by synthetic Syn Flinc<sup>TM</sup> fluid inclusion standards. A 100x objective was used during the microthermometry runs of the small inclusions. The microthermometry data were collected following the Fluid Inclusion Assemblage (FIA) approach described in Goldstein and Reynolds (1994) for carbonate minerals. The inconsistent homogenization temperatures and salinities obtained for these fluid inclusions, within the framework of an individual fluid inclusion assemblage (FIA) described by Goldstein and Reynolds (1994), indicate possible re-equilibration (stretched) of these inclusions and thus are not used in the interpretations. It is common for small inclusions (< 3 μm) to remain monophase all-liquid at room temperature due to their metastability (Goldstein and Reynolds, 1994). Thus, to eliminate the possible role of metastability, the samples were placed in a freezer for

several days following the procedures described in detail by Goldstein and Reynolds (1994). All-liquid inclusions remained unchanged and no vapor bubble was developed within them, which discards the metastability effect. In order to properly observe the phase transitions and determine the final melting temperature of ice in the all-liquid inclusions, they were rapidly heated up to ~200°C to stretch and nucleate a bubble at room temperature (Goldstein, 1990). The salinities are reported in equivalent weight percent NaCl (eq. wt. % NaCl) and were calculated based on the equation of Bodnar (1993). The homogenization temperatures obtained in all fluid inclusion assemblages indicate the minimum temperatures at which the fluids could have been trapped (Goldstein and Reynolds, 1994). No correction was made for pressure effects on entrapment temperatures since no data regarding the exact depth and pressure of entrapment are available. In absence of independent thermal indicators such as Conodont Alteration Index (CIA) and Vitrinite Reflectance (VR), the accuracy of pressure correction cannot be well constrained (Slobodník et al, 2006), and thus no correction was made for pressure effects on homogenization temperatures.

In order to perform a-high resolution petrography, Scanning Electron Microscope (SEM) and Back-scattered Scanning Electron Microscope (BSEM) analyses were conducted using a Jeol 6400 Scanning Electron Microscope (SEM) equipped with an Oxford EDS (Energy Dispersive System). Operating conditions were 15 kV and 1.2 nA, electron beam about 1  $\mu$ m in diameter and 100 s counting time; errors are  $\pm 2$ -5% for major elements and  $\pm 5$ -10% for minor components. The analysis focused mainly on detecting possible dolomite crystals inside the bed-perpendicular stylolites affecting the Cretaceous Scaglia Formation.

#### 4 Results

#### 4.1 Field observation and distribution of the dolomitized bodies

Dolomitization affected the Calcare Massiccio, Bugarone and Corniola Formations. There is no evidences of dolomitization in the overlying and immediate surrounding successions of the Calcare Massiccio, Bugarone and Corniola Formations (e.g. Maiolica and Scaglia Formations), though the base of Maiolica Formation is reported as dolomitized in the Central Apennines onshore (e.g. Pierantoni et al., 2013) and offshore areas (Murgia et al., 2004).

Dolomitized intervals are folded in the forelimb of the Montagna dei Fiori Anticline and are abruptly truncated by the Montagna dei Fiori Fault, which juxtaposes them against intensely foliated Scaglia, Bisciaro and Marne con Cerrogna Formations (Figs. 2 and 3). The distribution

of dolomitized intervals is wider in the Salinello valley creek (Figs. 1B1b, 2A2a) perhaps due to a better exposure. In the Corano Quarry location, dolomitization occur in the Calcare Massiccio and Bugarone Formations only as meter-sized dolostone geobodies in the footwall of the Montagna dei Fiori Fault (Fig. 4). The map pattern (Fig. 2) of dolostones indicates that their distribution is maximized in the Castel Manfrino-Osso Caprino hill area and fades out both southward and eastward.

Dolostone breccias in fault cores is typically clast supported, with angular and millimeter to centimeter sized fragments (Fig. 3C), changing to crackle breccia (Woodcock and Mort, 2008) away from the master slip surface. In the proximity of the master slip surface, dolostone fragments are sporadically overprinted by millimeter-sized dolomite veins. The breccia fragments, where cemented, are commonly surrounded by calcite.

Dolomitization does not follow a systematic pattern. The lateral extent of dolomitization is gradual. In some outcrops, dolomitization fronts show irregular outlines following, but also cross-cutting, the bedding surfaces (Fig. 5). Dolomitized intervals vary in thickness from a few meters to hundred meters affecting the totality of the exposed Calcare Massiccio and only the lower part of Corniola Formation, where no clay interlayers are present. In the Calcare Massiccio Formation, dolomitization does not follow a systematic pattern. In the northern side of the Osso Caprino hill (Fig. 2), the top of formation is dolomitized but moving toward the Salinello creek, a thick non dolomitized limestone is exposed. The same situation occurs on the opposite side of the creek and to the east of Castel Manfrino.

Dolomitized intervals in the Corniola Formation have a darker color relative to the host rock and are systematically more fractured than the hosting limestone. High amplitude (> 1 mm), bed-parallel stylolites are clearly visible in both limestones and dolostones (Fig. 5). However, in some dolostones only ghosts of stylolite traces can be seen. No apparent porosity could be observed in host rock limestones but The the dolostones locally contain porosity, appearing as millimetre- to centimetre-sized pores. Dolostone breccias in fault cores are typically clast-supported, with angular and millimeter- to centimeter-sized fragments (Fig. 3C), changing to crackle breccia (Woodcock and Mort, 2008) away from the main slip surface. In the proximity of the main slip surface, dolostone fragments are sporadically cross-cut by millimeter-sized dolomite veins. The breccia fragments, where cemented, are commonly surrounded by calcite cement.

## 4.2 Petrography

## 4.2.1 Early calcite cementation

The early diagenetic products in the studied intervals are generally non-ferroan calcite cements. The first calcite cements precipitated following a phase of bioclast micritization (*sensu* Bathurst, 1975) in grain-grain-supported intervals. In chronological order, they include: 1) fibrous cements (FC) riming the bioclasts, mostly in the peloidal facies of the Calcare Massiccio Formation (Fig. 6A6a). These cements are dull-dark brown to non-luminescent under cathodoluminescence; 2) mosaic cements (MC), commonly fill the intergranular pore spaces (Fig. 6B6b), and also occur as syntaxial overgrowths on echinoderm fragments. These cementsThey exhibit deformation twinning and show a well-developed dull-brown and orange concentrically-zoned cathodoluminescence pattern (Figs. 6C-6c and Dd). They contain only mono-phase all-liquid inclusions. All of these cements are postdated by dolomites and high amplitude bed-parallel stylolites (Fig. 6b).

# 4.2.2 Dolomitization

All the dolomite types are non-ferroan and dominantly fabric destructive. <u>Dolomitization</u> developed in all the facies types of the Calcare Massiccio and the overlaying Bugarone Formations, but only at the lower part of the Corniola Formation which consists of resedimented Calcare Massiccio breccias (turbiditic lobes).

The two first dolomite types (D1 and D2) are the dominant dolomite types in the studied outcrops. These dolomites are distributed within the damage zones of the ~ N-S and E-W Jurassic rift-related extensional faults and, in places, displaced by them (Fig. 2A2a, site 1). The third and fourth dolomite types (D3 and D4) are mainly observed within the damage zone of the Montagna dei Fiori Fault (NNW-SSE), and appear only as dolomitic pockets locally replacing the host rock and overprinting overgrowing D1 and D2 at the proximity of the ~ N-S and E-W extensional faults. The fifth dolomite type (D5) is found only within the brecciated zones associated with the Montagna dei Fiori Fault damage zone. The distinctive petrographic features of the recognized dolomite types are summarized below:

**Dolomite 1 (D1)** is a replacive dolomite which commonly appears as dispersed rhombs and aggregates, and locally rims fracture walls cemented by calcite (CV1) (Figs. 6E-6e and Ff). D1 postdates the micritic envelopes and early calcite cements, and predates high amplitude bed-parallel stylolites (Figs. 6G-6g and Hh). The crystals are fine to medium sized (< 350  $\mu$ m) and

with planar-e and planar-s textures, consisting of relatively turbid, rich in host rock solid-inclusions—rich, well-developed cuhedral to subhedral crystals,—. They show with—red luminescence when viewed under cathodoluminescence, occasionally developing a concentrical zonation.

Dolomite 2 (D2) is a replacive dolomite (Figs. 7A-7a and Bb), infrequently occluding existing pore spaces. Like D1, it also frequently predates high amplitude bed-parallel stylolites (Figs. 6G 6g and Hh). D2 generally exhibits a tightly closely packed texture with no or little intercrystalline porosity. The crystals are medium to coarse sized (≤ 500 μm) with planar-s to non-planar textures. They includeing a turbid core followed by a transparent subhedral to anhedral rim and trace quantities of saddle dolomite developing swiping-sweeping extinction. In some crystals, one additional turbid zone rich in host rock solid inclusions and fluid inclusions of mostly mono-phase is present. Cathodoluminescence observations enabled to recognize the presence of D1 in their turbid cores. D2 crystals are characterized by zones of bright red-pink luminescence separated by purple luminescence zones (Fig. 7b).

Dolomite 3 (D3) is present as small localized bodies in the Calcare Massiccio (at the Castel Manfrino reference section), in the Corniola Formation (at the Osso Caprino Road), and in the Calcare Massiccio and Bugarone Formations (at the Corano Quarry) (Figs. 1b and 2a). In the Corano Quarry the dolomitized Bugarone and Calcare Massiccio Formations are in the footwall of the Montagna dei Fiori Fault; and juxtaposed to the undolomitized, intensely foliated Scaglia Formation in (the hanging wall). The SEM and BSEM analysis performed on the samples from the immediate adjacent Scaglia Formation within the aforementioned fault damage zone did not indicate the presence of any dolomite in this formation. Within the Bugarone Formation in this fault damage zone, D3 locally cements the millimeter-sized angular breccias that are in turn affected by fault-parallel stylolites (Figs. 7C-7c and Dd). The SEM and BSEM analysis performed on the samples from the immediate adjacent Seaglia Formation within the aforementioned fault damage zone did not indicate the presence of any dolomite in this formation. D3 crystals are fine to medium sized (< 300 µm) mostly transparent euhedral to anhedralexhibiting planar-e to non-planar textures (< 300 µm), with minor development of saddle morphologies in of larger crystals (> 500 μm) with planar-c texture (Figs. 7E-7e to Hh). The euhedral to anhedral replacive crystals are generally replacive, displaying a faint core, which compared to previous dolomite types has fewer solid inclusions. The saddle crystals are

occasionally replacive but majorly appear as cement in fractures. They display typical curved and slightly serrated crystal terminations with swiping sweeping extinction. These saddle dolomites were only observed in the Castel Manfrino reference section. D3 generally exhibit a dull-dark purple color with bright orange zones and subzones in core and/or rims when viewed under cathodoluminescence (Figs. 7E-7e to Hh).

Dolomite 4 (D4) appears as a matrix replacive and dolomite cement surrounding porosity, and locally recrystallizing replacing D1 and D2 (Figs. 8A-8a to Ff). D4 also occludes bed\_bed\_parallel shear fractures and appears along the bed\_bed\_parallel stylolites (Figs. 9A-9a to Dd). In the Castel Manfrino reference section, some intercrystalline vuggy porosity is filled with fine dolomite rhombs including D4 with relics of D2 within their core (Figs. 8E-8e and Ff). The This porosity may be preserved or partially to completely filled by calcite (CV4C4). D4 crystals have a turbid, solid-inclusion rich core and transparent rim. They are fine to medium sized (< 200-350 μm), presenting subhedral planar-s to and infrequent euhedral crystals non-planar textures. D4 exhibits a distinct luminescence pattern including a purple zone and an irregular green subzone.

**Dolomite 5 (D5)** occurs as crystals cementing micro-veins that cross-cut precursor dolomite types including dolomitic breccia fragments. In cemented breccias, D5 is postdated by CV3C3.

D5 presents a planar-c texture is transparent, anhedral and is characterized by a bright red luminescence (Figs. 9E-9e and Ff).

# 4.2.3 Late calcite cementation

 Four generations of calcite veins postdating dolomitization and distributed only within the fault damage zones have been identified (Figs. 10 and 11):

1) Calcite vein 1 (CV1) occurs only in Calcare Massicio limestones and dolostones and is represented as centimeter-sized veins with thickness that does not exceed 1.5 cm. It is not clear whether the fracture opening and calcite precipitation was simultaneous (as shown in Ukar and Laubach, 2016). These veins are strata-bound, bedding-perpendicular veins—with irregular fracture walls, exhibiting white color in the outcrops. They are present within the syn-rift related extensional fault damage zones, postdatepostdating the first dolomite type (D1) and abutted riming the same fractures that abut the highby high amplitude bed-bed-parallel stylolites. CV1 often—usually shows blocky to elongated crystal morphologies and displays well-developed deformation twinning planes (Type II of Burkhard, 1993). This calcite exhibits concentrical

zonation and <u>dull\_brown</u> zones alternate with orange luminescence zones (Figs. <u>11A\_11a\_and Bb</u>).

2) Calcite vein 2 (CV2) exclusively occurs in the intensely deformed Scaglia Formation within the fault damage zones (Figs. 11b, c and d) and correspond to tension gashes associated with stylolites (sensu Nelson, 1981). The thickness of these veins does exceed 1 cm. They are usually discontinuous and branch to several microveins (thickness < 1mm) when their tips are not intersected by stylolites. CV2C2 veins are mostly recorded in foliated shear deformation zones with well-defined S-C fabrics, exhibiting blocky, elongated to fibrous shapes with strongly developed tightly spaced deformation twinning planes (Type II of Burkhard, 1993). CV2C2 displays yellow brown to orange luminescence with locally darker sector zones. The yellow brown to orange luminescence characteristic of CV2C2 is comparable withsimilar to those of encasing Scaglia host rocks (Figs. 11C-11c and Dd).

3) Calcite vein-3 (CC1V3) occurs as cement, filling the extensional faults Montagna dei Fiori master main fault plane and isolated veins within the extesional faultits damage zones. These veins are centimeter-sized with thicknesses of less than 2 cm. The breccias are generally clast-supported, but locally CV3C3 cements the brecciated fault-infillings containing angular fragments of host rock limestones, dolostones and earlier calcites. In the brecciated zones at the backlimb of the anticline (Montagna dei Fiori Fault), CV3C3 always passively overgrows D5 in fractures and never cuts it.postdates the last dolomitization phase (D5) with no evidence of physical disruption. CV3C3 exhibits a translucent white to translucent color in hand specimen. The crystals are blocky with no or weakly developed deformation twinning planes, and are characterized by a dark orange to brown luminescence with distinct darker sector zones (Figs. 11E-11e and Ff).

4) Calcite vein 4 (CV4C4) exists as <u>centimeter-sized</u> isolated veins, pore-filling as well as breccia cements postdating all the preceding dolomites and calcites in the <u>Montagna dei Fiori main fault plane</u>. The breccia fragments are <u>more oftenusually</u> dolostones. <u>CV4C4</u> has a <u>translucent white to translucent white</u> color in hand specimen with blocky crystal morphology and no evidence of subsequent deformation (e.g. deformation twinning planes), and is characterized by distinct concentrical zonation (Figs. <u>11G-11g</u> and <u>Hh</u>).

# 4.3 Geochemistry

# 4.3.1 Carbon and oxygen stable isotopes

The carbon and oxygen stable isotopic data ( $\delta^{13}$ C and  $\delta^{18}$ O) of host rocks, dolomites and calcites are given in Table 1 and shown in Figures 12A-12a and Bb. The marine stable isotopic compositions reported by Veizer et al. (1999) were used as marine reference values. Accordingly, Lower Jurassic marine limestones are characterized by  $\delta^{13}$ C values of -0.5 to +4.5% and  $\delta^{18}$ O values of -2.5 to +1.0% V-PDB. The  $\delta^{18}$ O values of the marine dolomites are known to be 3-4% V-PDB more enriched than those of co-genetic marine limestones (Land, 1980; Major et al., 1992; Horita, 2014). In order to avoid data ambiguity due to physical mixing, this analysis was not separately performed on early calcite cements (FC and MC). The  $\delta^{13}$ C and  $\delta^{18}$ O values measured on bulk samples of host rock limestones. Both  $\delta^{13}$ C and  $\delta^{18}$ O values of the host rocks are within the expected range of the Lower Jurassic marine limestones but the Corniola host rocks show slightly lower values comparing to those of Calcare Massiccio. In the Calcare Massiccio host rocks, the  $\delta^{13}$ C values plot between +2.4 and +3.1% and  $\delta^{18}$ O values are within the range of -1.6 and 0.0% V-PDB. The  $\delta^{13}$ C values in the Corniola host rocks are +2.0 and +2.5% while the  $\delta^{18}$ O values are -3.1 to -1.4% V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of the Scaglia host rocks range between +1.0 to +3.3% for  $\delta^{13}$ C and -2.2 to -1.0% V-PDB for  $\delta^{18}$ O. The obtained values obtained are characterized in the mean range of Upper Cretaceous to Paleogene marine limestones (Veizer et al., 1999; +1.0 to +4.5% for  $\delta^{13}$ C and -4.0 to +2.0% V-PDB for  $\delta^{18}$ O).

The  $\delta^{13}$ C values of CV1C1 are between +1.6 and +2.1% which plot within the range of reference values (Jurassic) but are slightly lower than the surrounding host rock values. The  $\delta^{18}$ O values are between -4.7 and -2.7% V-PDB which are lower than those of reference and host rock values.

The  $\delta^{13}$ C values of all dolomite types (+0.6 to +3.4‰) fall within the range of host rocks and Jurassic marine limestones (Veizer et al., 1999). The  $\delta^{18}$ O shows a wider range of values, somehow-overlapping but also lower than those of host rocks (-4.5 to -0.9‰ V-PDB) and those expected for the presumable-Lower Jurassic marine dolomites. The majority of values plot between -3.5 and -1.5‰ V-PDB. The small size and overgrowth nature of certain dolomite types (e.g. D2 and D5) limits their proper isolation for geochemical analyses. Only one sample from D1 dolomite could be measured for  $\delta^{13}$ C and  $\delta^{18}$ O values, showing +2.5 and -1.9‰ V-PDB, respectively. The  $\delta^{13}$ C and  $\delta^{18}$ O values of D3 dolomite range from +2.0 to +2.6‰ and -2.8 to -1.9‰ V-PDB, respectively, with values lower than those of the host rock.

D4 dolomite has  $\delta^{13}$ C values between +2.4 and +2.5‰, and  $\delta^{18}$ O values of -3.0 to -2.5‰ V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of CV2C2 are +1.2 to +3.1‰ and -1.7 to -1.7‰ V-PDB, respectively. The  $\delta^{13}$ C values of CV3C3 are between +0.5 and +2.4‰, and the  $\delta^{18}$ O values cover a range of -2.2 to 0.0‰ V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of CV4C4 are +3.8 to +4.9‰ and -9.4 to -9.1‰ V-PDB, respectively. The  $\delta^{13}$ C values are slightly higher but the  $\delta^{18}$ O values are considerably lower compared to preceding calcite generations and the measured values from host rocks.

# 4.3.2 87 Sr/ 86 Sr ratios

Samples from host rocks (i.e. Calcare Massiccio and Corniola Formations), dolomites (D1, D3 and D4) and the Scaglia Formation in juxtaposition with the dolostones were analyzed for their  $^{87}$ Sr/ $^{86}$ Sr isotopic ratios. The obtained ratios versus  $\delta^{18}$ O values of the analyzed samples are shown in Fig. 12C. The  $^{87}$ Sr/ $^{86}$ Sr ratios obtained from the Calcare Massiccio and Corniola limestones are 0.70766 and 0.70725 (n = 2), respectively, which is in agreement with the values of the Lower Jurassic marine carbonates (0.70704-0.70768) reported by McArthur et al. (2012). CV1 show a value equal to 0.70773.

All the dolomite types display higher  $^{87}$ Sr/ $^{86}$ Sr ratios when compared to the host rocks and reference values of the Lower Jurassic marine carbonates. D1 (replacive) and D4 cements show a comparable similar narrow range with values between 0.70784 and 0.70790, respectively. While, the The two D3 samples (replacive and cement) display higher  $^{87}$ Sr/ $^{86}$ Sr ratios (0.70858 and 0.70963, respectively). The  $^{87}$ Sr/ $^{86}$ Sr ratios obtained for dolomites do not show co-variation with corresponding  $\delta^{18}$ O values. The radiogenic Sr analysis was not performed on D2 and D5 since the physical mixing with other dolomite types could not be avoided.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the two-three marly limestone samples of Scaglia Formation are 0.70784 to 0.70790. The CV2C2 veins in Scaglia Formation show comparable similar ratios of 0.70779 and 0.70787. These values fit within the limits of values assigned by McArthur et al. (2012) for the Cenomanian-Bartonian (Scaglia age) marine carbonates (0.70730-0.70790).

# 4.4 Fluid inclusion microthermometry

The overview of microthermometry measurements is given in Table 1 and Figs. 13A to C. All the measured fluid inclusions are primary and occur in growth zones. Based on optical and fluorescence microscopy analysis of wafers all the inclusions are aqueous mono-phase (liquid)

and two-phase (liquid and vapor) with relatively consistent L:V ratio of 10-15% within a single FIA (fluid inclusion assemblage). Special care was taken to avoid the samples that occasionally displayed scattered mottled luminescence that may indicate recrystallization.

On the basis of optical microscopy analysis of wafers, D1 contain dominantly monophase aqueous inclusions with sizes greater than 5 µm. It is common for small inclusions (<3 µm) to remain monophase all liquid at room temperature due to their metastability (Goldstein and Reynolds, 1994). Thus, to eliminate the possible role of metastability, the samples were placed in a freezer for several days following the procedures described in detail by Goldstein and Reynolds (1994). All liquid inclusions remained unchanged and no vapor bubble was developed within them, which discards the metastability effect. In order to properly observe the phase transitions in the all liquid inclusions, they were rapidly heated up to ~ 200°C to stretch and nucleate a bubble at room temperature (Goldstein, 1990). All the inclusions froze at -65 to -49°C. The first melting (Te) was detected between -22 to -19.3°C. The final ice melting (Tm) appeared at temperatures between -7.7 and -2°C. Applying Bodnar's (1993) equation, the obtained final melting temperatures correspond to salinity ranges of 3.5 to 11.3 eq. wt. % NaCl.

D2 is characterized by the presence of mono-phase and infrequent two-phase inclusions generally within their growth zones. The homogenization temperature of two-phase inclusions varies between 58 and 71°C. Upon cooling, a complete freezing of the fluid phase is reached at -56 to -40°C. The first ice melting temperature was distinguished at -22°C. The final ice melting temperatures fall within -17.5 and -5°C, corresponding to salinities between 7.9 and 20.5 eq. wt. % NaCl.

D3 is commonly inclusion poor. The measureable inclusions were detected and examined only in saddle dolomite crystals. These crystals contain only two-phase aqueous inclusions. Their homogenization temperatures are within the narrow range of 70 to 73°C. The complete freezing and first ice melting temperatures could not be distinguished but the final ice melting temperature occurred at temperatures between -13 and -6°C equal to salinity ranges of 9.2 to 16.9 eq. wt.% NaCl. The first melting temperatures of fluid inclusions in D1, D2 and D3 were about -21°C, suggesting a H<sub>2</sub>O-NaCl fluid system.

D4 contains only two-phase aqueous inclusions. The homogenization temperatures in D4 vary between 79 and 105°C. Complete freezing of inclusions occurred at temperatures between -86 and -54 °C. The first ice melting was detected at -35 to -40°C indicating the

possible presence of divalent cations such as Ca<sup>2+</sup> and/or Mg<sup>2+</sup> in the fluids (Shepherd et al., 1985; Goldstein and Reynolds, 1994). The final ice melting temperatures fall within a range of -15 and -9°C corresponding to salinities of 12.8 to 18.6 eq. wt. % NaCl. A couple of inclusions show homogenization temperatures exceeding 120°C with salinities higher than 20 eq. wt. % NaCl. The inconsistent homogenization temperatures and salinities obtained for these fluid inclusions, within the framework of an individual fluid inclusion assemblage (FIA) described by Goldstein and Reynolds (1994), indicate possible re equilibration of these inclusions and thus are not used in the interpretations.

The obtained homogenization temperatures in all fluid inclusion assemblages indicate the minimum temperatures at which the fluids could have been trapped (Goldstein and Reynolds, 1994). No correction was made for pressure effects on entrapment temperatures since no data regarding the exact depth and pressure of entrapment are available. In absence of independent thermal indicators such as Conodont Alteration Index (CIA) and Vitrinite Reflectance (VR), the accuracy of pressure correction cannot be well constrained (Slobodník et al, 2006), and thus no correction was made for pressure effects on homogenization temperatures.

No measurable fluid inclusion could be identified in CV1C1 and CV2C2 due to intense deformation twinning. CV3C3 and CV4C4 contain only primary mono-phase aqueous inclusions, indicating an entrapment temperature of below about 40-50°C (Goldstein and Reynolds, 1994). A complete freezing of the inclusions in CV3C3 occurred at temperatures between -40 and -52.5°C. The first melting temperature was detected at about -21 to -22°C, suggesting a H<sub>2</sub>O-NaCl composition. The final melting temperatures range between -6.4 and -2.7°C, corresponding to salinities between 9.7 and 4.5 eq. wt. % NaCl. The majority of the values cluster between 7.8 and 5 eq. wt. % NaCl.

The complete freezing temperatures of the inclusions in CV4C4 fall within -46 and -35.5°C. The first melting temperature could not be determined with confidence but the final melting temperatures were reached at about -0.1 to -1.8°C, corresponding to salinities of 0.17 to 3.0 eq. wt. % NaCl.

#### 5 Discussion

# 5.1 Stable and radiogenic isotopic composition of the parental fluids

The  $\delta^{13}$ C values of all dolomite types mimic the range of host rock and Jurassic marine limestones and, consequently, they can be interpreted as largely rock-buffered. Their  $\delta^{18}$ O values

are partly comparable similar to those of their respective host rocks as well as Jurassic marine reference values but more depleted when compared to the presumable Jurassic marine dolomites. The relatively depleted  $\delta^{18}O_{dolomite}$  values could indicate the contribution of heated fluids in dolomitization process, although it could also relate to recrystallization of a precursor dolomite by fluids at higher temperature or  $^{18}O$ -depleted (Land, 1980; 1985). The absence of distinctive textural evidence in the analyzed samples such as enlarged crystal size and/or systematic mottled cathodoluminescence pattern, and their co-variation with  $\delta^{18}O$  values do not confirm recrystallization (Mazzullo, 1992 and ref. therein). Nevertheless, special care was taken to avoid the samples that occasionally displayed scattered mottled luminescence.

The oxygen isotope fractionation relation between water and dolomite (Land, 1983) was used to determine the most plausible parental fluids. In order to avoid erroneous results due to rock-buffered  $\delta^{18}$ O values, only the  $\delta^{18}$ O values of dolomite cements, especially from the bed bed-parallel veins containing D4 were used. These values may provide the closest approximation to the  $\delta^{18}$ O signature of the parental fluids (Barker and Cox, 2011). Accordingly, a  $\delta^{18}$ O value of  $\approx +2.5$  to +4% V-SMOW was calculated for D3, while this values increase to  $\approx +5$  to +7.5% V-SMOW for D4 (Fig. 13D13d). The calculated compositions of the potential parental fluids are progressively higher. The higher  $\delta^{18}$ O composition of the dolomitizing fluids relative to the Mesozoic seawater, which is estimated at -1.2 to -1% V-SMOW (Shackleton and Kennett, 1975; Marshall, 1992; Saelen et al., 1996), is compatible with fluids derived from or that had interacted with siliciclastic rocks, crystalline basement (Taylor, 1997) and/or evaporite-derived brines.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratios obtained for all dolomite types are higher than the Lower Jurassic marine carbonate values (0.70704-0.70768; McArthur et al., 2012). Since marine carbonates have very low rubidium (Rb) concentrations they produce negligible *in situ* radiogenic <sup>87</sup>Sr after their deposition (Stueber et al. 1972; Burke et al. 1982). Therefore, the higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios can be explained by the contribution of fluids originated or interacted with potassium rich siliciclastics siliciclastic rocks (K-feldspars), crystalline basement and/or stratigraphic levels with higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios (Emery and Robinson 1993; Banner, 2004). Taking into account that the Upper Triassic Burano Formation underlying the studied intervals as the basal detachment has <sup>87</sup>Sr/<sup>86</sup>Sr ratios between 0.70774 and 0.70794 (Boschetti et al., 2005), the <sup>87</sup>Sr/<sup>86</sup>Sr ratios (D1 and D4) can partially be explained by their contribution. However, this contribution cannot justify

much higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios recorded in D3, being higher than values reported for Phanerozoic seawater (McArthur et al., 2012), and the values recorded inobtained for the adjacent basinal deposits (i.e. Corniola and Scaglia Formations). Therefore, parental fluids most likely originated from or had interacted with the siliciclastics siliciclastic rocks underlying the Burano Formation (Verrucano Formation), if present, and/or with the crystalline basement with common elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.71500-0.72650; Del Moro et al., 1982). The significantly higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios in D3 in comparison with other studied dolomites indicates a higher influence of <sup>87</sup>Sr/<sup>86</sup>Sr-rich fluids either due to major changes in the permeability architecture of faults or availability of such fluids. The lack of any ferroan diagenetic phase minimizes the interaction of fluids produced by clay transformation/dewatering (i.e. smectite to illite transformation; Boles and Franks, 1979).

CV1C1 is characterized by  $\delta^{13}C$  and  $\delta^{18}O$  values lower than the host limestones (i.e. Calcare Massiccio), while its  ${}^{87}Sr/{}^{86}Sr$  ratio is comparable similar to them. The salinity and composition of the parental fluids cannot be inferred here since no measurable fluid inclusions were found within this cement. The  ${}^{87}Sr/{}^{86}Sr$  ratio being within the range of the corresponding host rocks and the reference values, points to a rock-buffered system for  ${}^{87}Sr/{}^{86}Sr$ .

The  $\delta^{13}$ C and  $\delta^{18}$ O values obtained for CV2C2, as well as  $^{87}$ Sr/ $^{86}$ Sr ratios, fall within the range of the Scaglia host rocks, thus reflecting their rock-buffered nature. This interpretation is further supported by the comparable similar luminescence characteristics of CV2C2 with that of encasing Scaglia host rocks. The fluids from which CV2C2 calcite precipitated, as expected for tension gashes, were most likely derived from carbonate dissolution during pressure-solution and stylolitization of host rock<sub>7</sub>, pointing to a closed fluid system in contrast with the subsequent vein generations.

cV3C3 is characterized by  $\delta^{13}$ C values within the Jurassic marine values but are generally lower than the host rocks, while their  $\delta^{18}$ O values partially overlap both the hosting limestones and dolostones. Microthermometry of fluid inclusions revealed only mono-phase aqueous inclusions and thus precipitation at relatively low temperature ( $\leq 40\text{-}50^{\circ}\text{C}$ ) with moderate salinity (4.5-9.7 eq. wt. % NaCl). Such levels of salinity can be assigned to evaporated seawater, residual brines or fluids derived from evaporite dissolution, and thus makes it difficult here to interpret their exact origin with the available data.

 $\overline{\text{CV4C4}}$  is the latest calcite phase, and records the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, respectively enriched and significantly depleted when compared to their hosting rocks and preceding

diagenetic products. Generally, the enrichment of  $^{13}$ C could suggest CO<sub>2</sub> outgassing due to evaporation or pressure changes (Friedman, 1970; Hendry et al., 2015) or bacterial fermentation (methanogenesis) of organic matter (Hudson, 1977) in low temperature diagenetic environments. The homogenization temperature of  $\frac{\text{CV4C4}}{\text{CV4}}$  being below about  $40\text{-}50^{\circ}\text{C}_{2}$  could support any of these processes. Their low  $\delta^{18}\text{O}$  values and fluid inclusions with salinities comparable similar to, but also significantly lower than, seawater reflect the contribution of meteoric fluids during precipitation of this calcite.

# 5.2 Origin of the dolomitizing fluids

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The contribution of brines that derived from highly evaporated seawater or evaporites is suggested by the elevated salinity values obtained from microthermometry of the fluid inclusions (3.5 to 20.5 eq. wt. % NaCl). Accordingly, two sources that could potentially provide such fluids can be proposed: 1) fluids related to the Late Messinian evaporites, associated with the overlying <u>Upper Miocene</u> Laga Formation, deposited during the <u>Upper Miocene time</u>, and their possible downward percolation through fault zones by density driven flow and/or seismic pumping mechanisms (Sibson, 1981; McCaig, 1988, 1990); or their tectonic involvement into the Apenninic thrust wedge during its propagation (underthrusting; Lobato et al., 1983); and 2) fluids related to the underlying décollement detachment horizon of the Burano evaporites (Upper Triassic) and their upward flow through fault zones during development of the Montagna dei Fiori Anticline. The first scenario is valid if the dolomitization would have occurred only from the Upper Miocene time onwards. Moreover, Several researchers (e.g. Vai and Ricci Lucchi, 1977; Bassetti et al., 1998; Roveri et al. 2001) have shown that the occurrence of primary shallow-water evaporites, which were dominantly gypsum, was limited only to the western and central parts of the northern Apennines consisting of thrust-top marginal basins. In contrast, evaporites never precipitated in parts of the central Apennines including the Montagna dei Fiori region (Marche area) (Roveri et al. 2001). Hence, the evaporitic horizons existing within the Laga Formation corresponds to resedimentation (gypsum debris) of those previously precipitated in the marginal basins. This interpretation makes the Messinian evaporites an unlikely source of Mg-rich brines. Moreover, taking Taking into account that the maximum burial-burial-related temperature of the Calcare Massiccio Formation did not exceed 80°C in the Montagna dei Fiori region (Ronchi et al., 2003), it's it is not unlikely that the downward percolation of relatively low-temperature brines derived from the Messinian evaporites, located

at the higher stratigraphic levels, could reach or exceed the high temperatures recorded in fluid inclusions of the <u>studied</u> dolomites in the <u>Calcare Massiccio Formation</u> (D4; up to 105°C), given that the homogenization temperatures reflect the minimum entrapment temperatures (Goldstein and Reynolds, 1994). Deep circulation of these brines, if <u>they</u> existed, can also be excluded by <u>the fact that</u> their limited <u>tectonic</u> involvement <u>within</u> the thrust wedge <u>being was</u> confined merely to the off shore wards of the Montagna dei Fiori region (Artoni, 2013).

Accordingly, the Upper Triassic Burano Formation, the basal detachment, appears as the most plausible source for the high salinity brines recorded in fluid inclusions, and likewise, the Mg-rich fluids could have been originated from post-evaporite brines associated with them (Carpenter, 1978; McCaffrey et al., 1987). The fluctuations in salinity may argue for different degrees of diverse range of fault connectivity, different degrees of rock-water interaction and contribution of pore waters of lower salinity (e.g. marine or meteoric).

# 5.3 Timing and structural controls on the evolution of parental fluids

A generalized paragenesis and the relative chronology of dolomitization in relation to the structural evolution of the Montagna dei Fiori Anticline are illustrated in Figs. 14 and 15. The structural episodes are based on the evolutionary stages of the Montagna dei Fiori Anticline suggested by Storti et al. (2018). The paragenesis is constructed on the basis of direct evidences recorded during observations at outcrop scale and microscopic observations (e.g. cross-cutting relationships between diagenetic phases, stylolites, fractures and other structural kinematics), and indirect evidences (e.g. regional geodynamics and burial history).

The occurrence of micritic envelopes and fibrous calcite cements (FC), in grain-grain-supported stratigraphic levels of the Calcare Massiccio Formation, is interpreted to be of eogenetic origin (i.e. marine phreatic diagenesis; Moore, 1989), reflecting an early diagenesis shortly after deposition. The well-developed dull brown and orange concentric cathodoluminescence pattern of the succeeding mosaic calcite cement (MC) suggests a progressive shift to more reducing conditions during precipitation in a phreatic diagenetic environment (as shown in Li et al., 2017). High amplitude bed-bed-parallel stylolites postdate both cements, which confirm their precipitation before significant burial. The observations made here are in agreement with earlier work by Giacometti and Ronchi (2000), interpreting that the Calcare Massiccio Formation was cemented during the early diagenetic stages.

D1, CV1C1 and D2 are postdated cut by well-developed, high amplitude bed-parallel stylolites. Presence of D1 and CV1C1 in bed-perpendicular veins typically abutted cut by these stylolites (see Figs. 6E-6e to Hh) support the interpretation that the first dolomitization event (D1 and D2) took place before significant burial and stylolite development,. being tThe latter and bed-perpendicular veins are dynamically compatible within the same stress field which is characterized by a vertical, load-related maximum principal axis of the stress ellipsoid (Fig. 15a). The dominantly mono-phase fluid inclusions within D1 and D2 are in agreement with precipitation temperatures below about 40-50°C, suggesting a relatively shallow to intermediate burial environment and hence supporting a pre-Apenninic orogeny age of precipitation from a mix of formational and extra-formational fluids with elevated 87Sr/86Sr ratios. The distribution of D1 and D2 localized nearby the rifting-related ~ N-S and E-W striking extensional faults and even their displacement along them (Fig. 2A2a, e.g. site 1), point to the possible contribution of these faults in occurrence of D1 and D2. These faults dominantly affect the Jurassic rocks older than the Maiolica Formation which is attributed to the post-rift deposits, therefore suggesting a pre-Maiolica age for these dolomite types. Although, an absolute age cannot be provided, based on the evidence discussed above, the circulation of Mg-rich fluids during this dolomitization event was most likely controlled by rifting-related Jurassic extensional fault zones cutting through the crystalline basement. Precipitation of D1 and D2 at the lower part of Corniola Formation which is known as the syn-rift deposit discards a pre-rift origin for these dolomites. The displacement of dolomites along the aforementioned faults is possibly related to their prolonged activation during Early to Late Jurassic. In addition to the role of these faults in channelizing the fluids, their mobilization must have been intensified by some deriving mechanisms. A thermal convection system derived from high hit flux during rifting was interpreted by Hollis et al. (2017) to be responsible for circulation of seawater in a syn-rift dolomitization case in the Hammam Faraun fault block (Suez Rift, Egypt). In such scenario, the salinity of the fluids and their <sup>87</sup>Sr/<sup>86</sup>Sr ratios are expected to be more or less within the range of seawater. Furthermore, this scenario seems unlikely in the studied area given the lack of a deep aquifer to accommodate the fault tips and promotes the lateral fluid flux from basin to the rift shoulders and vice versa. Taking into account that D1 and D2 are the volumetrically more relevant dolomites within the studied intervals, and assuming the likely role of syn-rift extensional faults (Early to Late Jurassic) in their precipitation, a dominantly syn-rift

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dolomitization process is proposed for the dolostones in the Montagna dei Fiori Anticline. Although the CL zonation pattern observed in D2 may indicate changes in flow condition or fluid composition, the lack of physical disruptions such as multiple fracturing suggests external regional controls rather than slip along the same faults (Eichhubl and Boles, 2000). The absence of pervasive syn-dolomitization fracturing and brecciation as well as zebra fabrics in these dolomites, perhaps indicate a relatively calm tectonic period during dolomite development (e.g. Hollis et al., 2017).

D3 and D4 both record elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios which accounts for their fault-controlled origin. However, their occurrence at the top of the Calcare Massiccio and overlaying Bugarone Formation (Corano Quarry site) which is < 1 m thick in Montagna dei Fiori region, and is marked as the final rift deposit (Cardello and Doglioni, 2015) discards a syn-rift origin for these dolomites. Moreover, D3 and D4 postdate the development of high amplitude bed-bed-parallel stylolites. The formation of stylolites requires an approximate overburden of 600 to 1500 m (Lind, 1993; Machel, 1999; Mountjoy et al., 1999; Schulz et al., 2016), corresponding to a late to post-Maiolica deposition time (Early Cretaceous time onwards). The presence of D3 and D4 dolomites in bed-bed-parallel fractures and as shear veins (D4) (Figs. 9a and b) suggests their association with contractional deformations, i.e. the most likely tectonic regime for explaining bed-perpendicular dilation. Therefore, the volumetrically minor second stage of dolomite precipitation may possibly be related to the Late- to post-Miocene compressional tectonics recorded in this region (e.g. Mazzoli et al., 2002; Artoni, 2013; Storti et al., 2018).

Dolostones containing D3 and D4 appear commonly as clast-supported breccias along fault zones pertaining to the Montagna dei Fiori Fault, then overprinted by fault-parallel stylolites (Figs. 3 and 7). Accordingly, the occurrence of these dolomites was probably synchronous with the incipient stages of fault development, predating fault buttressing (Storti et al., 2018). Homogenization temperatures recorded in D4 (up to 105°C), much higher than the maximum temperatures recorded in the host rocks (below about 80°C; Ronchi et al., 2003), suggest hydrothermal fluid circulation. The development of the Montagna dei Fiori Anticline at the toe of the Late Miocene Central Apennines thrust wedge could have favored the forelandward migration of hydrothermal fluids expelled from the more internal regions of the belt, similarly to what has been proposed for the Rocky Mountains foreland (i.e. squeegee flow model; Machel and Cavell. (1999). Such a migration may have possibly favored the precipitation

of D4 in bed-bed-parallel veins, generally considered as evidence for syn-compressional fluid overpressure (Sibson, 2001; Hiemstra and Goldstein, 2015). At this stage, in addition to dilation of the pre-existing ~ N-S and E-W striking rift-related extensional faults and their possible role in fluid migration, the excess of pore pressure at the base of the thrust ramp, in the fold hinge and during fold tightening could promote the localization of the fractures (Smith and Wiltschko, 1996; Ghisetti and Vezzani, 2000), with fluid migration within this zone and eventually dolomitization. These fractures could have been corridors that later on formed the insipient NW-SE Montagna dei Fiori Fault. Their localization at the back-limb cross-cutting the core, explaining best the distribution of D3 and D4 at this locality. The presence of only D5 only within the damage zone of the Montagna dei Fiori Fault, postdating dolostone brecciation and, in places, cementing breccia fragments, may suggest that D5 dolomite precipitation was associated with the late stage evolution of the Montagna dei Fiori Fault, predating late stage calcite precipitation. The shift from dolomite to calcite precipitation can be ascribed to attenuation of Mg-rich fluids and/or calcite saturation. This condition was perhaps initiated during the late stages of anticline evolution due to changes in fault conductivity sealing the upward migration of Mg-rich fluids. The presence of several generations of bed-bed-perpendicular stylolites bounding and intersecting CV2C2 veins (Fig. 10), supports the postulation that late stage calcite cements precipitated in close elosely associated association with the deformation history of the Scaglia Formation in the hanging wall of the Montagna dei Fiori Fault (Fig. 3). This deformation occurred, during buttressing against Calcare Massiccio and Corniola Formations in the footwall, and related with the positive inversion event induced by thrust-sheet stacking at depth (Storti et al., 2018). Precipitation of CV3C3 and CV4C4 in is interpreted to have occurred during uplift and cooling as revealed by their relatively low homogenization temperatures ( $\leq 40-50$ °C) of fluid inclusions trapped within these cements. Deformation twinning is either absent or weakly developed, reflecting the lack of significant tectonic deformation after calcite precipitation. These cements postdate the dolomitization events, high amplitude bed-bed-perpendicular and parallel stylolites, and are precipitated as cements bounding the breccia fragments within the damage zone of the Montagna dei Fiori Fault. Salinities calculated from their fluid inclusions, particularly in CV4C4, suggests precipitation from meteoric waters, which should have been

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favored during the late evolutionary stages of antiformal stacking beneath the Montagna dei Fiori

Anticline, and eventual late extensional slip along the Montagna dei Fiori Fault (Storti et al., 2018). The results obtained in this study are in relative agreement with the earlier work by Ronchi et al. (2003) and Murgia et al. (2004) in the Central Apennines, assigning dolomitization phases to the pre- and syn-orogenic deformations, although they did not specify the direct relation between the <u>local</u> structures and the different types of dolomite.

The textures of the studied dolomites vary from planar-e to non-planar, the preponderance of planar dolomite, as in D4, creates a rock with interesting poroperm characteristics (e.g. Woody et al., 1996; Wilson et al., 2007; Wenzhi et al., 2012). This case-study is certainly relevant for many potential reservoirs elsewhere in the world. Similar multistage burial dolomitization events enhancing the reservoir quality have been reported from the carbonate successions of the Jurassic in the Kopet-Dagh Basin, north eastern Iran (Adabi, 2009) and Devonian of the Rainbow sub-Basin, western Canada (Qing and Mountjoy, 1989; Lonnee, 1999).

## **6 Conclusions**

The Lower Jurassic limestones outcropping at the core of the Montagna dei Fiori Anticline (Central Apennines, Italy) are massively affected by dolomitization, in damage zones of the pre-orogenic faults inherited from the Tethyan rifting and the ones formed during the Apenninic orogeny. Cross-cutting relationships between deformation structures, and results from optical and cold cathodoluminescence petrography, fluid inclusion microthermometry, and isotope geochemistry, support the occurrence of two major dolomitization events. The first event is interpreted as <a href="having">having</a> developed during the late stages of Tethyan rifting in Jurassic and resulted in volumetrically significant dolostone geobodies. These dolostones are <a href="majorly-largely">majorly-largely</a> matrix replacive, and their precipitation initiated prior to the significant burial as reflected in their cross-cutting relationship with <a href="bed-bed-parallel">bed-bed-parallel</a> stylolites, and by homogenization temperatures in fluid inclusions that are dominantly below about 40-50°C. The second dolomitization event corresponds to volumetrically less relevant replacive dolomite and dolomite cements occluding fractures. These dolomites precipitated during hydrothermal fluid circulation associated with contractional tectonics during the Apenninic orogeny, possibly at the onset of the growth of the Montagna dei Fiori Anticline (Late Miocene).

Dolomitizing fluids in both events were most likely sourced from evaporitic brines associated to the underlying Burano evaporites and their interaction with siliciclastic rocks and/or the crystalline basement.

Author contributions. M. Mozafari participated in fieldwork, performed petrographic and microthermometric analyses, provided their interpretation, and wrote the manuscript; R. Swennen participated in fieldwork, discussed the results of the diagenetic study, and critically reviewed the manuscript; F. Balsamo contributed to collect and interpret structural data, discussed structural diagenesis data interpretation, and critically reviewed the manuscript; H. El Desouky collected <sup>87</sup>Sr/<sup>86</sup>Sr data; F. Storti conceived the research, contributed to collect and interpret structural data, discussed structural diagenesis data interpretation, and critically reviewed the manuscript; C. Taberner participated in fieldwork, discussed the results of the diagenetic study and their framing into the proposed structural evolution, and critically reviewed the manuscript.

Acknowledgments. This research was performed by collaboration between Parma and KU Leuven universities in the framework of a research project (PT12432 and GFSTE 1100942) funded by Shell Global Solutions International (Carbonate Research Team, now Geology and New Reservoir Types Team). We thank E.M. Selmo (Parma University) and M. Joachimski (University of Erlangen, Germany) for the stable carbon and oxygen analysis. G. Davis (VU Amsterdam, the Netherlands) is thanked for the strontium isotope analysis. A. Comelli and H. Nijs are kindly thanked for the careful preparation of the wafers and thin sections. L. Barchi is gratefully appreciated for his help in SEM analysis. We gratefully acknowledge A. Koopman for the constructive discussions during field work. We appreciate D. Smith (Energie Beheer Nederland, the Netherlands) for the careful reviewing of the manuscript. We are very grateful to reviewers J. Hendry and E. Ukar for their suggestions that allowed us to significantly improve the manuscript.

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## 1251 Table captions

- 1252 Table. 1. Stable carbon and oxygen isotopes, <sup>87</sup>Sr/<sup>86</sup>Sr ratios, and fluid inclusion
- microthermometry data (not pressure corrected) of host rocks and diagenetic phases in the
- Montagna dei Fiori Anticline. Stable carbon and oxygen isotopes values are expressed in
- 1255 % V-PDB and salinity values in eq. wt. % NaCl.

## Figure captions

Fig. 1. Aa) Simplified regional map (modified after Ghisetti and Vezzani, 1997) showing the tectonic outlines of the Central Apennines and the study area (rectangle). Bb) Schematic geological map of the Montagna dei Fiori Anticline showing the distribution of dolostones (modified after Storti et al., 2017a). Cc) Lithostratigraphical column of the successions exposed in Montagna dei Fiori (modified after Mattei, 1987; Di Francesco et al, 2010; Storti et al., 2018). Letter B stands for the Bugarone Formation. Lithologies are mentioned in the text. Note that the thickness of the not-outcropping formations (Triassic evaporites and the crystalline basement) is not to scale. Dd) Regional Geological geological transect across present day Central Apennines and the Adriatic Sea (modified after Fantoni and Franciosi, 2010) with vertical exaggeration of 2:1. The dashed rectangle indicates the Montagna dei Fiori Anticline region.

Fig. 2. Aa, Bb) Geological map of the central sector of the Montagna dei Fiori Anticline, and cross-section oriented parallel (a-b) to the hinge line representing the tectono-stratigraphic architecture of the faulted anticline (modified after Storti et al., 2017a). The stereonets (Schmidt equal area projection lower hemisphere) provide the attitude of the extensional faults. The locations of the corresponding field sites are indicated by numbers letters. c) At this location, well exposed N-S striking extensional fault zones offset the dolomitized Corniola Formation. The fault zone is characterized by near-horizontal stylolites localized in the footwall damage zone (4 fault data). d, e and f) These locations consist of mostly ~ E-W striking extensional fault zones. Particularly the boundary fault zones delimiting Calcare Massiccio Formation in the main horst block is evident (site d: 20 fault data; site e: 24 fault data; site f: 9 fault data). g and h) At these locations, dip-slip slickenlines support major extensional movements related to the Montagna dei Fiori Fault. Contractional deformation structures are preserved in the bed-perpendicular

stylolites, shear surfaces and tension gashes arranged as S-C arrays (site g: 21 fault data; site h: 14 fault data). Equal area projection, lower hemisphere.

Fig. 3. Aa) Field photograph showing the deformed Scaglia Formation in the hanging wall (HW) and brecciated, dolomitized Calcare Massiccio Formation in the footwall (FW) of the Montagna dei Fiori Fault. The red arrow indicates the sense of fault movement. Bb) A hand specimen from the deformed Scaglia formation showing the intensity of the abundant pressure solutions seems (TS), indicated by arrows, and their abutting relationship withcross-cutting calcite veins (CV2C2). Cc) A transmitted light photomicrograph of the dolomitized, brecciated Calcare Massiccio Formation. Note all the breccia fragments are composed of dolomite (D4 here).

Fig. 4. Field photographs (Corano Quarry) showing the field relations between dolostones (only D3 here), host limestones and the Montagna dei Fiori Fault: Aa) Panoramic view showing the spatial relationship between limestones and dolostones (orange) in the damage zone of the Montagna dei Fiori Fault (F). Note that the limestones and including dolostones of the Calcare Massiccio and Bugarone Formations on the footwall (FW) and marly limestones of the Scaglia Formation on the hangingwall (HW) are intensely deformed. Bb) Plan view of the dolomitized Calcare Massiccio limestone in the footwall damage zone: intersected by calcite veins (CV1C1), which are partially dolomitized, and affected by bed-bed-perpendicular stylolites (arrows). Cc) Distinct transition (dashed line) between dolomitized and undolomitized Calcare Massiccio limestone in the footwall damage zone.

Fig. 5. Field photograph (Aa) and a simplified sketch (Bb) in field site d showing of a dolomitic pocket (grey color) within the folded Calcare Massiccio (grey color) and their its relation with bed-bed-parallel stylolites within the Calcare Massiccio Formation (hammer is 40 cm long). Note C1 is the only calcite cement here.

Fig. 6. <u>Undolomitized and dolomitized Calcare Massiccio Formation in field site d: Aa)</u>
Transmitted light image showing a micritic peloid rimmed by the fibrous cements (FC) which are <u>followed overgrown</u> by the mosaic cements (MC). <u>Bb</u>) Transmitted light image showing mosaic cements (MC) in a peloidal limestone over-printed by high amplitude <u>bed-bed-parallel</u>

stylolites (dotted white line). Note the core of some of the peloids is partially cemented as well. Cc, Dd) Respectively, transmitted light and corresponding cathodoluminescence image of FC and MC cements. Ec) Transmitted light photomicrograph showing D1 crystals (arrows) rimming lining a fracture which is cemented by CV1C1. The fracture is in turn affected by a bed-bed-parallel stylolite. Ff) Cathodoluminescence image showing D1 scattered in the host rock and riming the fracture. Gg, Hh) Respectively, transmitted light and corresponding cathodoluminescence image showing part of a bed-bed-parallel stylolite (dotted white line) overprinting D1 and D2 crystals.

Fig. 7. Aa, Bb) Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image showing the zoned rhombs of D2 with the remnants of D1 preserved in their cloudy core sampled from dolomitized Calcare Massiccio Formation in field site d. The pore space is occluded by D4. Cc, Dd) D3 cementing angular breccia fragments of the Bugarone Formation in the damage zone of the Montagna dei Fiori Fault in the Corano Quarry site. Note the breccia is overprinted by a fault-fault-parallel bed-bed-perpendicular stylolite. Ec, Ff) Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image showing the euhedral to subhedral crystals of D3 entirely replacing the matrix and also present as cement developing a bright subzone and rim sampled from dolomitized Corniola Formation in Osso-caprino road. Gg, Hh) D3 with a saddle crystal outline (SD) postdating calcite cements (MC) and a zoned D2 crystal. The saddle morphology is outlined by a dotted white line.

Fig. Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image of dolomite types: Aa, Bb) The cross-cutting relationship between D3 and D4 sampled from dolomitized Corniola Formation in Osso-caprino road. Note the presence of D3 within the core of dolomite crystals overgrown by D4. Cc, Dd) Successions of dolomite types sampled from dolomitized Calcare Massiccio Formation in field site f. Note the green CL color of D4 crystals. Typically, luminescent dolomites are known to show yellow, orange to red colors (Machel et al., 1991). Green luminescence in carbonates including dolomite have been attributed by a number of researchers to the incorporation of three valent rare earth elements (REE) such as Dy3+ and U3+ as luminescence activators within their crystal lattice (Luczaj and Goldstein, 2000). Another possibility is the emplacement of Mn<sup>2+</sup>, with yellow

luminescence, in Ca<sup>2+</sup> sites with blue luminescence in the dolomite crystal lattice instead of preferential incorporation in the Mg<sup>2+</sup> site (Sommer, 1972b; Amieux, 1982; Walker et al., 1989; Habermann et al., 1999). Accordingly, non-stoichiometric, Ca-rich and poorly ordered dolomites may favor Mn<sup>+2</sup> incorporation into their Ca<sup>2+</sup> site. Ee, Ff) Vuggy porosity rimmed by D4 (green CL). Note the porosity is filled with fine dolomite rhombs including traces of D2 in their core and D4 overgrowths.

Fig. 9. Photomicrographs showing respectively, transmitted light and corresponding cathodoluminescence image of D4 and D5 in relation to stylolites and fracturing: Aa, Bb) D4, exploiting a bed-bed-parallel stylolite that crossed-cuts D1 and D2 sampled from dolomitized Calcare Massiccio Formation in field site d. Cc, Dd) A sub-horizontal fracture cemented by D4 sampled from dolomitized Corniola Formation in field site f. Ee, Ff) D5 microveins (arrows) intersecting all the predating dolomite types in the footwall brecciated zone of the Montagna dei Fiori Fault-, sampled from dolomitized Calcare Massiccio Formation in Castel Manfrino site.

Fig. 10. Field photographs showing the major calcite vein settings observed in Montagna dei Fiori: Aa) Cross-sectional view of bed normal Calcite vein 1 (CV1C1) abutting bed-bed-parallel stylolites in folded beds of the Calcare Massiccio Formation. Bb) Plan view of the Calcite vein 2 (CV2C2) intensely affecting the deformed Scaglia (Rossa) Formation. Cc, Dd) Cross-sectional view of the Scaglia Formation, intensely affected by pressure solution seams of tectonic origin crossed-over by populations of bed-perpendicular Calcite veins (CV3C3) in en echelon extensional arrays.

Fig. 11. Aa) Cathodoluminescence and transmitted light (in set) image showing blocky to elongated crystals of CV1C1 with zoned CL pattern in the Corano Quarry site. Bb) Transmitted light image showing intensely twinned CV1C1 crystals overprinted by euhedral to subhedral crystals of D3 in the Corano Quarry site. Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image: Cc, Dd) CV2C2 in the Scaglia Formation abutted by a bed-bed-perpendicular stylolite (indicated by white arrows and dashed line) in the Corano Quarry site. The crystals display blocky to fibrous morphologies, deformation twinning, and a similar orange luminescence pattern comparable withsimilar to the adjacent host rock. Ee, Ff)

CV3C3 cementing the breccia fragments in the damage zone of the Montagna dei Fiori Fault. The crystals are blocky and show faint deformation twinning. They are brown-orange with distinct darker luminescence sector zones. Gg, Hh) CV4C4 present as a cement within a polygonal pore space rimmed by dolomite, sampled from dolomitized Calcare Massiccio Formation in field site f. Note the blocky crystals, absence of deformation twinning and distinct concentric luminescence zonation pattern. CV4C4 is corroded and followed by a late telogenetic calcite.

Fig. 12. A, B) Overview of the  $\delta^{13}$ C and  $\delta^{18}$ O values of dolomites (Aa) host rocks from Montagna dei Fiori as well as calcite veins (Bb). The stable isotope value of Lower Jurassic marine limestones based on Veizer et al. (1999) is indicated by a dashed rectangle in subset B. The  $\delta^{18}$ O values of the marine dolomites are considered to be 3-4‰ V-PDB higher than those of marine limestones (Land, 1980; Major et al., 1992; Horita, 2014). Cc) Cross-plot of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and corresponding  $\delta^{18}$ O values of host rocks, dolomites and calcite veins compared with Lower Jurassic marine carbonates  ${}^{87}$ Sr/ ${}^{86}$ Sr (dashed rectangle) framework reported by McArthur et al. (2012).

Fig. 13. Overview of microthermometry analysis of primary inclusions in Montagna dei Fiori: Aa) Frequency distribution of the Tm<sub>ice</sub> (°C) in dolomite phasestypes. Bb) Frequency distribution of the Th (°C) in dolomite phasestypes. Cc) Salinity (eq. wt. % NaCl) versus Th (°C) of dolomite and calcite phases. Dd) Isotopic fractionation diagram from Land (1983) used to determine the isotopic composition (% V-SMOW) of parental fluids in equilibrium with dolomites in Montagna dei Fiori.

Fig. 14. A) Generalized paragenesis of diagenetic phases in relation to deformational stages and burial history of the Calcare Massiccio Formation in the Montagna dei Fiori Anticline. The deformational stages are from Storti et al. (2018), and the burial curve is based on Ronchi et al. (2003). The burial curve was made based on paleo-depth, paleo-temperatures, sedimentation rate and paleo-heat flow.

Fig. 15. Sketch showing the successive fault-related diagenetic phases, of most importantly dolomitization, recorded in the carbonate succession exposed at the core of the Montagna dei Fiori Anticline (not scaled). Different diagenetic phases are indicated with different colors. Aa) The first dolomitization event is pre-orogenic (syn-rift), triggered from the fluids channelized along Jurassic ~ E-W and ~ N-S striking extensional faults. This event occurred during burial compaction and development of bed-bed-parallel stylolites (BS). It is represented by scattered dolomite rhombs (D1) followed by calcite cementation (CVICI). The dolomitization continued with precipitation of larger crystals of D2. **Bb**) Second dolomitization event: syn-orogenic (early folding/ faulting) dolomitization from fluids that migrated from more internal regions of the thrust belt and were channelized along the basal detachment level into the fold core. This dolomitization event presents matrix replacive and cements displaying infrequent saddle outlines (SD) in pore spaces, within bed-bed-parallel veins and shear fractures. These dolostones postdate compaction but are affected by bed-bed-perpendicular stylolites (TS) generated by horizontal to sub-horizontal layer layer-parallel shortening related to the growth of the Montagna dei Fiori Anticline. Cc) Extensional collapse of the anticline and development of the Montagna dei Fiori Fault, followed by buttressing of the Scaglia against Calcare Massiccio and Corniola Formations during positive inversion induced by continuing underthrusting at depth. Precipitation of D5 in micro-veins and cements in breccia zones, followed by late stage calcite cementation in the Montagna dei Fiori Fault damage zone (CV2C2, CV3C3 and CV4C4).

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	Stable isotopes		Sr isotopes	Fluid inclusion microthermometry		
	$\delta^{13}$ C	$\delta^{18}O$	<sup>87</sup> Sr/ <sup>86</sup> Sr	Th (°C)	Salinity	n
Calcare Massiccio Fm.	+2.4 to +3.1	-1.6 to 0.0	0.70766	-	-	
Corniola Fm.	+2.0 to +2.5	-3.1 to -1.4	0.70725	-	-	
Scaglia Fm.	+1.0 to +3.1	-2.2 to -1.0	0.70784-0.70791	-	-	
D1	+2.5	-1.9	0.70789	≤ 40-50	3.5 to 11.3	<u>27</u>
CV1	+1.6 to +2.1	-4.7 to -2.7	0.70773	-	-	Ξ
D2	-	-	-	$ \leq 40-50 \text{ to} $	7.9 to 20.5	<u>37</u>
D3	+2.0 to +2.6	-2.8 to -1.9	0.70859-0.70964	70 to 73	9.2 to 16.9	9
D4	+2.4 to +2.5	-3.0 to -2.5	0.70790	79 to 105	12.8 to 18.6	<u>7</u>
CV2	+1.2 to +3.1	-1.7 to -1.6	0.70779 - 0.70787	-	-	
CV3	+0.5 to +2.4	-2.2 to 0.0	-	≤ 40 <b>-</b> 50	4.5 to 9.7	9
CV4	+3.8 to +4.9	-9.4 to -9.1	-	≤ 40-50	0.17 to 3.0	<u>19</u>

Table. 1

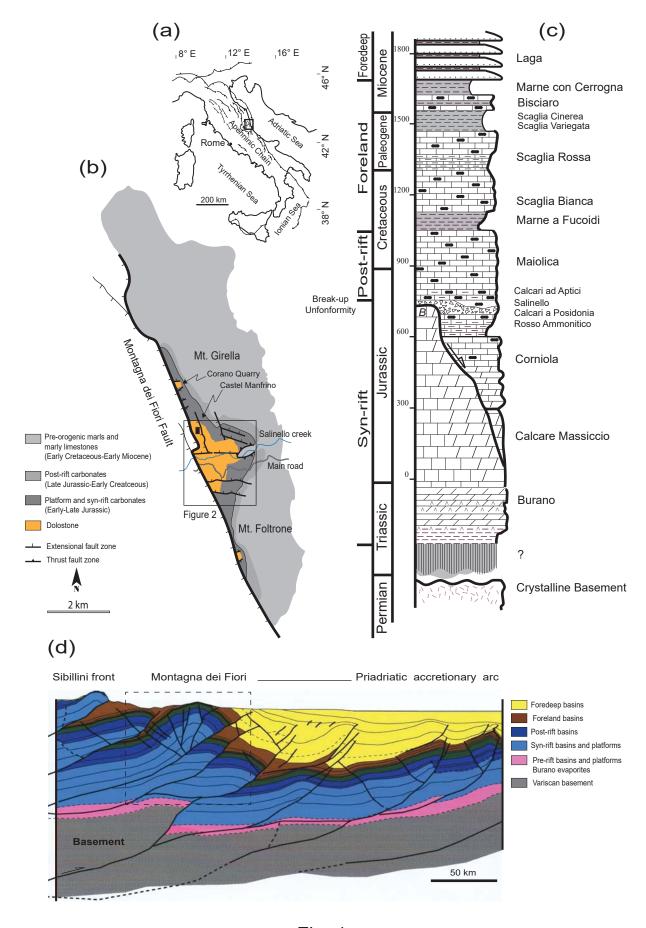


Fig. 1

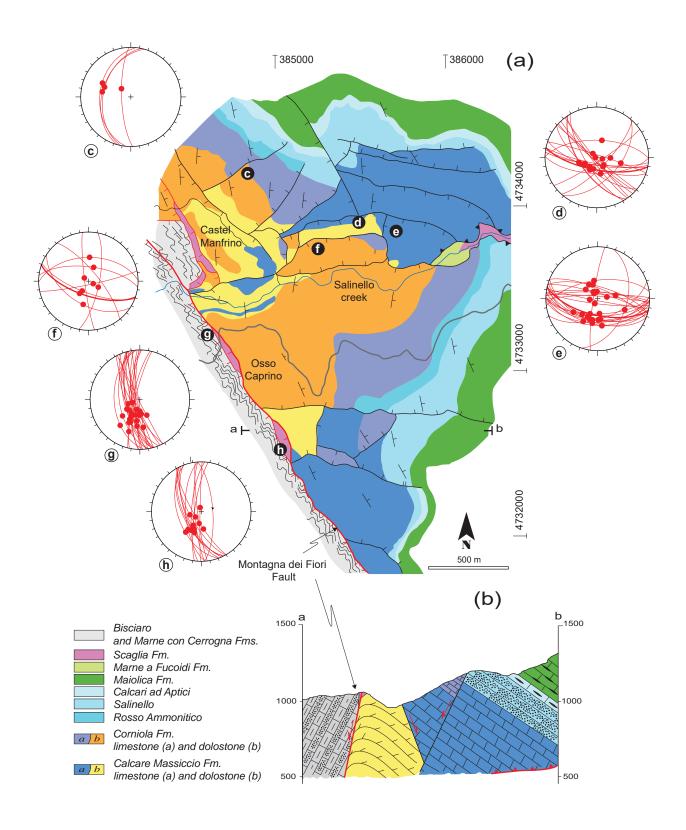


Fig. 2

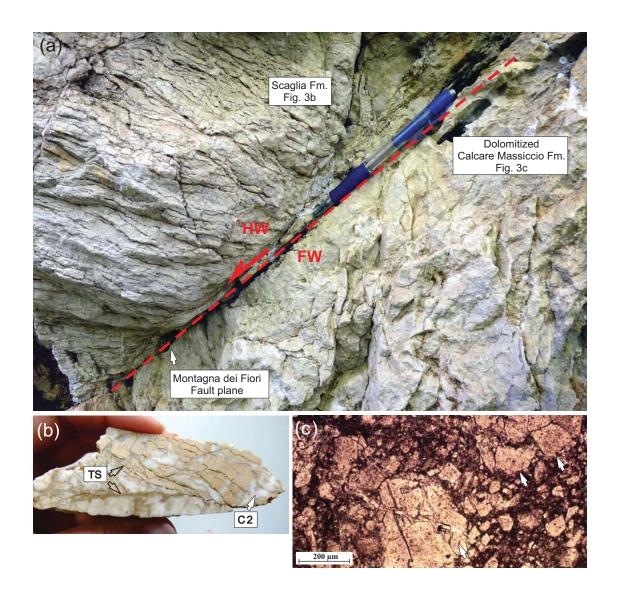


Fig. 3

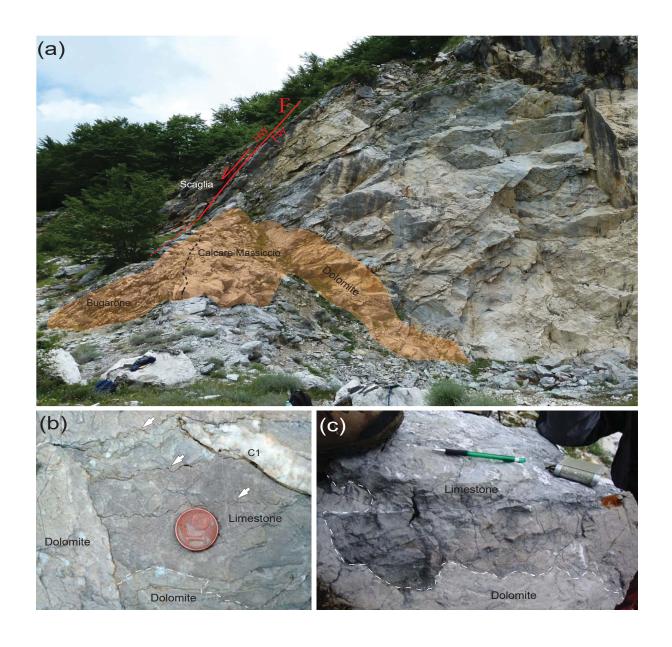


Fig. 4

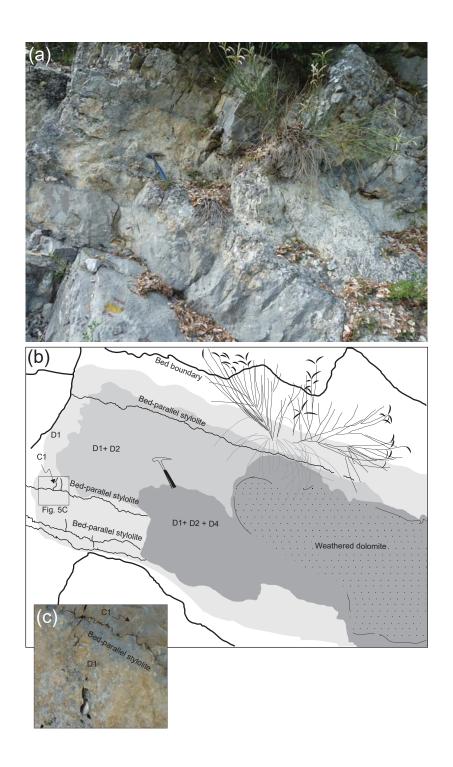


Fig. 5

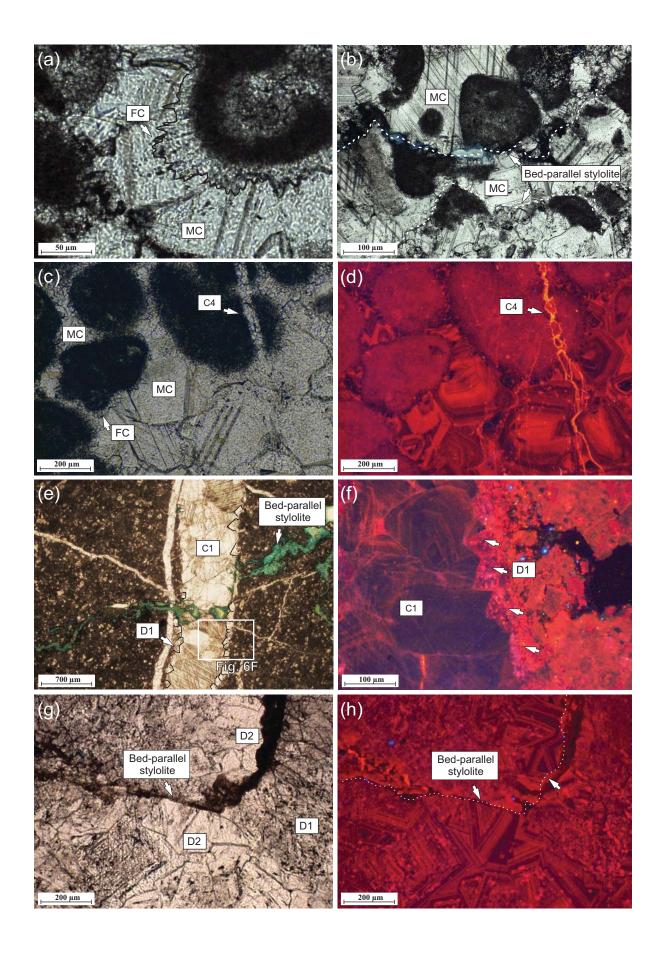


Fig. 6

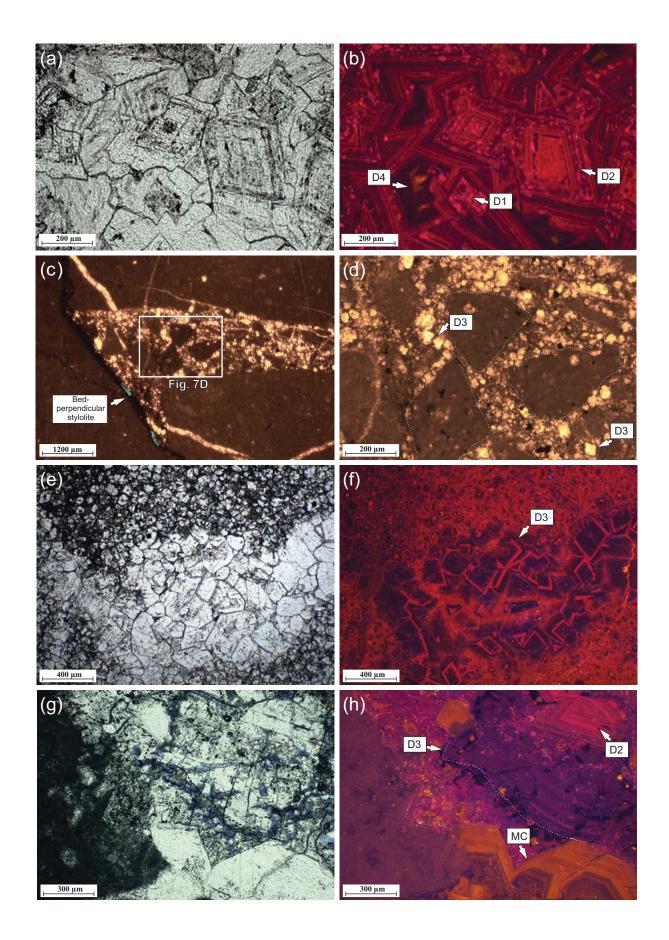


Fig. 7

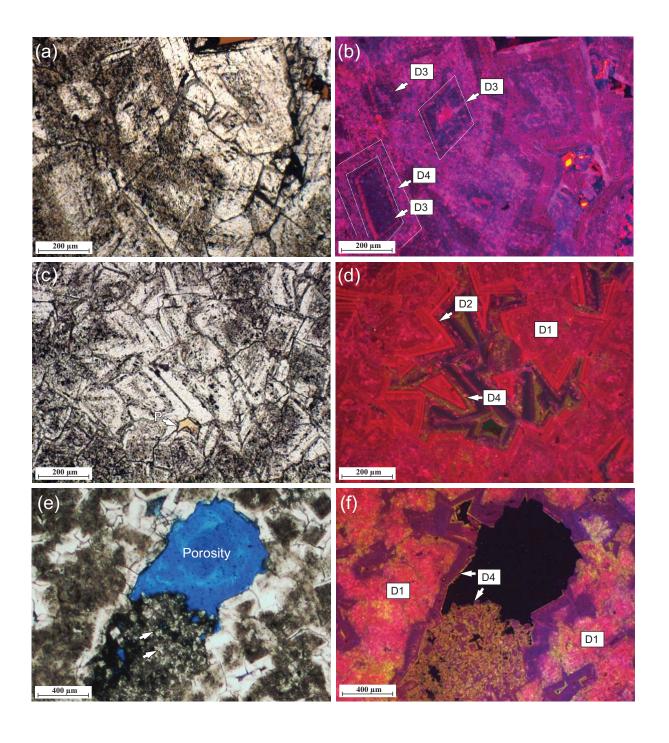


Fig. 8

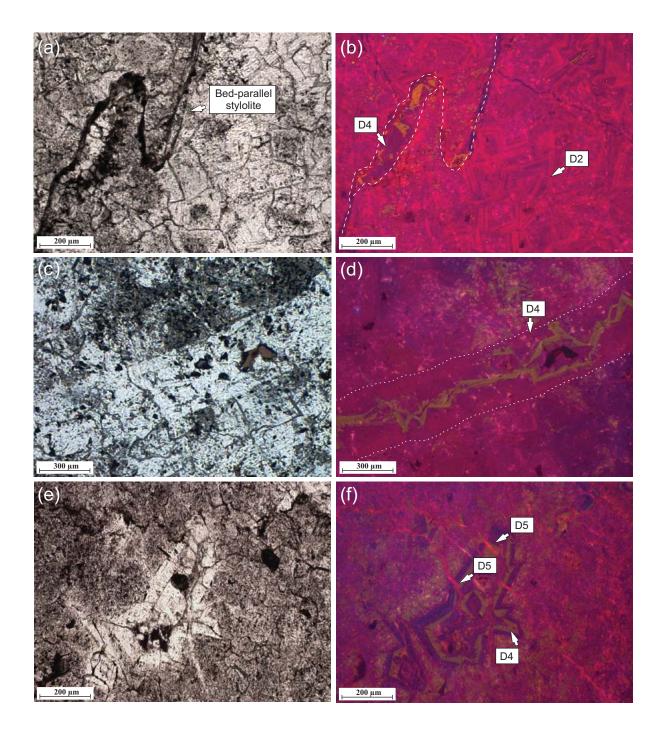


Fig. 9

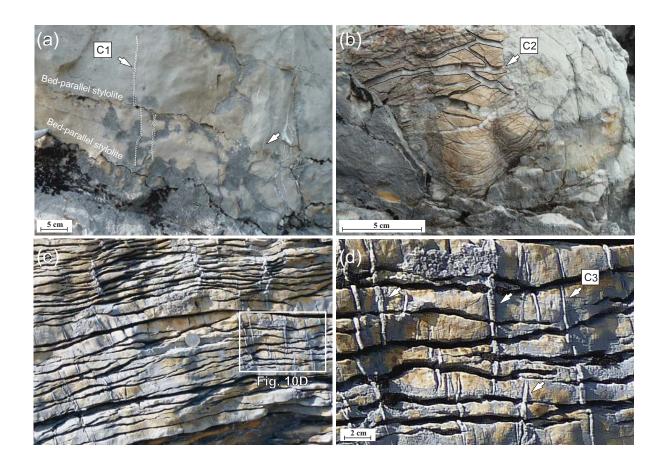


Fig. 10

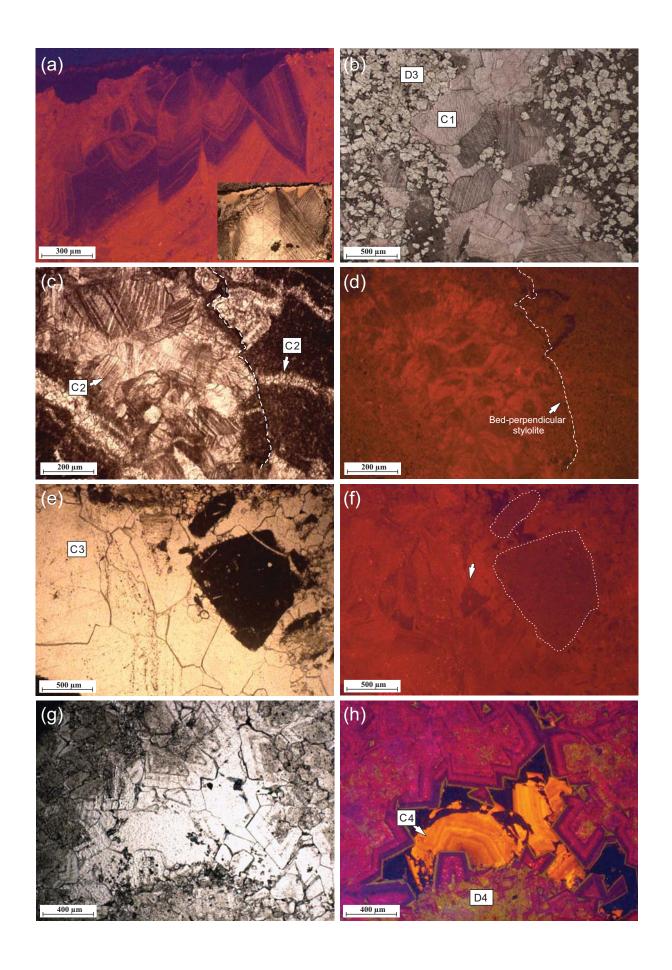


Fig. 11

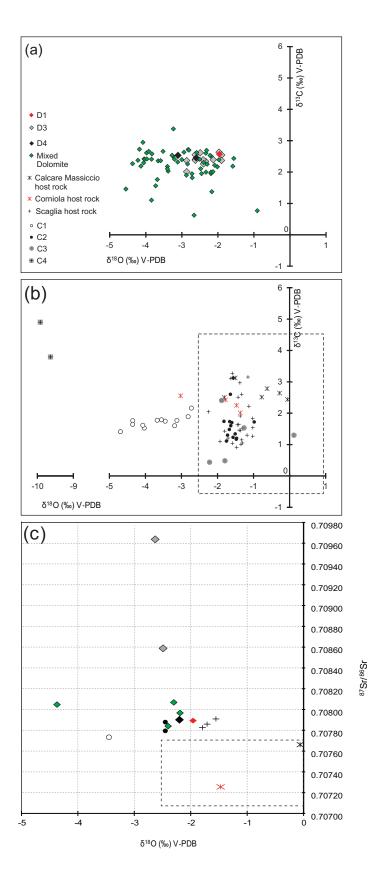


Fig. 12

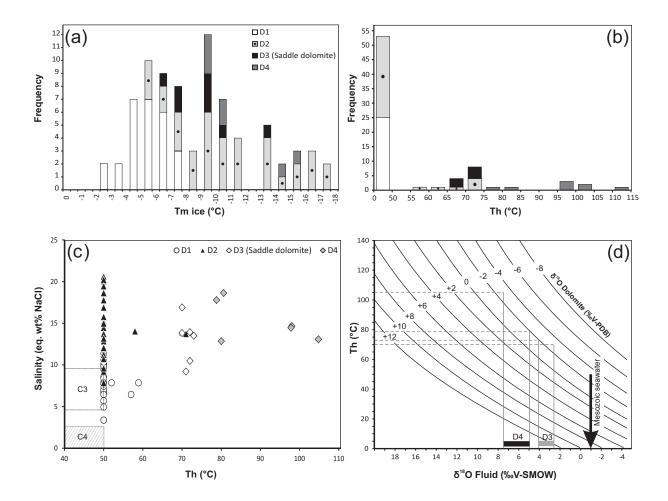


Fig. 13

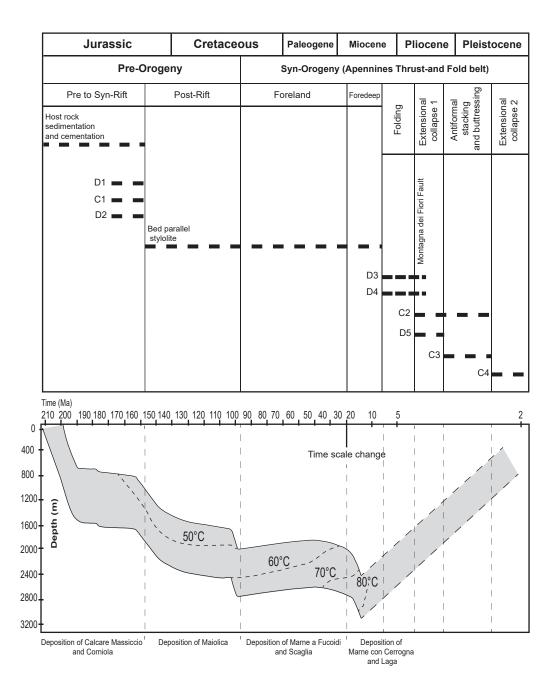


Fig. 14

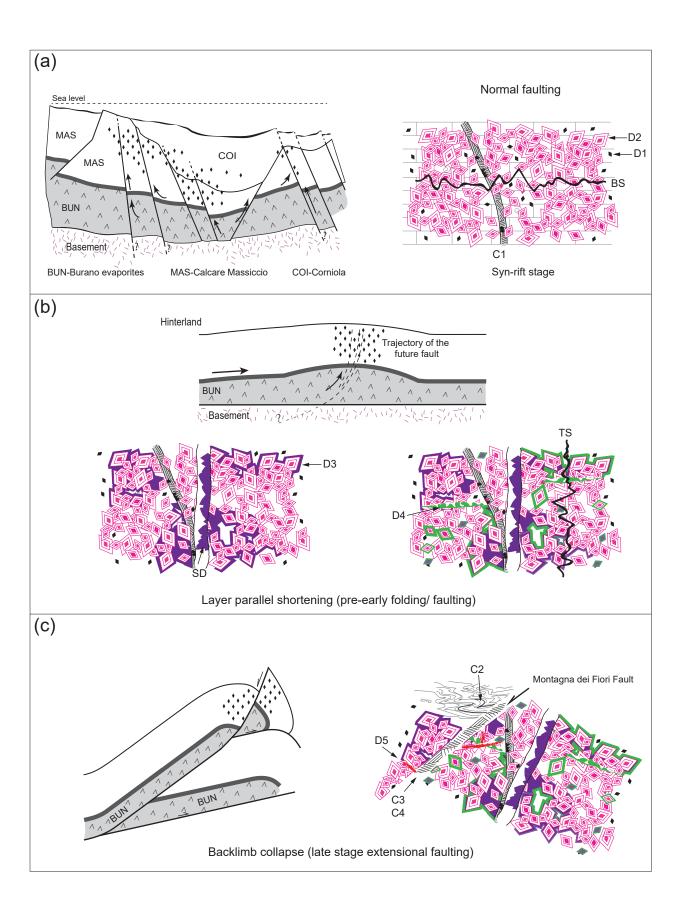


Fig. 15

# Review of "Fault-related dolomitization in the Montagna dei Fiori Anticline (Central Apennines, Italy): Record of a dominantly pre-orogenic fluid migration. Se-2018-136

This manuscript presents field, petrographic and geochemical data from non-stratabound dolomites in a complex tectonic setting, and interprets their geofluid origin (parent fluids, timing) in the context of the tectonostratigraphic history.

It is coherent and logically organised. Aspects of the written English need minor improvement (punctuation, plurals, word order, etc); it will benefit from a final revision by a native English speaker.

The data are generally of good quality, and the interpretations are mostly justified from the results presented. In any study such as this, with limitations imposed by the ability to sample all the phases, there is necessarily some latitude or flexibility in the deductions that can be made. However, the authors do a good job of considering alternative possibilities for the fluid sources and timings.

My only issue with the paper is that the authors have not really considered whether there are wider implications or generic advances that can be made from the research. It presents itself as a case study, albeit one with a good integration of structural and diagenetic data. But what is the wider impact that will attract a non-specialist readership? Within the paper the authors all but admit that their findings are only modestly advanced from those of Ronchi and co-workers fifteen years ago (lines 638-642). I had hoped to see more progression in the science, and maybe the authors need to more thoroughly and critically evaluate the Ronchi model in the light of their new data. They could also work the structural data more – rather than just considering fault orientations and timings, what about the character and extent of the damage zones associated with different fault types / generations, and their relationship to the size and shape of dolomite bodies? What determines the lateral extent of dolomites? Is it other faults / fractures, or a gradual reaction front?

One generic aspect that the authors could address is implications for reservoir potential in analogues for this setting. The preponderance of planar dolomite is significant because planar dolomite is usually very beneficial for porperm (unlike many examples of hydrothermal dolomitization that feature tight nonplanar dolomites). Are there dolomitised plays in the Middle East that this study could be compared to (Zagros Mountains for example?), or maybe in Mexico?

Another factor of interest, largely by-passed in the text, is what drove the fluid circulation necessary to cause massive dolomitization when the low temperatures argue against a hydrothermal syn-rift system. Can the authors attempt a mass balance to estimate the order of magnitude fluid volumes needed? Maybe the dolomitization occurred in the down-flowing (cool) limb of a convection cell established on syn-rift faults that breached contemporary sea bed? Or does the dolomite zoning imply a pulsed fluid flow associated with strain cycling or seismic valving? I recommend the recent papers by Hollis and others on the Hammam Faraun fault and related syn-rift dolomitization. Are the D1-2 dolomites formed in a similar manner to this geologically younger example? Likewise, with the later dolomitization, which structures would have been open during compressional tectonics and able to serve as conduits for substantial fluid volumes?

If the authors address these issues their paper, which is already technically good, it will have much greater impact and interest across the sedimentary and structural geoscience community.

I have some more **specific comments** – these are tagged by line number or Figure number:

Line 43: The paper describes the role of evaporite-sourced fluids in the dolomitization process, but I am not sure that it illustrates a controlling role of evaporitic detachments. These may have influenced the tectonic development, but if it is believed that they directly controlled the dolomitization this needs to be specifically discussed later in the paper. Emphasized more in the text

Note the abstract is quite long-winded. It would be good to make it more succinct and punchier. Addressed

Line 69: The Castel Manfrino Dolostones are not labelled in Fig. 1 or Fig. 2b. Added in Fig.1

Line 73, 76: Did Ronchi (2003) base her study on the mapping of Mattei (1987)? Maybe there needs to be a couple of sentences describing Ronchi's findings so that it can be more clearly shown that the understanding has moved on. Added to text

Line 79-83: This is very long-winded and vague. It either needs to be shortened or to include specific details. The sentence is shortened.

Line 129: Given that the early dolomitization (D1-2) is later ascribed to the syn-rift stage, it would be useful to briefly describe the facies and architectural character of the syn-rift carbonates. For example, were they preferentially developed on footwall highs, in which case there was likely a juxtaposition of permeable high energy facies against faults that later hosted fluid flow? Addressed

Line 135-137: It may be a matter of debate, but the authors need to either provide the conflicting evidence or at least express a view and justify it. The sentence is deleted as further discussion is not the focus of this research

Line 152: Can the Montagna dei Fiori fault be indicated / labelled on Fig. 1d? Addressed

Line 164: Ground truthing implies that the features had previously been mapped out using remote data. If so, this should be included in the methods. Addressed

Line 167: So far as I can see, the Sibley and Gregg (1987) terminology (planar-e, planar-s, nonplanar) is <not> used anywhere in the paper, so either it needs to be incorporated or this sentence should be removed. The sentence and related references are removed

Line 186: Can the reproducibility  $(\pm 0.1\%)$  be smaller than the precision  $(\pm 0.2\%)$ ? The inter-lab reproducability is  $\pm 0.1\%$  means the measurement for the same sample in two different labs has a difference of  $\pm 0.1\%$ 

Line 224: Bugarone Formation is not shown on Fig. 1 or Fig 2. Addressed Line 231: Is the wider distribution of dolomitized intervals related to the topography of the valley and the exposures? If not, what is the relationship? Addressed

Line 238: I suggest not using "overprinted", which implies the original fabric / lithology is lost. Why not just use "cross-cut"? (or even just "cut") Addressed

Line 258 and elsewhere: "Dull" is not a colour! Addressed

Line 261 onwards: There could be a bit more detail on the dolomite distribution and fabric with respect to host rock facies. Is it all texturally destructive, is there any textural or mineralogical selectivity, were grainy or muddy facies preferentially dolomitized (controls by permeability versus reactive surface area......?) Addressed

Line 272: There is an issue because CV1, CV2 etc. are introduced before they have been defined and described. I suggest starting section 4.2 with a paragenetic summary to alleviate this problem. Addressed, paragenesis is presented in Fig. 14.

Line 278: By using "frequently" the text suggests that sometimes (infrequently) D2 post-dates bed-parallel stylolites. Is that the case? Addressed

Line 284-285: This sentence needs a figure citation. Addressed

Line 297: Repetition of "euhedral to anhedral" (cf. line 295) – note this is not Sibley and Gregg terminology. Nor is "tightly packed texture" in line 279. Addressed

Line 305: I do not think one dolomite can "recrystallize" another. Recrystallization is a solid-state process that increased mineral stability. To demonstrate it might need data on the ordering, crystallinity and stoichiometry of D1/2 versus D4 (do the authors have any XRD data?). What is more likely is that D4 has locally replaced D1 and D2 by a dissolution-precipitation mechanism. However, the text lacks a clear description of the evidence for replacement. I recall papers by Mazzullo and by Machel that discuss this – it would be good to list the criteria for this case. Addressed

Line 330: In Fig. 11C, D the dolomite does not appear to be yellow-orange, it looks more like orange-brown. Addressed

Line 332: How wide was the extensional fault master plane? Please supply the range of widths (and lengths where possible) of the different vein generations. It is addressed for vein generations.

Line 335-336: What is meant by "with no evidence of physical disruption"? Does it mean that CV3 always passively overgrows D5 in voids and never cuts it? If so, it is easier to say this. Addessed

Line 336: Translucent is not a colour. Addressed

Line 334: What colours are the zones? Addressed

Line 367-368: Rather than "the presumable Lower Jurassic marine dolomites" — which are hypothetical — it is better to say the values are lower than those expected for Lower Jurassic seawater dolomites. Addressed

Line 391: "While....." indicates there should be a second part to the sentence. Addressed

Line 396: What is the lithology of these samples? Addressed

Line 401: Please add a sentence or two on the fluid inclusion petrography and distribution – do inclusions follow growth zones or are they randomly distributed? Are they all primary or are some pseudosecondary? What are their shapes and what are the liquid:vapour ratios in the 2-phase examples? Also, in reporting the results for different cements please give the number of inclusions the ranges are based on (n=). Addressed

Line 409-410: What is the purpose of nucleating a bubble for measurement of freezing temperatures? Addressed

Line 477-478: This sentence appears out of place or at least needs clarification. More than two values are needed to demonstrate a progression. Addressed

Line 503-507: Yes, this makes sense if the veins are filling tension gashes associated with stylolites – such as system is likely to be buffered by the dissolving carbonate. Maybe make this point more explicitly, and contrast with vein types that were more extensive and would have allowed allochthonous fluids to pass through with minimal host-rock interaction. Addressed

Line 518: Hendry et al. (2015) did not discuss  $^{13}$ C enrichment from  $CO_2$  outgassing due to evaporation. They made the point that negative covariance in C and O isotopes within veins could be due to precipitation during  $CO_2$  outgassing related to pressure changes. Addressed

Line 524-551: This is good but is a very long paragraph. Can it be made more succinct? Addressed

Line 550-551: The final sentence needs rewriting; what was confined, the thrust wedge or the fluids? Addressed

Line 556: In the preceding section there is very little mention of fluid mixing. Could the poorly correlated Th, salinity and stable isotopic data reflect precipitation from allochthonous fluids as they mixed with in situ fluids (and cooled)? Degrees of mixing (and of water-rock interaction) may have different from fault to fault

- is it really likely that the hydrogeological systems was as simple as is being presented here? The obtained

data show no systematic variations from fault to fault. Thus, existance of different local hydrological systems cannot be addressed. The sentence is revised ad completed

Line 575-579: Please rewrite this sentence – it tries to say too many things at the same time. Addressed Line 584: Doesn't the displacement of D1-2 on these faults indicate that the dolomite formed before faulting? What is the critical evidence that it is genuinely syn-rift? The syn-rift deposits (Corniola Formation) is affected by these dolomites. Addressed more in the text

Line 590: if D1-2 were related to basement-cutting faults, why are the Sr isotope values much less elevated than for D3 and D4? There is no other alternative for radiogenic Sr source. This is the case for all of the dolomite types. Maybe less basement deriven fluids were involved in D1.

Line 656-657: Please explain how hydrothermal fluids were able to circulate in the compressional tectonic regime – which structures were able to be in tension and therefore transmissive rather than sealing?

Addressed

Line 1139: The cross-cutting relationship in Fig. 8a, b is not very evident. Addressed Lines 1142-1148: Should this discussion be in the main text rather than in the caption? This has been made to avoid a longer discussion.

Fig. 2b: It would help if the colours and ornaments matched Fig. 8a (e.g. Salinello Fm). The text size needs to be increased for better legibility. Addressed

The stereonet data are good, but very little use is made of them in the text of the paper. Addressed in the figure caption

Fig. 5: Please increase the text size and make 5c larger – it is too small to see clearly. Addressed

Figs 6-9, 11: Some of the CL images could be a bit sharper and maybe with increased contrast to better discriminate the dolomite types. Addressed

Fig. 12: The symbols for D3 vs. CV3 and mixed dolomite vs. CV1 are too similar (especially given the small size). I am also not clear how Fig. 12b relates to Fig. 12a; maybe split the legend between the two plots according to what is in them – that might help. Addressed

Fig. 14: How were the burial temperatures in the burial history determined? What assumptions are they based on? Addressed

Fig. 15: I like this figure but I'm still not sure what the fluid flow pathway is in (b). Maybe a broader tectonic context diagram is needed showing expulsion of fluids from the foreland (if that is where they are coming from?). The fluids were migrated from hinterland (now indicated on the sketch) rather than forland.

I hope these comments are helpful, and I look forward to seeing the paper published in revised form.

Jim Hendry

Tullow Oil Ltd, Dublin

## **Specific comments:**

- 1) Abstract: The abstract can be shortened substantially, yet it is missing key information. It provides too much detail of some aspects of this work but lacks equivalent detail in other cases. For example, why are calcite-filled veins not mentioned here? Weren't they a main focus of this study? A more succinct and balanced abstract is required. Also, the abstract would benefit from a "punchline" or statement of the broader implications of this work at the end. What did you learn about the extent of dolomitization near faults? How is this relevant for porosity/permeability evolution and fluid flow in dolomitized, carbonate-hosted hydrocarbon reservoirs and aquifers? Addressed
- 2) Introduction: You may want to consider adding a short statement about why some fault-zones become dolomitized but others don't. What are the requirements? What can you learn from outcrops that you cannot from core alone? I would say that the main benefit would be the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D. Addition of such a field-relations analysis would greatly improve the impact of this work. Addressed
- 3) Geologic setting: This section is a bit long and could be shortened. Addressed
- 4) Methodology: A few things are missing:
  - o How large of a geographic area did you sample? Addressed
  - How did you decide which areas to sample for isotopic analyses? Did you image them first? How? How confident are you that you didn't mix different cements when sampling? Addressed
  - O How many fluid inclusions in your FIAs? What was your reproducibility and error? How did you make sure you did not measure stretched inclusions? Addressed
  - O Documentation of where hand samples came from is very poor. This can be improved by showing the location of the thin sections on outcrop photos, and their spatial relationship with faults etc. These might need to be included in an appendix due to space restrictions, but it is important. Explained in author response

#### 5) Field observations

- o What is the spatial distribution of the dolomitized geobodies? Addressed
- o And of the veined sections?
- o 6 outcrop locations are marked on Figure 2 but distributions of the different types of cements are only shown in one image (figure 5b). These are very important relations to assess fluid pathways and the evolution of dolomitization. Addressed
- What are the orientations of CV1–CV4 cement-bearing fractures? Shown in Storti et al. (2018)

#### 6) Petrography

O How much calcite cement is there in the breccias? What are the textures? Why are these not included in your diagenetic evolution analysis? How do cements in breccias relate to those in host rocks? Are cements in the host rocks affected by brecciation? Show examples. Addressed

- How did dolomitization affect porosity in both host rock and fault rocks? How
  does porosity compare between limestones and dolostones? Addressed
- Some of the petrographic relationships mentioned need to be backed by images (see my line-specific comments) Addressed
- The order in which dolomite cements and vein-calcite cements are mentioned needs to be improved.
- o What is the relationship between MC and D1/D2? Where is this documented? Addressed
- What is the distribution of CV cements in the host rock (see Laubach, 2003)? This should be properly documented and reported. I don't think vein cement is an appropriate term for these calcite cements. Also, keep in mind that the occlusion of fracture porosity by postkinematic cements can significantly postdate the timing of the opening of the fracture (see Ukar and Laubach, 2016). In other words: the timing of fracturing and cementation are not the same. Keep that in mind in your descriptions. Addressed
- o The observation of CV3 in breccias is quite interesting. Document and show images. What other cements are there in breccias? How did you establish the relative timing of these cements and others? Breccia cements should not be referred to as vein cements. Explained in author response
- o What are the spatial distributions of the different cement types? Addressed

# 7) Geochemistry

- o What are the isotopic characteristics of MC and fibrous cements? Addressed
- o Interpretations, especially for Sr ratios, should be moved to the discussion.

#### 8) Fluid inclusions

- o Show images of the different types of fluid inclusions, especially the FIAs.
- O The graphs used to summarize fluid-inclusion thermometric results are not appropriate because key information is lost. Same for salinity. Please replot the data so that the temperature range for each individual FIA is shown. Did you measure an equal amount of FIAs for each type of cement? Otherwise, frequency would not very meaningful in Fig. 13 because it would be sample and cement availability dependent.
- Why are CV temperatures not shown in these graphs? For a higher focus on dolomitization case study

#### 9) Discussion

- o This section can be significantly shortened by avoiding repetition of results.
- I think parental fluid calculations should be shown in the results section, not in the discussion. To emphasize on the nature of parental fluids, we prefer to keep SMOW values in discussion section
- Use parallel writing style for stable isotopes and Sr discussion.???
- O D3 shows significantly higher Sr/Sr than D4. How can both be related to the same event and derived from similar fault-related fluids? D1 and D2 are also fault-related. Why the differences in isotopic signatures, especially if all are related to basement-rooted faults??? Addressed

- The association of D3 and D4 with bed-parallel and shear fractures is mentioned for the first time in the discussion. This needs to be mentioned in the results. Are the cements themselves sheared? Show evidence. Addressed in petrography
- O Discuss the spatial distribution of the different cement and vein/breccia types. What do they indicate about fluid-flow patterns? The breccia types in MDF are not diverse. More details on bereccia is out of focus of this study.
- o The orientation of CV1–CV4-bearing fractures needs to be taken into account in the structural interpretation. A detailed structural interpretation is discussed in Storti et al. 2018. Its now more emphasized in this manuscript.
- Section 5.3: Without a better documentation of the orientations and field relations of the different cements and fracture types it is difficult to assess the validity of the inferred paragenetic sequence and the association of the different cements and structures with tectonic events. Some of the spatial and cross-cutting relationships between different types of cements are first mentioned in this section. Such descriptions should be moved to the results section.
- O What is the driver for fluid circulation? Why are they Mg-rich fluids? What do fluid-inclusion salinities indicate? Addressed in section 5.2
- O Why do you go from dolomite replacement and cementation to calcit cementation? Addressed
- O How are your findings relevant for porosity/permeability evolution and fluid flow in dolomitized, carbonate-hosted hydrocarbon reservoirs and aquifers associated with similar reservoir-scale structures? Addressed
- O How are your conclusions applicable to dolomitization processes associated with faults in general? How far can dolomitizing fluids travel and to what extent do they alter the mechanics and porosity/permeability of the host rock? What are the consequences for fluid-flow in these rocks? Addressed

#### Conclusions

10)

- o More thought needs to go into the conclusions section.
- o I don't think enough data are presented in this study, especially of cross-cutting relationships and orientations of the different "deformation structures" to support the structural interpretation presented in the conclusions. For example, where is the evidence that the opening-mode fractures (no orientations or relationships within the anticline are reported!) and normal faults mentioned in this study are associated with contractional tectonics of the Apenninic orogeny? All are discussed in details in Storti et al. 2018.

Lines 29-31: This needs to be re-written. Layer-parallel shortening would not give place to layer-parallel stylolites. Extensional faulting by itself either. Involvement in the Apenninic thrust wedge of what? Addressed

<sup>11)</sup> Figures and figure captions need work, especially the model shown in Figure 15 (see comments in figure caption).

Lines 48-54: May I suggest you take a look at the recently published Ferraro et al. (2019) paper for a description of the diagenetic evolution of carbonate fault rocks in the central and southern Apennines? Addressed

Lines 54-58: You may want to consider adding a short statement about why some fault zones become dolomitized but others don't. What are the requirements? Addressed

Lines 58-61: What can you learn from outcrops that you cannot from core alone? I would say that the main benefit would be the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D. Perhaps a missed opportunity in this work?

Line 67: I don't see Bugarone in Figure 1. Addressed

Line 69: I don't see catel Manfrino Dolostones in Figures 1 or 2. All the dolomitized intervals are called

#### Castel Manfrino Dolostones

Lines 72-73: How is your study better than Ronchi (2003)? Addressed

Lines 76-78: In Figure 2 it appears that dolomitized bodies are found quite far away from faults, beyond the typical lateral extent of fault damage zones. What is the explanation? Why are some faults associates with dolomitization while others aren't? Does it have to do with age of faults? Other factors? This would be a good topic for the discussion.

Line: 84: I would have liked to see more "field mapping" of the extent of D1–D5 and CV1–CV4 in this work.

Line 87: This sentence should start with a different word than "therefore". What provides insights? How? Addressed

Lines 88-89. Yes. This needs to be discussed in the discussion. Addressed

Lines 90-92: Yes. This needs to be discussed in the discussion. Addressed

Line 96: evolution of the Apennines has been proposed to be the result of Addressed

Line 98: since the Late Cretaceous Addressed

Line 103: The Central Apennines involve OK

Line 110: lower part of the Burano Formation Addressed

Line 115: Deposition of the Hettangian–Sinemurian Calcare Massiccio Formation, with a total thickness ... Addressed

Line 117: following facies are present Addressed

Line 125: deepening-upward trend Addressed

Line 137: olistolith model This sentence is deleted

Lines 138-145: So, does this evidence favor the fault-related model or does this evidence provide an

alternative model? Why does this sentence start with 'However''? This sentence is deleted

Line 151: at a high angle Addressed

Line 162-163: 60 samples distributed across how big of an area? Addressed

Line 164: What structures? Addressed

Line 187: Vienna Pee Dee Belemnite Addressed

Line 215: In order to perform high resolution Addressed

Lines 220-221: bed-perpendicular stylolites Addressed

Lines 224-230: This belongs in the Geological Setting. Addressed

Line 225: There is no evidence of dolomitization Addressed

Lines 231-234: Location names need to be included in figure captions. Addressed

Lines 235-239: This seems out of place. Start by describing mesoscale relations and distributions

of dolomitized geobodies. Then focus on hand-sample and petrographic details. Addressed

Line 235: in fault cores are typically Addressed

Line 237: is "main slip surface" a better term? Addressed

Line 238: cut by rather than overprinted. Are dolomite-filled veins intra- or intergranular?

Line 239: calcite cement Addressed

Line 241: cross-cutting bedding surfaces Addressed

Line 242: from a few meters to hundreds of meters Addressed

Line 243: and the lower part of Addressed

Line 246: High amplitude (>1 mm), bed-parallel stylolites Addressed

Line 247-248: How does porosity differ between limestones and dolostones?

Line 253: grain-supported intervals Addressed

Lines 259-260: Evidence? Addressed

Line 265: we can't see the displacement mentioned in Figure 2A, site 1

Line 267-268: Are they overprinting or overgrowing? Show evidence. We also cannot see the distribution of the different cements at outcrop scale.

271-272: On what basis did you establish that the replacive dolomite within the host rock (D1) and lining fractures is the same?

Lines 275-276: solid inclusions of what? Insert figure call out for concentric zonation. Addressed

Line 281: sweeping extinction Addressed

Line 282: In some crystals, one... what types of solid and fluid inclusions? Addressed

Lines 286-291: Mark locations on map/figure captions and call out the figure. Addressed

Line 290-291: Scaglia Formation in the hanging wall. Addressed

Lines 293-295: This needs to be moved up Addressed

Line 305: bed-parallel shear fractures Addressed

Lines 308 on: There is a problem with CV introduction. What does it stand for? Must introduce them in chronological order. If the calcite cement is in veins it is most likely in the host rock as well (see Laubach, 2003). I don't think calling it vein cement is appropriate. Addressed

Line 308: What porosity? Addressed

Lines 318-320: Show outcrop photo?

Line 319: bed-perpendicular rather than bedding because that's what you use elsewhere. Make sure term usage is consistent throughout. Addressed

Line 321: bed-parallel stylolites. CV1 usually shows (often means time. Correct elsewhere in the manuscript). Addressed

Lines 324-326: Show image of CV2 in tension gashes Addressed

Line 332: extensional fault's master (main?) plane Addressed

Line 339-340: More evidence that the use of CV to refer to calcite cements that occur in a variety of textures and petrographic relations is not appropriate.

Lines 361-364: Why is this mentioned here and not with the rest of the calcite cements? Its ordered based on relative timig

Line 396: I see 3 values plotted for Scaglia. Addressed

Lines 398-399: Interpretation. Move to discussion. Same comment for previous

paragraphs.Addressed

Lines 401-411: This belongs in the Methods section. Addressed

Lines 409 and 439: all-liquid inclusions Addressed

Lines 439-445: This belongs in the Methods section. Addressed

Lines 469-470: This belongs in the methods/results. Why did you avoid them? Could mottled

D be a different type than those reported? Addressed

Lines 471-474: Move to methods. Report parental fluid calculations in the results section.

Line 478: Progressively higher than what? Fixed

Line 481: siliciclastic rocks,... Correct here and elsewhere. Addressed

Line 493:, or values recorded... Add references. Addressed

Lines 499 and 505: Replace comparable with similar. Here and elsewhere. Addressed

Line 507: stylolitization of the host rock (otherwise we do not know what dissolution etc. you are referring to). Addressed

Lines 527-528: fluids related to Late Messinian... overlying Upper Miocene Laga Formation and their possible...Addressed

Line 543: burial-related temperature Addressed

Line 544: it is unlikely that the.. Addressed

Line 546: located at higher stratigraphic levels Addressed

Line 564: calcite cements (FC) in grain-supported stratigraphic levels of the CMF is interpreted to be... Addressed

Line 570: bed-parallel stylolties Addressed

Line 574 and 575: are cut by Addressed

Line 579: Figure 15A call out. Addressed

Line 585: We cannot see the distribution described in Figure 2A.

Line 587: attributed to post-rift Addressed

Line 588: Although an absolute age cannot be provided, Addressed

Line 603: bed-parallel fractures. This is the first mention of shear veins for D4. Are the

cements sheared? Show evidence. Cements are not sheared. Addressed

Line 604: Contractional deformations? How? Describe relationships better. Bed-perpendicular dilation alone would not cause shear.

Lines 608-610: First mention of this. Move to results.

Lines 618-619: bed-parallel veins Addressed

Line 622: fragments suggests that... late-stage evolution Addressed

Line 624: bed-perpendicular stylolites Addressed

Line 624-629. This is way too long. In any case, there is new information here that needs to be moved to the results section. Addressed

Line 629: low homogenization temperatures of fluid inclusions trapped within these cements Addressed

Lines 638-642: So, how is your study better? How are your conclusions applicable to dolomitization processes associated with faults in general?

Figures: Documentation of where samples came from is poor. Locations of samples need to be shown on outcrop photos and/or detailed maps. Add in appendix if space is limited.

Figure 1: Tiny name in a) is unreadable. Mark location of cross-section (A-A') shown in d).

Figure 2: Add names of each field site to the figure caption. Addressed

Figure 3: The picture in a) is too close up to see the context. Mark distribution of D1 etc. as in Fig 5d. Why isn't there more on these breccias (c) in the manuscript? Explain what arrows point to. Pressure solution seams. You are not showing intensity (it would be a number). Perhaps say showing abundant pressure solution seams. What are the abutting relationships? Which abuts which? Move arrow in b) so that the vein is actually visible. Are the other white pods also considered "veins"?

Figure 4: Show spatial distribution of D1, D3, CV1... etc. at the outcrop scale. The sentence seems to say that CV1 veins are dolomitized. Is that what you really mean? What is the dolomite type in b) and c)? Good opportunity to show cross-cutting relationships summarized in Figure 14.

Figure 5: What field site(s) and formation(s) are these from? In b) the zone shown in c) is marked as only having D1 but as D1 + D2 in c). Which one is correct? Any CV2-CV4 here? Addressed

Figure 6: What field site is this? rimmed by fibrous cements (FC), which are overgrown by mosaic cements (MC). overprinted bed-parallel stylolites. D1cements lining a fracture. What do

arrows point to in f) If it is D1, then what is to the right of it? Line 1123: which is cemented by CV1 in the center. Addressed

Figure 7: What field site(s) and formation(s) are these from? What is beyond D3 in e) and f)? Is D3 only present in breccias in this site? What is the CL signal of D3 in breccias and how did you establish correspondence with D3 in host rocks? What is the context of the sample? in e) and f) Addressed

Figure 8: What field site(s) and formation(s)? D3 and D4 are not cross-cutting but it appears that D4 overgrows D3. What is the D4 arrow in b) exactly pointing to? What cement is in the rhomb on the upper right corner? d) I am having a hard time seeing the microfracture. What CV is this? Or do you have dolomite-filled veins as well? Where are these described? What other cements are in e) and f) and what do arrows point to? Lines 1141-1150 belongs in the discussion.

#### Addressed

Figure 9: What field site(s) and formation(s)? If D4 also occurs in fractures why is it not called vein cement as in your CV scheme? What other cements and/or host rock are in these photographs? Add labels. Addressed

Figure 10: These photographs are too close up to see the context. Outlining obscures fractures in a). c-d) These do not look like tension gashes to me (as mentioned in text?). Mislabeled as CV2 on the picture (?) but CV3 in the figure caption. Addressed

Figure 11: What field site(s) and formation(s)? What is a) a sample of? And the rest? Show field context. Addressed

Figure 12: Why aren't these figures in color? The symbols are too similar and they are hard to distinguish from one another. I would assign a color to each formation and a symbol to each diagenetic feature. Addressed

Figure 13: These plots are not very useful because key information is lost. Plot homogeneization and ice melting T ranges so that variability within individual FIAs is captured. Color would help, Also, where are the data for CV cements?

Figure 15: The fracture in a) would not have that orientation if sigma 1 were vertical. Indicate which fault you are referring to in b). The vein in b) would not develop in that orientation if sigma 1 were horizontal. Also, keep in mind that the timing of cementation of the veins by postkinematic cements (see Ukar and Laubach, 2016) postdates timing of opening of the fracture. Don't mix the two! I had no idea that CV4 is restricted to the MdFF until now, because it is not mentioned anywhere in the text. How do you reconcile D3 to be surrounding breccia clasts within the MdFF in this model and sequence? Addressed

Estibalitz Ukar Research Associate Jackson School of Geosciences The University of Texas at Austin Dear Dr. Hendry and Dr. Ukar,

Thank you for the very constructive comments. They not only helped us to improve the quality of the manuscript but also our knowledge of dolomitizataion process. We have tried our best to address your suggestions in this new version of the manuscript.

Regarding the advancement of our research in comparison with the work previously presented by Ronchi et al. (2003), the current study gives much more details about the dolomite characterization and their relation to the structural evolution of the anticline on the regional and local scale. Furthermore, the obtained geochemical and microthermometry analyses do not confirm the role of marly or shaly basinal successions in providing the Mg-rich fluids during the first event of dolomitization (i.e. syn-rift), as proposed by Ronchi et al. (2003). We have tried to be modest in criticizing the latter authors limited research since the current research was build up on their findings. Another important question about the studied dolomites was the role of Scaglia Formation in providing the Mg-rich fluids during compression, because this formation is juxtaposed with the dolostones by the Montagna dei Fiori Fault. Our results do not support this hypothesis.

During our research, we also performed some other advance analyses such as clumped isotopes and U/Pb dating. However, the consecutive overgrowth pattern of dolomites and difficulties in isolating them to get enough and good quality samples increased the uncertainty in the results. Therefore, we decided not to include those data in the manuscript.

In the Montagna dei Fiori Anticline, the structures and their relative chronology are very complicated. A comprehensive structural study on the evolution of the Montagna dei Fiori Anticline was performed parallel with the current study, and published by Storti et al. (2018) in Tectonics. The target of the current study was to focus on dolomitization, and to use the structural model proposed by Storti et al. (2018) to deduce the most likely timing for dolomitization.

The distribution of dolomitization and sampled locations are way larger than the out crop photo scale. The dolomitized intervals are tens of meters mostly exposed in vertical to subvertical outcrops. To be able to show their 3D distribution properly a photogrammetry or LiDAR imaging is required.

The brecciated zones are mostly clast-support with minor calcite and negligible dolomite cement. Moreover, a detailed classification of breccia is not the focus of this research and does not give relevant information regarding this dolomitization case study.

This new version of the manuscript has been reviewed by a native English speaker.

Best regards,

Mozafari et al.

- 1 Fault-controlled dolomitization in the Montagna dei Fiori Anticline (Central Apennines,
- 2 Italy): Record of a dominantly pre-orogenic fluid migration
- 3 Mahtab Mozafari<sup>1</sup>, Rudy Swennen<sup>2</sup>, Fabrizio Balsamo<sup>1</sup>, Hamdy El Desouky<sup>2,3</sup>, Fabrizio Storti<sup>1</sup>
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- 12 (Fabrizio.Storti@unipr.it)

#### **Abstract**

The Lower Jurassic platform and basinal deposits exposed in the Montagna dei Fiori Anticline (Central Apennines, Italy) are pervasively affected by dolomitization. Based on the integration of field work, petrography, and geochemistry, two fault-related dolomitization events were recognized and interpreted as having occurred before and during the Apenninic orogeny, respectively. Fluid inclusion analysis indicates moderate to elevated salinity values of 3.5 to 20.5 and 12.8 to 18.6 eq. wt. % NaCl, in the first and the second event, respectively. The estimated salinities, in combination with  $\delta^{18}$ O values and  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios, suggest significant involvement of evaporitic fluids in both events, most likely derived from the underlying Upper Triassic Burano Formation. In addition, the  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios up to 0.70963 suggest the circulation of deepsourced fluids that interacted with siliciclastics siliciclastic rocks and/or the crystalline basement during the dolomitization events. The first dolomitization event which is also considered as the most pervasive one started prior to the significant burial conditions, as reflected in homogenization temperatures of their fluid inclusions being mostly below about 40-50°C.

Two major dolomite types (D1 and D2) were recognized as pertaining to this the first event, both postdated by high amplitude bed-parallel stylolites.—, supporting This relationship supports a syn-burial, pre layer-parallel shortening dolomitization, interpreted as controlled by the extensional fault pattern affecting the carbonate succession before its involvement in the

Apenninic thrust wedge. A possible geodynamic framework for this dolomitization event is Early to Late Jurassic rift-related extensional tectonism. The second dolomitization event (D3, <u>D4 and D5)</u> initiated with a dolomite type (D3) is characterized by a slight-temperature upturn (up to 73°C), followed by a second type (D4) with markedly higher homogenization temperatures (up to 105°C), and interpreted as associated with the inflow of hydrothermal fluids, possibly related to major changes in the permeability architecture of faults during early- to synthrusting and folding activity. Eventually, D4 was overprinted by a late generation of dolomite veins (D5) interpreted as associated with late orogenic extensional faulting in the backlimb of the Montagna dei Fiori Anticline. Based on the timing of deformation in the Montagna dei Fiori Anticline, D3 to D5the second dolomitization event likely occurred in Late Miocene to Pliocene times. The findings regarding characteristics and timing of dolomitization here illustrates the long-term controlling role of the eveporitic evaporitic detachments in dolomitization process. Our data This study shows that the Mg-rich fluids that were most likely derived from these evaporites may prime the tectonically involved successions for repeated dolomitization, and <u>hence</u> formation of potential reservoirs <u>in-during</u> sequential tectonic modifications (extensional vs. compressional).

## 1 Introduction

Fault-controlled dolomitization has been the focus of attention in many studies during the last decades due to its influential role in modifying the petrophysical properties of rocks and, hence, anisotropy in fluid migration pathways, and, ultimately on reservoir quality (e.g. Purser et al., 1994; Montanez, 1994; Zempolich and Hardie, 1997; Vandeginste et al., 2005; Davies and Smith, 2006; Sharp et al. 2010). The mechanical and hydrological behaviour of fault zones are in turn influenced by fluid-rock interactions and diagenetic modifications (e.g. Gale et al., 2004; Laubach et al., 2010; Clemenzi et al., 2015; Ferraro et al., 2019). It follows that the mutual interplay between fault activity and fluid driven-rock-fluid interaction can trigger dolomitization of carbonates when exposing to Mg saturated or oversaturated fluids and, consequently, variations in physico-chemical properties of fluids through time and space.

-Leaking or sealing behaviours of fault zones during deformation are key controls for fault-related fluid circulation. A detailed understanding of such an interplay is thus necessary to improve our capability of making reliable predictions of fault-related dolomitization in carbonate reservoirs. Studying outcrop analogues provides fundamental support to meet this requirement

(e.g. Swennen et al., 2012; Dewit et al., 2014; Bistacchi et al., 2015)., and the opportunity to assess the spatial distribution of dolomitized zones, and individual diagenetic events, in 3D (e.g. Swennen et al., 2012; Dewit et al., 2014; Bistacchi et al., 2015).

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The Lower Jurassic to Lower Cretaceous Umbria-Marche passive margin carbonate succession, in the Central Apennines (Italy), is intensely affected by localized dolomitization both in the onshore fold-and-thrust belt and in offshore foredeep and foreland areas (e.g. Murgia et al., 2004; Pierantoni et al., 2013). The dolomitized intervals which are the focus of this study are well-exposed in the core of the Montagna dei Fiori Anticline (e.g. Ronchi et al., 2003), where the dolomitized Lower Jurassic intervals (Calcare Massiccio, Bugarone and Corniola Formations) and their relationships with fault zones allow to study the mutual influence between deformation structures and dolomitized intervals (Fig. 1). These intervals, known as the Castel Manfrino Dolostones (Crescenti, 1969; Mattei, 1987; Koopman, 1983), have been previously studied by Ronchi et al. (2003) only at its reference section, exposed at the Castel Manfrino location (Fig. 1b), in the central sector of the Montagna dei Fiori Anticline (Fig. 2). A fault-controlled dolomitization model and the relative timing of dolomitization were proposed by Ronchi (2003)the latter authors. based on the homogenization temperatures obtained from microthermometry of the fluid inclusions, and their relation with the thermal history of the area studied. However, no clear relation between dolomitization and structural evolution of the Montagna dei Fiori Anticline on a local scale was provided to confidently link the occurrence of dolomitization to a particular tectonic event. Moreover, the nature and origin of the dolomitizing fluids were not well constrained. Recent re-evaluation of dolostone distribution in the Montagna dei Fiori Anticline (Storti et al., 2017a), showed that the dimension of the dolomitized geobodies (Fig. 2) is much more significant than what was previously mapped by Mattei (1987). Dolostones are distributed within fault damage zones and in the laterally adjacent carbonate rocks, and in intersection areas between fault sets, for a total area in map view of more than 1.5 km<sup>2</sup> (Storti et al., 2017a).

The structural pattern of the Montagna dei Fiori Anticline documents the overprinting of extensional and contractional deformation along major fault zones. Although challenging, the The preserved structural framework in this anticline provides an opportunity to study the direct but complex regional tectonic controls on dolomitization in carbonate successions undergoing multiple deformation events, from rifting to folding and thrusting. This contribution integrates

field mapping, new petrographic, geochemical, and microthermometric analyses, with structural studies (Storti et al., 2018) to characterize the temporal record of fault-controlled diagenetic phases and, more specifically, dolomitization in the carbonatic succession outcropping in the Montagna dei Fiori Anticline. Therefore provides insights into the structural controls on regional fluid flow and their chemical evolution through time. These findings might be of relevance for exploration and reservoir quality prediction in the region of onshore and offshore the Apennines and Southern Alps, both onshore and offshore. Moreover, this work provides additional evidence of the potential influence of fluids derived from evaporitic detachment levels in modifications of geochemical trends and petrophysical properties of the overlying carbonate rocks.

## 2 Geological setting

The Montagna dei Fiori Anticline is a NNW-SSE striking, thrust-related fold located at the mountain front of the Central Apennines (Fig. 1). The geodynamic evolution of the Apennines is generally knownhas been proposed to be the result of the superposition of NE-SW compression (in present-day geographic coordinates), related to the convergence between Eurasia and Africa plates since the Late Cretaceous times (Elter et al., 1975; Dewey et al., 1989; Patacca et al., 1992), on a rifting-related tectono-sedimentary architecture produced by Early Jurassic extension (e.g., Centamore et al., 1971). In such a framework, the Central Apennines developed during Miocene to Plio-Pleistocene times (e.g. Parotto and Praturlon, 1975; Barchi et al., 1998; Mazzoli et al., 2002; Bollati et al., 2012).

The Central Apennines involves the Umbria-Marche succession, which essentially includes Triassic to Miocene carbonates and marls, covered by Miocene to Pliocene synorogenic clastic sediments (Fig. 1). The pre-orogenic succession, from bottom to top, includes Late Triassic evaporites, dolomites and limestones (of the Burano Formation), which the basal detachment runs within its evaporitic interval (Ghisetti and Vezzani, 2000), Early to Late Jurassic platform and basinal limestones and dolostones (Calcare Massiccio, Corniola, Rosso Ammonitico, Calcari a Posidonia and Calcari ad Aptici Formations), and Cretaceous to Early Miocene basinal carbonates (Maiolica, Marne a Fucoidi, Scaglia and Biscaro Formations). In general, the lower part of the Burano Formation is overlaid by the fluvio-deltaic siliciclastics siliciclastic rocks of the Verrucano Formation (Middle-Late Triassic) (Tongiorgi et al., 1977; Ghisetti and Vezzani, 2000; Tavani et al., 2008). Nevertheless, the existence of these siliciclastic rocks in the Montagna dei Fiori area is not yet provedproven. Syn-

orogenic deposits include Miocene marls and turbiditic sandstones (Marne con Cerrogna and Laga Formations) (Artoni, 2013 and references therein).

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The deposition of the Calcare Massiccio Formation, (dated as Hettangian-Sinemurian) and with a total thickness varying between 300 to 700 m (Pialli, 1971), records an important extension pulse in the evolution of Tethyan rifting. The following facies are observed in the lower part of the Calcare Massiccio Formationthis formation which has been interpreted as having been deposited in a peritidal environment: consists of oncoid-rich-peloidal pack- to grainstones in alternation with peloidal wacke- to packstones including horizons of algal bindstones (Calcare Massiccio A; Brandano et al., 2016). The upper part is made up of beds of skeletal and coated grain wacke- to grainstones including microoncoids, echinoderms, calcareous and siliceous sponges, bivalves, gastropods and ammonites (Calcare Massiccio B; Brandano et al., 2016). It The lower part has been interpreted as having been deposited in a peritidal environment, while the upper part corresponds to lower to middle shelf depositional environments, characterized by a general deepening deepening upward trend associated with extensional faulting and drowning of the platform, coupled with subsidence and deposition of the overlying Corniola Formation in the pelagic areas. Overall, the Early Jurassic rifting led to the growth of the Calcare Massiccio Formation in a carbonate platform setting, followed by faulting and drowning, and development of pelagic intrabasins filled by syn-rift sediments (Fig. 1c; Bernoulli et al. 1979; Santantonio and Carminati, 2011). The syn-rift sediments include pelagic limestones of the Bugarone and Corniola Formations. Condensed pelagic limestones of the Bugarone Formation (Lower Pliensbachian-Lower Tithonian; Bugarone Group in Pierantoni et al., 2013) occur at the top of the Calcare Massiccio Formation where it formed fault-controlled highs marking the regional drowning of the carbonate platform (Santantonio and Carminati, 2011). The pelagic limestones of the Corniola Formation (Sinemurian-Toarcian; Colacicchi et al., 1975; Morettini et al., 2002; Bosence et al., 2009; Marino and Santantonio, 2010; Brandano et al., 2016) occur within the fault-controlled (half)grabens in lateral continuation with the Calcare Massiccio Formation. The Corniola Formation in the lower part consists of turbiditic lobes which originated from tectonic brecciation of the Calcare Massiccio Formation. The upper part consists of a well-bedded pelagic mudstone with chert nodules (Di Francesco et al., 2010). In the Montagna dei Fiori, the geologic framework of the outcropping Calcare Massiccio Formation is still a matter of debate between a

fault-related tectonosedimentary pattern (Mattei, 1987; Storti et al., 2017b), and a gravity-driven, olistolith hypothesis (Di Francesco et al, 2010; Santantonio et al., 2017). However, recent

## 2.1 Structural Framework

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The Montagna dei Fiori Anticline is intersected by two major fault categories (Storti et al., 2018), which based on the chronological order include: detailed work in the Salinello valley (Storti et al., 2017a; 2018) Firstly, ~ E-W and ~ N-S striking fault zones showing extensional kinematics bounding the documented that major outcrops of Calcare Massiccio are bounded by mostly ~ E-W and ~ N-S striking fault zones showing extensional kinematics and dominantly affecting the Jurassic rocks older than the Maiolica Formation (Fig. 2A2a, e.g. sites 1 to 4). Overprinting relations indicate that ~ E-W deformation structures are systematically younger than the ~ N-S ones. Similar trends were observed in syn-rift fault zones in other anticlines of the Central Apennines (e.g. Cooper and Burbi, 1986; Alvarez, 1989; Chilovi et al., 2002). Such a tectonosedimentary inheritance was involved in the growth of the Montagna dei Fiori Anticline, which initiated during the Late Miocene (Mazzoli et al., 2002; Artoni, 2003) and progressively evolved into the upper thrust sheet of a well-developed antiformal stack until Plio-Pleistocene times (e.g. Ghisetti et al., 1993; Calamita et al., 1994; Artoni, 2013). The second set of faults is A a major structural feature trending parallel to the Montagna dei Fiori Anticline and dissecting it is the Montagna dei Fiori Fault, a NNW-SSE striking extensional fault system cutting at a high angle through the folded footwall rocks, typically at the forelimb-crest transition (Figs. 1, 2). This fault consists of two partially overlapping main fault zones with an extensional stratigraphic separation exceeding 900 m, and This fault system juxtaposes intensely deformed Late Miocene sediments in the hanging wall, against dolomitized and undolomitized Lower Jurassic and Cretaceous limestones in the footwall (Figs. 1 and 2). The development of the Montagna dei Fiori Fault has been alternatively interpreted as either a pre- (e.g. Calamita et al., 1994, Mazzoli, 2002; Scisciani et al., 2002) or late-folding (Ghisetti and Vezzani, 2000) feature. More recently, the origin of the Montagna dei Fiori Fault has been ascribed to the mutual interaction between horizontal shortening and uplift, and episodic gravitational re-equilibration during antiformal stacking underneath the anticline during Plio-Pleistocene times (Storti et al., 2018). The dolomitized intervals are exposed in the damage zones of the both aforementioned fault categories.

## 3 Methodology

The fieldwork covered an area of over 4 km<sup>2</sup> to delineate the distribution of dolostones.

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The stratigraphic and deformational features of dolostones were analyzed in more than 60 outcrops. The distribution of dolomitized intervals as well as their cross-cutting relationships with bedding planes, stylolites, veins and structures-faults were ground-trutheddocumented and sampled. For petrographic analyses, 130 polished thin sections were studied with standard petrographic methods (transmitted and UV-fluorescent light microscopy). Dolomite crystal morphology and texture is based on the classification proposed by Sibley and Gregg (1987).

The rock slabs and thin sections were stained using Alizarine Red S and potassium ferricyanide (Dickson, 1966) to discriminate dolomite from calcite and evaluate their iron content. Cold cathodoluminescence microscopy (CL) was carried out on representative thin sections (n = 80) at KU Leuven University (Belgium) using a Technosyn cathodoluminescence device (8-15 kV, 200-400  $\mu$ A gun current, 0.05 Torr vacuum and 5 mm beam width).

 $\delta^{13}$ C and  $\delta^{18}$ O analysis were carried out on 117 samples. To ensure the sampling quality and avoid physical mixing of different diagenetic phases, the thin section images were mapped and the sampling targets were determined. Nevertheless, some diagenetic phases could not be isolated due to their sequential overgrowth and small size. Powder samples (150 - 200 µg) were obtained by applying a New Wave Research micromilling device and a dental drill at KU Leuven University (Belgium). The analysis was conducted at Parma University (Italy) and the Friedrich-Alexander-Universität (Erlangen-Nürnberg, Germany) laboratories using Finnigan DeltaPlus V and ThermoFinnigan 252 mass spectrometers, respectively. The carbonate powders were reacted with 100% phosphoric acid at constant temperature of 75°C. Several additional CO<sub>2</sub> reference gases (NBS18, NBS19, MAB99, and a pure Carrara marble) with known isotopic ratio were analyzed during the measurements to determine the  $\delta^{13}$ C and  $\delta^{18}$ O values of the sample. Reproducibility was checked by replicate analysis of laboratory standards and was better than  $\pm 0.1\%$  for  $\delta^{13}$ C and  $\pm 0.2\%$  for  $\delta^{18}$ O at Parma University and  $\pm 0.04$  for  $\delta^{13}$ C and  $\pm 0.05\%$  for δ<sup>18</sup>O at Friedrich-Alexander-Universität. Oxygen isotope composition of dolomites was corrected using the acid fractionation factors given by Rosenbaum and Sheppard (1986). Duplicate homogeneous samples measured in both labs for inter-laboratory reproducibility-show  $\delta^{13}$ C and  $\delta^{18}$ O values within the acceptable range of error deviation (±0.1%) both for  $\delta^{13}$ C and 8<sup>48</sup>O. All carbon and oxygen values are reported in per mil, relative to the "Vienna Pee Dee Belemnite Vienna PDB scale" (V-PDB).

A total number of 21 samples were analyzed for their <sup>87</sup>Sr/<sup>86</sup>Sr ratios. The analyses were conducted at the Department of Analytical Chemistry, Ghent University (Belgium) and at the Vrije Universiteit Amsterdam (the Netherlands). NIST SRM 987 was used as the international Sr standard in both labs. At Ghent University, 15 sample powders (20 mg) were collected using a dental drill device. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio measurements were performed using a Thermo Scientific Neptune Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) instrument. Within the external precision, repeated analyses of the international Sr standard yielded an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.710271 \pm 0.000023$  (2SD, n = 43), in agreement with the accepted <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.710248 for this reference sample (Thirlwall, 1991). At Vrije Universiteit Amsterdam, 6 sample powders (2 - 3 mg) were collected using a New Wave Research micromilling device. Analyses were performed using a ThermoElectron Triton plus TIMS instrument. In order to monitor and document the system's performance, repeated analyses of the international Sr standard (n = 58) were carried out on load sizes of 10 ng and 100 ng which yielded average <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 0.710245±0.000022 (2SD) and 0.710242±0.000008 (2SD), respectively. In both labs mass discrimination correction was performed via internal normalization using Russell's exponential law and the accepted value (0.1194; Steiger and Jager, 1977) of the invariant <sup>86</sup>Sr/<sup>88</sup>Sr ratio.

Fluid inclusion microthermometry analysis was performed on 11 doubly polished wafers (80-130 μm in thickness). Measurements were carried out at Parma University (Italy) using Linkam THMSG-600 and Linkam MDS-600 heating-cooling stages coupled with a Leica DM 2500 microscope. The final melt (Tm<sub>ice</sub>) and homogenization temperatures (T<sub>h</sub>) were reproducible within 0.5°C and 5°C, respectively. The stages were calibrated by synthetic Syn Flinc<sup>TM</sup> fluid inclusion standards. A 100x objective was used during the microthermometry runs of the small inclusions. The microthermometry data were collected following the Fluid Inclusion Assemblage (FIA) approach described in Goldstein and Reynolds (1994) for carbonate minerals. The inconsistent homogenization temperatures and salinities obtained for these fluid inclusions, within the framework of an individual fluid inclusion assemblage (FIA) described by Goldstein and Reynolds (1994), indicate possible re-equilibration (stretched) of these inclusions and thus are not used in the interpretations. It is common for small inclusions (< 3 μm) to remain monophase all-liquid at room temperature due to their metastability (Goldstein and Reynolds, 1994). Thus, to eliminate the possible role of metastability, the samples were placed in a freezer for

several days following the procedures described in detail by Goldstein and Reynolds (1994). All-liquid inclusions remained unchanged and no vapor bubble was developed within them, which discards the metastability effect. In order to properly observe the phase transitions and determine the final melting temperature of ice in the all-liquid inclusions, they were rapidly heated up to ~200°C to stretch and nucleate a bubble at room temperature (Goldstein, 1990). The salinities are reported in equivalent weight percent NaCl (eq. wt. % NaCl) and were calculated based on the equation of Bodnar (1993). The homogenization temperatures obtained in all fluid inclusion assemblages indicate the minimum temperatures at which the fluids could have been trapped (Goldstein and Reynolds, 1994). No correction was made for pressure effects on entrapment temperatures since no data regarding the exact depth and pressure of entrapment are available. In absence of independent thermal indicators such as Conodont Alteration Index (CIA) and Vitrinite Reflectance (VR), the accuracy of pressure correction cannot be well constrained (Slobodník et al, 2006), and thus no correction was made for pressure effects on homogenization temperatures.

In order to perform a-high resolution petrography, Scanning Electron Microscope (SEM) and Back-scattered Scanning Electron Microscope (BSEM) analyses were conducted using a Jeol 6400 Scanning Electron Microscope (SEM) equipped with an Oxford EDS (Energy Dispersive System). Operating conditions were 15 kV and 1.2 nA, electron beam about 1  $\mu$ m in diameter and 100 s counting time; errors are  $\pm 2$ -5% for major elements and  $\pm 5$ -10% for minor components. The analysis focused mainly on detecting possible dolomite crystals inside the bed-perpendicular stylolites affecting the Cretaceous Scaglia Formation.

#### 4 Results

#### 4.1 Field observation and distribution of the dolomitized bodies

Dolomitization affected the Calcare Massiccio, Bugarone and Corniola Formations. There is no evidences of dolomitization in the overlying and immediate surrounding successions of the Calcare Massiccio, Bugarone and Corniola Formations (e.g. Maiolica and Scaglia Formations), though the base of Maiolica Formation is reported as dolomitized in the Central Apennines onshore (e.g. Pierantoni et al., 2013) and offshore areas (Murgia et al., 2004).

Dolomitized intervals are folded in the forelimb of the Montagna dei Fiori Anticline and are abruptly truncated by the Montagna dei Fiori Fault, which juxtaposes them against intensely foliated Scaglia, Bisciaro and Marne con Cerrogna Formations (Figs. 2 and 3). The distribution

of dolomitized intervals is wider in the Salinello valley creek (Figs. 1B1b, 2A2a) perhaps due to a better exposure. In the Corano Quarry location, dolomitization occur in the Calcare Massiccio and Bugarone Formations only as meter-sized dolostone geobodies in the footwall of the Montagna dei Fiori Fault (Fig. 4). The map pattern (Fig. 2) of dolostones indicates that their distribution is maximized in the Castel Manfrino-Osso Caprino hill area and fades out both southward and eastward.

Dolostone breccias in fault cores is typically clast supported, with angular and millimeter to centimeter sized fragments (Fig. 3C), changing to crackle breccia (Woodcock and Mort, 2008) away from the master slip surface. In the proximity of the master slip surface, dolostone fragments are sporadically overprinted by millimeter-sized dolomite veins. The breccia fragments, where cemented, are commonly surrounded by calcite.

Dolomitization does not follow a systematic pattern. The lateral extent of dolomitization is gradual. In some outcrops, dolomitization fronts show irregular outlines following, but also cross-cutting, the bedding surfaces (Fig. 5). Dolomitized intervals vary in thickness from a few meters to hundred meters affecting the totality of the exposed Calcare Massiccio and only the lower part of Corniola Formation, where no clay interlayers are present. In the Calcare Massiccio Formation, dolomitization does not follow a systematic pattern. In the northern side of the Osso Caprino hill (Fig. 2), the top of formation is dolomitized but moving toward the Salinello creek, a thick non dolomitized limestone is exposed. The same situation occurs on the opposite side of the creek and to the east of Castel Manfrino.

Dolomitized intervals in the Corniola Formation have a darker color relative to the host rock and are systematically more fractured than the hosting limestone. High amplitude (> 1 mm), bed-parallel stylolites are clearly visible in both limestones and dolostones (Fig. 5). However, in some dolostones only ghosts of stylolite traces can be seen. No apparent porosity could be observed in host rock limestones but The the dolostones locally contain porosity, appearing as millimetre- to centimetre-sized pores. Dolostone breccias in fault cores are typically clast-supported, with angular and millimeter- to centimeter-sized fragments (Fig. 3C), changing to crackle breccia (Woodcock and Mort, 2008) away from the main slip surface. In the proximity of the main slip surface, dolostone fragments are sporadically cross-cut by millimeter-sized dolomite veins. The breccia fragments, where cemented, are commonly surrounded by calcite cement.

## 4.2 Petrography

## 4.2.1 Early calcite cementation

The early diagenetic products in the studied intervals are generally non-ferroan calcite cements. The first calcite cements precipitated following a phase of bioclast micritization (*sensu* Bathurst, 1975) in grain-grain-supported intervals. In chronological order, they include: 1) fibrous cements (FC) riming the bioclasts, mostly in the peloidal facies of the Calcare Massiccio Formation (Fig. 6A6a). These cements are dull-dark brown to non-luminescent under cathodoluminescence; 2) mosaic cements (MC), commonly fill the intergranular pore spaces (Fig. 6B6b), and also occur as syntaxial overgrowths on echinoderm fragments. These cementsThey exhibit deformation twinning and show a well-developed dull-brown and orange concentrically-zoned cathodoluminescence pattern (Figs. 6C-6c and Dd). They contain only mono-phase all-liquid inclusions. All of these cements are postdated by dolomites and high amplitude bed-parallel stylolites (Fig. 6b).

## 4.2.2 Dolomitization

All the dolomite types are non-ferroan and dominantly fabric destructive. <u>Dolomitization</u> developed in all the facies types of the Calcare Massiccio and the overlaying Bugarone Formations, but only at the lower part of the Corniola Formation which consists of resedimented Calcare Massiccio breccias (turbiditic lobes).

The two first dolomite types (D1 and D2) are the dominant dolomite types in the studied outcrops. These dolomites are distributed within the damage zones of the ~ N-S and E-W Jurassic rift-related extensional faults and, in places, displaced by them (Fig. 2A2a, site 1). The third and fourth dolomite types (D3 and D4) are mainly observed within the damage zone of the Montagna dei Fiori Fault (NNW-SSE), and appear only as dolomitic pockets locally replacing the host rock and overprinting overgrowing D1 and D2 at the proximity of the ~ N-S and E-W extensional faults. The fifth dolomite type (D5) is found only within the brecciated zones associated with the Montagna dei Fiori Fault damage zone. The distinctive petrographic features of the recognized dolomite types are summarized below:

**Dolomite 1 (D1)** is a replacive dolomite which commonly appears as dispersed rhombs and aggregates, and locally rims fracture walls cemented by calcite (CV1) (Figs. 6E-6e and Ff). D1 postdates the micritic envelopes and early calcite cements, and predates high amplitude bed-parallel stylolites (Figs. 6G-6g and Hh). The crystals are fine to medium sized (< 350  $\mu$ m) and

with planar-e and planar-s textures, consists consisting of relatively turbid, rich in host rock solid-inclusions rich, well-developed cuhedral to subhedral crystals, They show with red luminescence when viewed under cathodoluminescence, occasionally developing a concentrical zonation.

Dolomite 2 (D2) is a replacive dolomite (Figs. 7A-7a and Bb), infrequently occluding existing pore spaces. Like D1, it also frequently predates high amplitude bed-parallel stylolites (Figs. 6G 6g and Hh). D2 generally exhibits a tightly closely packed texture with no or little intercrystalline porosity. The crystals are medium to coarse sized (≤ 500 μm) with planar-s to non-planar textures. They includeing a turbid core followed by a transparent subhedral to anhedral rim and trace quantities of saddle dolomite developing swiping-sweeping extinction. In some crystals, one additional turbid zone rich in host rock solid inclusions and fluid inclusions of mostly mono-phase is present. Cathodoluminescence observations enabled to recognize the presence of D1 in their turbid cores. D2 crystals are characterized by zones of bright red-pink luminescence separated by purple luminescence zones (Fig. 7b).

Dolomite 3 (D3) is present as small localized bodies in the Calcare Massiccio (at the Castel Manfrino reference section), in the Corniola Formation (at the Osso Caprino Road), and in the Calcare Massiccio and Bugarone Formations (at the Corano Quarry) (Figs. 1b and 2a). In the Corano Quarry the dolomitized Bugarone and Calcare Massiccio Formations are in the footwall of the Montagna dei Fiori Fault; and juxtaposed to the undolomitized, intensely foliated Scaglia Formation in (the hanging wall). The SEM and BSEM analysis performed on the samples from the immediate adjacent Scaglia Formation within the aforementioned fault damage zone did not indicate the presence of any dolomite in this formation. Within the Bugarone Formation in this fault damage zone, D3 locally cements the millimeter-sized angular breccias that are in turn affected by fault-parallel stylolites (Figs. 7C-7c and Dd). The SEM and BSEM analysis performed on the samples from the immediate adjacent Seaglia Formation within the aforementioned fault damage zone did not indicate the presence of any dolomite in this formation. D3 crystals are fine to medium sized (< 300 µm) mostly transparent euhedral to anhedralexhibiting planar-e to non-planar textures (< 300 µm), with minor development of saddle morphologies in of larger crystals (> 500 μm) with planar-c texture (Figs. 7E-7e to Hh). The euhedral to anhedral replacive crystals are generally replacive, displaying a faint core, which compared to previous dolomite types has fewer solid inclusions. The saddle crystals are

occasionally replacive but majorly appear as cement in fractures. They display typical curved and slightly serrated crystal terminations with swiping sweeping extinction. These saddle dolomites were only observed in the Castel Manfrino reference section. D3 generally exhibit a dull-dark purple color with bright orange zones and subzones in core and/or rims when viewed under cathodoluminescence (Figs. 7E-7e to Hh).

Dolomite 4 (D4) appears as a matrix replacive and dolomite cement surrounding porosity, and locally recrystallizing replacing D1 and D2 (Figs. 8A-8a to Ff). D4 also occludes bed\_bed\_parallel shear fractures and appears along the bed\_bed\_parallel stylolites (Figs. 9A-9a to Dd). In the Castel Manfrino reference section, some intercrystalline vuggy porosity is filled with fine dolomite rhombs including D4 with relics of D2 within their core (Figs. 8E-8e and Ff). The This porosity may be preserved or partially to completely filled by calcite (CV4C4). D4 crystals have a turbid, solid-inclusion rich core and transparent rim. They are fine to medium sized (< 200-350 μm), presenting subhedral planar-s to and infrequent euhedral crystals non-planar textures. D4 exhibits a distinct luminescence pattern including a purple zone and an irregular green subzone.

**Dolomite 5 (D5)** occurs as crystals cementing micro-veins that cross-cut precursor dolomite types including dolomitic breccia fragments. In cemented breccias, D5 is postdated by CV3C3.

D5 presents a planar-c texture is transparent, anhedral and is characterized by a bright red luminescence (Figs. 9E-9e and Ff).

## 4.2.3 Late calcite cementation

 Four generations of calcite veins postdating dolomitization and distributed only within the fault damage zones have been identified (Figs. 10 and 11):

1) Calcite vein 1 (CV1) occurs only in Calcare Massicio limestones and dolostones and is represented as centimeter-sized veins with thickness that does not exceed 1.5 cm. It is not clear whether the fracture opening and calcite precipitation was simultaneous (as shown in Ukar and Laubach, 2016). These veins are strata-bound, bedding-perpendicular veins—with irregular fracture walls, exhibiting white color in the outcrops. They are present within the syn-rift related extensional fault damage zones, postdatepostdating the first dolomite type (D1) and abutted riming the same fractures that abut the highby high amplitude bed-bed-parallel stylolites. CV1 often—usually shows blocky to elongated crystal morphologies and displays well-developed deformation twinning planes (Type II of Burkhard, 1993). This calcite exhibits concentrical

zonation and <u>dull\_brown</u> zones alternate with orange luminescence zones (Figs. <u>11A\_11a\_and Bb</u>).

2) Calcite vein 2 (CV2) exclusively occurs in the intensely deformed Scaglia Formation within the fault damage zones (Figs. 11b, c and d) and correspond to tension gashes associated with stylolites (sensu Nelson, 1981). The thickness of these veins does exceed 1 cm. They are usually discontinuous and branch to several microveins (thickness < 1mm) when their tips are not intersected by stylolites. CV2C2 veins are mostly recorded in foliated shear deformation zones with well-defined S-C fabrics, exhibiting blocky, elongated to fibrous shapes with strongly developed tightly spaced deformation twinning planes (Type II of Burkhard, 1993). CV2C2 displays yellow brown to orange luminescence with locally darker sector zones. The yellow brown to orange luminescence characteristic of CV2C2 is comparable withsimilar to those of encasing Scaglia host rocks (Figs. 11C-11c and Dd).

3) Calcite vein-3 (CC1V3) occurs as cement, filling the extensional faults Montagna dei Fiori master main fault plane and isolated veins within the extesional faultits damage zones. These veins are centimeter-sized with thicknesses of less than 2 cm. The breccias are generally clast-supported, but locally CV3C3 cements the brecciated fault-infillings containing angular fragments of host rock limestones, dolostones and earlier calcites. In the brecciated zones at the backlimb of the anticline (Montagna dei Fiori Fault), CV3C3 always passively overgrows D5 in fractures and never cuts it.postdates the last dolomitization phase (D5) with no evidence of physical disruption. CV3C3 exhibits a translucent white to translucent color in hand specimen. The crystals are blocky with no or weakly developed deformation twinning planes, and are characterized by a dark orange to brown luminescence with distinct darker sector zones (Figs. 11E-11e and Ff).

4) Calcite vein 4 (CV4C4) exists as <u>centimeter-sized</u> isolated veins, pore-filling as well as breccia cements postdating all the preceding dolomites and calcites in the <u>Montagna dei Fiori main fault plane</u>. The breccia fragments are <u>more oftenusually</u> dolostones. <u>CV4C4</u> has a <u>translucent white to translucent white</u> color in hand specimen with blocky crystal morphology and no evidence of subsequent deformation (e.g. deformation twinning planes), and is characterized by distinct concentrical zonation (Figs. <u>11G-11g</u> and <u>Hh</u>).

# 4.3 Geochemistry

# 4.3.1 Carbon and oxygen stable isotopes

The carbon and oxygen stable isotopic data ( $\delta^{13}$ C and  $\delta^{18}$ O) of host rocks, dolomites and calcites are given in Table 1 and shown in Figures 12A-12a and Bb. The marine stable isotopic compositions reported by Veizer et al. (1999) were used as marine reference values. Accordingly, Lower Jurassic marine limestones are characterized by  $\delta^{13}$ C values of -0.5 to +4.5% and  $\delta^{18}$ O values of -2.5 to +1.0% V-PDB. The  $\delta^{18}$ O values of the marine dolomites are known to be 3-4% V-PDB more enriched than those of co-genetic marine limestones (Land, 1980; Major et al., 1992; Horita, 2014). In order to avoid data ambiguity due to physical mixing, this analysis was not separately performed on early calcite cements (FC and MC). The  $\delta^{13}$ C and  $\delta^{18}$ O values measured on bulk samples of host rock limestones. Both  $\delta^{13}$ C and  $\delta^{18}$ O values of the host rocks are within the expected range of the Lower Jurassic marine limestones but the Corniola host rocks show slightly lower values comparing to those of Calcare Massiccio. In the Calcare Massiccio host rocks, the  $\delta^{13}$ C values plot between +2.4 and +3.1% and  $\delta^{18}$ O values are within the range of -1.6 and 0.0% V-PDB. The  $\delta^{13}$ C values in the Corniola host rocks are +2.0 and +2.5% while the  $\delta^{18}$ O values are -3.1 to -1.4% V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of the Scaglia host rocks range between +1.0 to +3.3% for  $\delta^{13}$ C and -2.2 to -1.0% V-PDB for  $\delta^{18}$ O. The obtained values obtained are characterized in the mean range of Upper Cretaceous to Paleogene marine limestones (Veizer et al., 1999; +1.0 to +4.5% for  $\delta^{13}$ C and -4.0 to +2.0% V-PDB for  $\delta^{18}$ O).

The  $\delta^{13}$ C values of CV1C1 are between +1.6 and +2.1% which plot within the range of reference values (Jurassic) but are slightly lower than the surrounding host rock values. The  $\delta^{18}$ O values are between -4.7 and -2.7% V-PDB which are lower than those of reference and host rock values.

The  $\delta^{13}$ C values of all dolomite types (+0.6 to +3.4‰) fall within the range of host rocks and Jurassic marine limestones (Veizer et al., 1999). The  $\delta^{18}$ O shows a wider range of values, somehow-overlapping but also lower than those of host rocks (-4.5 to -0.9‰ V-PDB) and those expected for the presumable-Lower Jurassic marine dolomites. The majority of values plot between -3.5 and -1.5‰ V-PDB. The small size and overgrowth nature of certain dolomite types (e.g. D2 and D5) limits their proper isolation for geochemical analyses. Only one sample from D1 dolomite could be measured for  $\delta^{13}$ C and  $\delta^{18}$ O values, showing +2.5 and -1.9‰ V-PDB, respectively. The  $\delta^{13}$ C and  $\delta^{18}$ O values of D3 dolomite range from +2.0 to +2.6‰ and -2.8 to -1.9‰ V-PDB, respectively, with values lower than those of the host rock.

D4 dolomite has  $\delta^{13}$ C values between +2.4 and +2.5‰, and  $\delta^{18}$ O values of -3.0 to -2.5‰ V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of CV2C2 are +1.2 to +3.1‰ and -1.7 to -1.7‰ V-PDB, respectively. The  $\delta^{13}$ C values of CV3C3 are between +0.5 and +2.4‰, and the  $\delta^{18}$ O values cover a range of -2.2 to 0.0‰ V-PDB. The  $\delta^{13}$ C and  $\delta^{18}$ O values of CV4C4 are +3.8 to +4.9‰ and -9.4 to -9.1‰ V-PDB, respectively. The  $\delta^{13}$ C values are slightly higher but the  $\delta^{18}$ O values are considerably lower compared to preceding calcite generations and the measured values from host rocks.

# 4.3.2 87 Sr/ 86 Sr ratios

Samples from host rocks (i.e. Calcare Massiccio and Corniola Formations), dolomites (D1, D3 and D4) and the Scaglia Formation in juxtaposition with the dolostones were analyzed for their  $^{87}$ Sr/ $^{86}$ Sr isotopic ratios. The obtained ratios versus  $\delta^{18}$ O values of the analyzed samples are shown in Fig. 12C. The  $^{87}$ Sr/ $^{86}$ Sr ratios obtained from the Calcare Massiccio and Corniola limestones are 0.70766 and 0.70725 (n = 2), respectively, which is in agreement with the values of the Lower Jurassic marine carbonates (0.70704-0.70768) reported by McArthur et al. (2012). CV1 show a value equal to 0.70773.

All the dolomite types display higher  $^{87}$ Sr/ $^{86}$ Sr ratios when compared to the host rocks and reference values of the Lower Jurassic marine carbonates. D1 (replacive) and D4 cements show a comparable similar narrow range with values between 0.70784 and 0.70790, respectively. While, the The two D3 samples (replacive and cement) display higher  $^{87}$ Sr/ $^{86}$ Sr ratios (0.70858 and 0.70963, respectively). The  $^{87}$ Sr/ $^{86}$ Sr ratios obtained for dolomites do not show co-variation with corresponding  $\delta^{18}$ O values. The radiogenic Sr analysis was not performed on D2 and D5 since the physical mixing with other dolomite types could not be avoided.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the <u>two-three marly limestone</u> samples of Scaglia Formation are 0.70784 to 0.70790. The <u>CV2C2</u> veins in Scaglia Formation show <u>comparable similar</u> ratios of 0.70779 and 0.70787. These values fit within the limits of values assigned by McArthur et al. (2012) for the Cenomanian-Bartonian (Scaglia age) marine carbonates (0.70730-0.70790).

## 4.4 Fluid inclusion microthermometry

The overview of microthermometry measurements is given in Table 1 and Figs. 13A to C. All the measured fluid inclusions are primary and occur in growth zones. Based on optical and fluorescence microscopy analysis of wafers all the inclusions are aqueous mono-phase (liquid)

and two-phase (liquid and vapor) with relatively consistent L:V ratio of 10-15% within a single FIA (fluid inclusion assemblage). Special care was taken to avoid the samples that occasionally displayed scattered mottled luminescence that may indicate recrystallization.

On the basis of optical microscopy analysis of wafers, D1 contain dominantly monophase aqueous inclusions with sizes greater than 5 µm. It is common for small inclusions (<3 µm) to remain monophase all liquid at room temperature due to their metastability (Goldstein and Reynolds, 1994). Thus, to eliminate the possible role of metastability, the samples were placed in a freezer for several days following the procedures described in detail by Goldstein and Reynolds (1994). All liquid inclusions remained unchanged and no vapor bubble was developed within them, which discards the metastability effect. In order to properly observe the phase transitions in the all liquid inclusions, they were rapidly heated up to ~ 200°C to stretch and nucleate a bubble at room temperature (Goldstein, 1990). All the inclusions froze at -65 to -49°C. The first melting (Te) was detected between -22 to -19.3°C. The final ice melting (Tm) appeared at temperatures between -7.7 and -2°C. Applying Bodnar's (1993) equation, the obtained final melting temperatures correspond to salinity ranges of 3.5 to 11.3 eq. wt. % NaCl.

D2 is characterized by the presence of mono-phase and infrequent two-phase inclusions generally within their growth zones. The homogenization temperature of two-phase inclusions varies between 58 and 71°C. Upon cooling, a complete freezing of the fluid phase is reached at -56 to -40°C. The first ice melting temperature was distinguished at -22°C. The final ice melting temperatures fall within -17.5 and -5°C, corresponding to salinities between 7.9 and 20.5 eq. wt. % NaCl.

D3 is commonly inclusion poor. The measureable inclusions were detected and examined only in saddle dolomite crystals. These crystals contain only two-phase aqueous inclusions. Their homogenization temperatures are within the narrow range of 70 to 73°C. The complete freezing and first ice melting temperatures could not be distinguished but the final ice melting temperature occurred at temperatures between -13 and -6°C equal to salinity ranges of 9.2 to 16.9 eq. wt.% NaCl. The first melting temperatures of fluid inclusions in D1, D2 and D3 were about -21°C, suggesting a H<sub>2</sub>O-NaCl fluid system.

D4 contains only two-phase aqueous inclusions. The homogenization temperatures in D4 vary between 79 and 105°C. Complete freezing of inclusions occurred at temperatures between -86 and -54 °C. The first ice melting was detected at -35 to -40°C indicating the

possible presence of divalent cations such as Ca<sup>2+</sup> and/or Mg<sup>2+</sup> in the fluids (Shepherd et al., 1985; Goldstein and Reynolds, 1994). The final ice melting temperatures fall within a range of -15 and -9°C corresponding to salinities of 12.8 to 18.6 eq. wt. % NaCl. A couple of inclusions show homogenization temperatures exceeding 120°C with salinities higher than 20 eq. wt. % NaCl. The inconsistent homogenization temperatures and salinities obtained for these fluid inclusions, within the framework of an individual fluid inclusion assemblage (FIA) described by Goldstein and Reynolds (1994), indicate possible re equilibration of these inclusions and thus are not used in the interpretations.

The obtained homogenization temperatures in all fluid inclusion assemblages indicate the minimum temperatures at which the fluids could have been trapped (Goldstein and Reynolds, 1994). No correction was made for pressure effects on entrapment temperatures since no data regarding the exact depth and pressure of entrapment are available. In absence of independent thermal indicators such as Conodont Alteration Index (CIA) and Vitrinite Reflectance (VR), the accuracy of pressure correction cannot be well constrained (Slobodník et al, 2006), and thus no correction was made for pressure effects on homogenization temperatures.

No measurable fluid inclusion could be identified in CV1C1 and CV2C2 due to intense deformation twinning. CV3C3 and CV4C4 contain only primary mono-phase aqueous inclusions, indicating an entrapment temperature of below about 40-50°C (Goldstein and Reynolds, 1994). A complete freezing of the inclusions in CV3C3 occurred at temperatures between -40 and -52.5°C. The first melting temperature was detected at about -21 to -22°C, suggesting a H<sub>2</sub>O-NaCl composition. The final melting temperatures range between -6.4 and -2.7°C, corresponding to salinities between 9.7 and 4.5 eq. wt. % NaCl. The majority of the values cluster between 7.8 and 5 eq. wt. % NaCl.

The complete freezing temperatures of the inclusions in CV4C4 fall within -46 and -35.5°C. The first melting temperature could not be determined with confidence but the final melting temperatures were reached at about -0.1 to -1.8°C, corresponding to salinities of 0.17 to 3.0 eq. wt. % NaCl.

#### 5 Discussion

### 5.1 Stable and radiogenic isotopic composition of the parental fluids

The  $\delta^{13}$ C values of all dolomite types mimic the range of host rock and Jurassic marine limestones and, consequently, they can be interpreted as largely rock-buffered. Their  $\delta^{18}$ O values

are partly comparable similar to those of their respective host rocks as well as Jurassic marine reference values but more depleted when compared to the presumable Jurassic marine dolomites. The relatively depleted  $\delta^{18}O_{dolomite}$  values could indicate the contribution of heated fluids in dolomitization process, although it could also relate to recrystallization of a precursor dolomite by fluids at higher temperature or  $^{18}O$ -depleted (Land, 1980; 1985). The absence of distinctive textural evidence in the analyzed samples such as enlarged crystal size and/or systematic mottled cathodoluminescence pattern, and their co-variation with  $\delta^{18}O$  values do not confirm recrystallization (Mazzullo, 1992 and ref. therein). Nevertheless, special care was taken to avoid the samples that occasionally displayed scattered mottled luminescence.

The oxygen isotope fractionation relation between water and dolomite (Land, 1983) was used to determine the most plausible parental fluids. In order to avoid erroneous results due to rock-buffered  $\delta^{18}$ O values, only the  $\delta^{18}$ O values of dolomite cements, especially from the bed bed-parallel veins containing D4 were used. These values may provide the closest approximation to the  $\delta^{18}$ O signature of the parental fluids (Barker and Cox, 2011). Accordingly, a  $\delta^{18}$ O value of  $\approx +2.5$  to +4% V-SMOW was calculated for D3, while this values increase to  $\approx +5$  to +7.5% V-SMOW for D4 (Fig. 13D13d). The calculated compositions of the potential parental fluids are progressively higher. The higher  $\delta^{18}$ O composition of the dolomitizing fluids relative to the Mesozoic seawater, which is estimated at -1.2 to -1% V-SMOW (Shackleton and Kennett, 1975; Marshall, 1992; Saelen et al., 1996), is compatible with fluids derived from or that had interacted with siliciclastic rocks, crystalline basement (Taylor, 1997) and/or evaporite-derived brines.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratios obtained for all dolomite types are higher than the Lower Jurassic marine carbonate values (0.70704-0.70768; McArthur et al., 2012). Since marine carbonates have very low rubidium (Rb) concentrations they produce negligible *in situ* radiogenic <sup>87</sup>Sr after their deposition (Stueber et al. 1972; Burke et al. 1982). Therefore, the higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios can be explained by the contribution of fluids originated or interacted with potassium rich siliciclastics siliciclastic rocks (K-feldspars), crystalline basement and/or stratigraphic levels with higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios (Emery and Robinson 1993; Banner, 2004). Taking into account that the Upper Triassic Burano Formation underlying the studied intervals as the basal detachment has <sup>87</sup>Sr/<sup>86</sup>Sr ratios between 0.70774 and 0.70794 (Boschetti et al., 2005), the <sup>87</sup>Sr/<sup>86</sup>Sr ratios (D1 and D4) can partially be explained by their contribution. However, this contribution cannot justify

much higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios recorded in D3, being higher than values reported for Phanerozoic seawater (McArthur et al., 2012), and the values recorded inobtained for the adjacent basinal deposits (i.e. Corniola and Scaglia Formations). Therefore, parental fluids most likely originated from or had interacted with the siliciclastics siliciclastic rocks underlying the Burano Formation (Verrucano Formation), if present, and/or with the crystalline basement with common elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.71500-0.72650; Del Moro et al., 1982). The significantly higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios in D3 in comparison with other studied dolomites indicates a higher influence of <sup>87</sup>Sr/<sup>86</sup>Sr-rich fluids either due to major changes in the permeability architecture of faults or availability of such fluids. The lack of any ferroan diagenetic phase minimizes the interaction of fluids produced by clay transformation/dewatering (i.e. smectite to illite transformation; Boles and Franks, 1979).

CV1C1 is characterized by  $\delta^{13}C$  and  $\delta^{18}O$  values lower than the host limestones (i.e. Calcare Massiccio), while its  ${}^{87}Sr/{}^{86}Sr$  ratio is comparable similar to them. The salinity and composition of the parental fluids cannot be inferred here since no measurable fluid inclusions were found within this cement. The  ${}^{87}Sr/{}^{86}Sr$  ratio being within the range of the corresponding host rocks and the reference values, points to a rock-buffered system for  ${}^{87}Sr/{}^{86}Sr$ .

The  $\delta^{13}$ C and  $\delta^{18}$ O values obtained for CV2C2, as well as  $^{87}$ Sr/ $^{86}$ Sr ratios, fall within the range of the Scaglia host rocks, thus reflecting their rock-buffered nature. This interpretation is further supported by the comparable similar luminescence characteristics of CV2C2 with that of encasing Scaglia host rocks. The fluids from which CV2C2 calcite precipitated, as expected for tension gashes, were most likely derived from carbonate dissolution during pressure-solution and stylolitization of host rock<sub>7</sub>, pointing to a closed fluid system in contrast with the subsequent vein generations.

cV3C3 is characterized by  $\delta^{13}$ C values within the Jurassic marine values but are generally lower than the host rocks, while their  $\delta^{18}$ O values partially overlap both the hosting limestones and dolostones. Microthermometry of fluid inclusions revealed only mono-phase aqueous inclusions and thus precipitation at relatively low temperature ( $\leq 40\text{-}50^{\circ}\text{C}$ ) with moderate salinity (4.5-9.7 eq. wt. % NaCl). Such levels of salinity can be assigned to evaporated seawater, residual brines or fluids derived from evaporite dissolution, and thus makes it difficult here to interpret their exact origin with the available data.

 $\overline{\text{CV4C4}}$  is the latest calcite phase, and records the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, respectively enriched and significantly depleted when compared to their hosting rocks and preceding

diagenetic products. Generally, the enrichment of  $^{13}$ C could suggest CO<sub>2</sub> outgassing due to evaporation or pressure changes (Friedman, 1970; Hendry et al., 2015) or bacterial fermentation (methanogenesis) of organic matter (Hudson, 1977) in low temperature diagenetic environments. The homogenization temperature of  $\frac{\text{CV4C4}}{\text{CV4}}$  being below about  $40\text{-}50^{\circ}\text{C}_{2}$  could support any of these processes. Their low  $\delta^{18}\text{O}$  values and fluid inclusions with salinities comparable similar to, but also significantly lower than, seawater reflect the contribution of meteoric fluids during precipitation of this calcite.

### 5.2 Origin of the dolomitizing fluids

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The contribution of brines that derived from highly evaporated seawater or evaporites is suggested by the elevated salinity values obtained from microthermometry of the fluid inclusions (3.5 to 20.5 eq. wt. % NaCl). Accordingly, two sources that could potentially provide such fluids can be proposed: 1) fluids related to the Late Messinian evaporites, associated with the overlying <u>Upper Miocene</u> Laga Formation, deposited during the <u>Upper Miocene time</u>, and their possible downward percolation through fault zones by density driven flow and/or seismic pumping mechanisms (Sibson, 1981; McCaig, 1988, 1990); or their tectonic involvement into the Apenninic thrust wedge during its propagation (underthrusting; Lobato et al., 1983); and 2) fluids related to the underlying décollement detachment horizon of the Burano evaporites (Upper Triassic) and their upward flow through fault zones during development of the Montagna dei Fiori Anticline. The first scenario is valid if the dolomitization would have occurred only from the Upper Miocene time onwards. Moreover, Several researchers (e.g. Vai and Ricci Lucchi, 1977; Bassetti et al., 1998; Roveri et al. 2001) have shown that the occurrence of primary shallow-water evaporites, which were dominantly gypsum, was limited only to the western and central parts of the northern Apennines consisting of thrust-top marginal basins. In contrast, evaporites never precipitated in parts of the central Apennines including the Montagna dei Fiori region (Marche area) (Roveri et al. 2001). Hence, the evaporitic horizons existing within the Laga Formation corresponds to resedimentation (gypsum debris) of those previously precipitated in the marginal basins. This interpretation makes the Messinian evaporites an unlikely source of Mg-rich brines. Moreover, taking Taking into account that the maximum burial-burial-related temperature of the Calcare Massiccio Formation did not exceed 80°C in the Montagna dei Fiori region (Ronchi et al., 2003), it's it is not unlikely that the downward percolation of relatively low-temperature brines derived from the Messinian evaporites, located

at the higher stratigraphic levels, could reach or exceed the high temperatures recorded in fluid inclusions of the <u>studied</u> dolomites in the <u>Calcare Massiccio Formation</u> (D4; up to 105°C), given that the homogenization temperatures reflect the minimum entrapment temperatures (Goldstein and Reynolds, 1994). Deep circulation of these brines, if <u>they</u> existed, can also be excluded by <u>the fact that</u> their limited <u>tectonic</u> involvement <u>within</u> the thrust wedge <u>being was</u> confined merely to the off shore wards of the Montagna dei Fiori region (Artoni, 2013).

Accordingly, the Upper Triassic Burano Formation, the basal detachment, appears as the most plausible source for the high salinity brines recorded in fluid inclusions, and likewise, the Mg-rich fluids could have been originated from post-evaporite brines associated with them (Carpenter, 1978; McCaffrey et al., 1987). The fluctuations in salinity may argue for different degrees of diverse range of fault connectivity, different degrees of rock-water interaction and contribution of pore waters of lower salinity (e.g. marine or meteoric).

# 5.3 Timing and structural controls on the evolution of parental fluids

A generalized paragenesis and the relative chronology of dolomitization in relation to the structural evolution of the Montagna dei Fiori Anticline are illustrated in Figs. 14 and 15. The structural episodes are based on the evolutionary stages of the Montagna dei Fiori Anticline suggested by Storti et al. (2018). The paragenesis is constructed on the basis of direct evidences recorded during observations at outcrop scale and microscopic observations (e.g. cross-cutting relationships between diagenetic phases, stylolites, fractures and other structural kinematics), and indirect evidences (e.g. regional geodynamics and burial history).

The occurrence of micritic envelopes and fibrous calcite cements (FC), in grain-grain-supported stratigraphic levels of the Calcare Massiccio Formation, is interpreted to be of eogenetic origin (i.e. marine phreatic diagenesis; Moore, 1989), reflecting an early diagenesis shortly after deposition. The well-developed dull brown and orange concentric cathodoluminescence pattern of the succeeding mosaic calcite cement (MC) suggests a progressive shift to more reducing conditions during precipitation in a phreatic diagenetic environment (as shown in Li et al., 2017). High amplitude bed-bed-parallel stylolites postdate both cements, which confirm their precipitation before significant burial. The observations made here are in agreement with earlier work by Giacometti and Ronchi (2000), interpreting that the Calcare Massiccio Formation was cemented during the early diagenetic stages.

D1, CV1C1 and D2 are postdated cut by well-developed, high amplitude bed-parallel stylolites. Presence of D1 and CV1C1 in bed-perpendicular veins typically abutted cut by these stylolites (see Figs. 6E-6e to Hh) support the interpretation that the first dolomitization event (D1 and D2) took place before significant burial and stylolite development,. being tThe latter and bed-perpendicular veins are dynamically compatible within the same stress field which is characterized by a vertical, load-related maximum principal axis of the stress ellipsoid (Fig. 15a). The dominantly mono-phase fluid inclusions within D1 and D2 are in agreement with precipitation temperatures below about 40-50°C, suggesting a relatively shallow to intermediate burial environment and hence supporting a pre-Apenninic orogeny age of precipitation from a mix of formational and extra-formational fluids with elevated 87Sr/86Sr ratios. The distribution of D1 and D2 localized nearby the rifting-related ~ N-S and E-W striking extensional faults and even their displacement along them (Fig. 2A2a, e.g. site 1), point to the possible contribution of these faults in occurrence of D1 and D2. These faults dominantly affect the Jurassic rocks older than the Maiolica Formation which is attributed to the post-rift deposits, therefore suggesting a pre-Maiolica age for these dolomite types. Although, an absolute age cannot be provided, based on the evidence discussed above, the circulation of Mg-rich fluids during this dolomitization event was most likely controlled by rifting-related Jurassic extensional fault zones cutting through the crystalline basement. Precipitation of D1 and D2 at the lower part of Corniola Formation which is known as the syn-rift deposit discards a pre-rift origin for these dolomites. The displacement of dolomites along the aforementioned faults is possibly related to their prolonged activation during Early to Late Jurassic. In addition to the role of these faults in channelizing the fluids, their mobilization must have been intensified by some deriving mechanisms. A thermal convection system derived from high hit flux during rifting was interpreted by Hollis et al. (2017) to be responsible for circulation of seawater in a syn-rift dolomitization case in the Hammam Faraun fault block (Suez Rift, Egypt). In such scenario, the salinity of the fluids and their <sup>87</sup>Sr/<sup>86</sup>Sr ratios are expected to be more or less within the range of seawater. Furthermore, this scenario seems unlikely in the studied area given the lack of a deep aquifer to accommodate the fault tips and promotes the lateral fluid flux from basin to the rift shoulders and vice versa. Taking into account that D1 and D2 are the volumetrically more relevant dolomites within the studied intervals, and assuming the likely role of syn-rift extensional faults (Early to Late Jurassic) in their precipitation, a dominantly syn-rift

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dolomitization process is proposed for the dolostones in the Montagna dei Fiori Anticline. Although the CL zonation pattern observed in D2 may indicate changes in flow condition or fluid composition, the lack of physical disruptions such as multiple fracturing suggests external regional controls rather than slip along the same faults (Eichhubl and Boles, 2000). The absence of pervasive syn-dolomitization fracturing and brecciation as well as zebra fabrics in these dolomites, perhaps indicate a relatively calm tectonic period during dolomite development (e.g. Hollis et al., 2017).

D3 and D4 both record elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios which accounts for their fault-controlled origin. However, their occurrence at the top of the Calcare Massiccio and overlaying Bugarone Formation (Corano Quarry site) which is < 1 m thick in Montagna dei Fiori region, and is marked as the final rift deposit (Cardello and Doglioni, 2015) discards a syn-rift origin for these dolomites. Moreover, D3 and D4 postdate the development of high amplitude bed-bed-parallel stylolites. The formation of stylolites requires an approximate overburden of 600 to 1500 m (Lind, 1993; Machel, 1999; Mountjoy et al., 1999; Schulz et al., 2016), corresponding to a late to post-Maiolica deposition time (Early Cretaceous time onwards). The presence of D3 and D4 dolomites in bed-bed-parallel fractures and as shear veins (D4) (Figs. 9a and b) suggests their association with contractional deformations, i.e. the most likely tectonic regime for explaining bed-perpendicular dilation. Therefore, the volumetrically minor second stage of dolomite precipitation may possibly be related to the Late- to post-Miocene compressional tectonics recorded in this region (e.g. Mazzoli et al., 2002; Artoni, 2013; Storti et al., 2018).

Dolostones containing D3 and D4 appear commonly as clast-supported breccias along fault zones pertaining to the Montagna dei Fiori Fault, then overprinted by fault-parallel stylolites (Figs. 3 and 7). Accordingly, the occurrence of these dolomites was probably synchronous with the incipient stages of fault development, predating fault buttressing (Storti et al., 2018). Homogenization temperatures recorded in D4 (up to 105°C), much higher than the maximum temperatures recorded in the host rocks (below about 80°C; Ronchi et al., 2003), suggest hydrothermal fluid circulation. The development of the Montagna dei Fiori Anticline at the toe of the Late Miocene Central Apennines thrust wedge could have favored the forelandward migration of hydrothermal fluids expelled from the more internal regions of the belt, similarly to what has been proposed for the Rocky Mountains foreland (i.e. squeegee flow model; Machel and Cavell. (1999). Such a migration may have possibly favored the precipitation

of D4 in bed-bed-parallel veins, generally considered as evidence for syn-compressional fluid overpressure (Sibson, 2001; Hiemstra and Goldstein, 2015). At this stage, in addition to dilation of the pre-existing ~ N-S and E-W striking rift-related extensional faults and their possible role in fluid migration, the excess of pore pressure at the base of the thrust ramp, in the fold hinge and during fold tightening could promote the localization of the fractures (Smith and Wiltschko, 1996; Ghisetti and Vezzani, 2000), with fluid migration within this zone and eventually dolomitization. These fractures could have been corridors that later on formed the insipient NW-SE Montagna dei Fiori Fault. Their localization at the back-limb cross-cutting the core, explaining best the distribution of D3 and D4 at this locality. The presence of only D5 only within the damage zone of the Montagna dei Fiori Fault, postdating dolostone brecciation and, in places, cementing breccia fragments, may suggest that D5 dolomite precipitation was associated with the late stage evolution of the Montagna dei Fiori Fault, predating late stage calcite precipitation. The shift from dolomite to calcite precipitation can be ascribed to attenuation of Mg-rich fluids and/or calcite saturation. This condition was perhaps initiated during the late stages of anticline evolution due to changes in fault conductivity sealing the upward migration of Mg-rich fluids. The presence of several generations of bed-bed-perpendicular stylolites bounding and intersecting CV2C2 veins (Fig. 10), supports the postulation that late stage calcite cements precipitated in close elosely associated association with the deformation history of the Scaglia Formation in the hanging wall of the Montagna dei Fiori Fault (Fig. 3). This deformation occurred, during buttressing against Calcare Massiccio and Corniola Formations in the footwall, and related with the positive inversion event induced by thrust-sheet stacking at depth (Storti et al., 2018). Precipitation of CV3C3 and CV4C4 in is interpreted to have occurred during uplift and cooling as revealed by their relatively low homogenization temperatures ( $\leq 40-50$ °C) of fluid inclusions trapped within these cements. Deformation twinning is either absent or weakly developed, reflecting the lack of significant tectonic deformation after calcite precipitation. These cements postdate the dolomitization events, high amplitude bed-bed-perpendicular and parallel stylolites, and are precipitated as cements bounding the breccia fragments within the damage zone of the Montagna dei Fiori Fault. Salinities calculated from their fluid inclusions, particularly in CV4C4, suggests precipitation from meteoric waters, which should have been

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favored during the late evolutionary stages of antiformal stacking beneath the Montagna dei Fiori

Anticline, and eventual late extensional slip along the Montagna dei Fiori Fault (Storti et al., 2018). The results obtained in this study are in relative agreement with the earlier work by Ronchi et al. (2003) and Murgia et al. (2004) in the Central Apennines, assigning dolomitization phases to the pre- and syn-orogenic deformations, although they did not specify the direct relation between the <u>local</u> structures and the different types of dolomite.

The textures of the studied dolomites vary from planar-e to non-planar, the preponderance of planar dolomite, as in D4, creates a rock with interesting poroperm characteristics (e.g. Woody et al., 1996; Wilson et al., 2007; Wenzhi et al., 2012). This case-study is certainly relevant for many potential reservoirs elsewhere in the world. Similar multistage burial dolomitization events enhancing the reservoir quality have been reported from the carbonate successions of the Jurassic in the Kopet-Dagh Basin, north eastern Iran (Adabi, 2009) and Devonian of the Rainbow sub-Basin, western Canada (Qing and Mountjoy, 1989; Lonnee, 1999).

### **6 Conclusions**

The Lower Jurassic limestones outcropping at the core of the Montagna dei Fiori Anticline (Central Apennines, Italy) are massively affected by dolomitization, in damage zones of the pre-orogenic faults inherited from the Tethyan rifting and the ones formed during the Apenninic orogeny. Cross-cutting relationships between deformation structures, and results from optical and cold cathodoluminescence petrography, fluid inclusion microthermometry, and isotope geochemistry, support the occurrence of two major dolomitization events. The first event is interpreted as <a href="having">having</a> developed during the late stages of Tethyan rifting in Jurassic and resulted in volumetrically significant dolostone geobodies. These dolostones are <a href="majorly-largely">majorly-largely</a> matrix replacive, and their precipitation initiated prior to the significant burial as reflected in their cross-cutting relationship with <a href="bed-bed-parallel">bed-bed-parallel</a> stylolites, and by homogenization temperatures in fluid inclusions that are dominantly below about 40-50°C. The second dolomitization event corresponds to volumetrically less relevant replacive dolomite and dolomite cements occluding fractures. These dolomites precipitated during hydrothermal fluid circulation associated with contractional tectonics during the Apenninic orogeny, possibly at the onset of the growth of the Montagna dei Fiori Anticline (Late Miocene).

Dolomitizing fluids in both events were most likely sourced from evaporitic brines associated to the underlying Burano evaporites and their interaction with siliciclastic rocks and/or the crystalline basement.

Author contributions. M. Mozafari participated in fieldwork, performed petrographic and microthermometric analyses, provided their interpretation, and wrote the manuscript; R. Swennen participated in fieldwork, discussed the results of the diagenetic study, and critically reviewed the manuscript; F. Balsamo contributed to collect and interpret structural data, discussed structural diagenesis data interpretation, and critically reviewed the manuscript; H. El Desouky collected <sup>87</sup>Sr/<sup>86</sup>Sr data; F. Storti conceived the research, contributed to collect and interpret structural data, discussed structural diagenesis data interpretation, and critically reviewed the manuscript; C. Taberner participated in fieldwork, discussed the results of the diagenetic study and their framing into the proposed structural evolution, and critically reviewed the manuscript.

Acknowledgments. This research was performed by collaboration between Parma and KU Leuven universities in the framework of a research project (PT12432 and GFSTE 1100942) funded by Shell Global Solutions International (Carbonate Research Team, now Geology and New Reservoir Types Team). We thank E.M. Selmo (Parma University) and M. Joachimski (University of Erlangen, Germany) for the stable carbon and oxygen analysis. G. Davis (VU Amsterdam, the Netherlands) is thanked for the strontium isotope analysis. A. Comelli and H. Nijs are kindly thanked for the careful preparation of the wafers and thin sections. L. Barchi is gratefully appreciated for his help in SEM analysis. We gratefully acknowledge A. Koopman for the constructive discussions during field work. We appreciate D. Smith (Energie Beheer Nederland, the Netherlands) for the careful reviewing of the manuscript. We are very grateful to reviewers J. Hendry and E. Ukar for their suggestions that allowed us to significantly improve the manuscript.

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## 1251 Table captions

- 1252 Table. 1. Stable carbon and oxygen isotopes, <sup>87</sup>Sr/<sup>86</sup>Sr ratios, and fluid inclusion
- microthermometry data (not pressure corrected) of host rocks and diagenetic phases in the
- Montagna dei Fiori Anticline. Stable carbon and oxygen isotopes values are expressed in
- 1255 % V-PDB and salinity values in eq. wt. % NaCl.

## Figure captions

Fig. 1. Aa) Simplified regional map (modified after Ghisetti and Vezzani, 1997) showing the tectonic outlines of the Central Apennines and the study area (rectangle). Bb) Schematic geological map of the Montagna dei Fiori Anticline showing the distribution of dolostones (modified after Storti et al., 2017a). Cc) Lithostratigraphical column of the successions exposed in Montagna dei Fiori (modified after Mattei, 1987; Di Francesco et al, 2010; Storti et al., 2018). Letter B stands for the Bugarone Formation. Lithologies are mentioned in the text. Note that the thickness of the not-outcropping formations (Triassic evaporites and the crystalline basement) is not to scale. Dd) Regional Geological geological transect across present day Central Apennines and the Adriatic Sea (modified after Fantoni and Franciosi, 2010) with vertical exaggeration of 2:1. The dashed rectangle indicates the Montagna dei Fiori Anticline region.

Fig. 2. Aa, Bb) Geological map of the central sector of the Montagna dei Fiori Anticline, and cross-section oriented parallel (a-b) to the hinge line representing the tectono-stratigraphic architecture of the faulted anticline (modified after Storti et al., 2017a). The stereonets (Schmidt equal area projection lower hemisphere) provide the attitude of the extensional faults. The locations of the corresponding field sites are indicated by numbers letters. c) At this location, well exposed N-S striking extensional fault zones offset the dolomitized Corniola Formation. The fault zone is characterized by near-horizontal stylolites localized in the footwall damage zone (4 fault data). d, e and f) These locations consist of mostly ~ E-W striking extensional fault zones. Particularly the boundary fault zones delimiting Calcare Massiccio Formation in the main horst block is evident (site d: 20 fault data; site e: 24 fault data; site f: 9 fault data). g and h) At these locations, dip-slip slickenlines support major extensional movements related to the Montagna dei Fiori Fault. Contractional deformation structures are preserved in the bed-perpendicular

stylolites, shear surfaces and tension gashes arranged as S-C arrays (site g: 21 fault data; site h: 14 fault data). Equal area projection, lower hemisphere.

Fig. 3. Aa) Field photograph showing the deformed Scaglia Formation in the hanging wall (HW) and brecciated, dolomitized Calcare Massiccio Formation in the footwall (FW) of the Montagna dei Fiori Fault. The red arrow indicates the sense of fault movement. Bb) A hand specimen from the deformed Scaglia formation showing the intensity of the abundant pressure solutions seems (TS), indicated by arrows, and their abutting relationship withcross-cutting calcite veins (CV2C2). Cc) A transmitted light photomicrograph of the dolomitized, brecciated Calcare Massiccio Formation. Note all the breccia fragments are composed of dolomite (D4 here).

Fig. 4. Field photographs (Corano Quarry) showing the field relations between dolostones (only D3 here), host limestones and the Montagna dei Fiori Fault: Aa) Panoramic view showing the spatial relationship between limestones and dolostones (orange) in the damage zone of the Montagna dei Fiori Fault (F). Note that the limestones and including dolostones of the Calcare Massiccio and Bugarone Formations on the footwall (FW) and marly limestones of the Scaglia Formation on the hangingwall (HW) are intensely deformed. Bb) Plan view of the dolomitized Calcare Massiccio limestone in the footwall damage zone: intersected by calcite veins (CV1C1), which are partially dolomitized, and affected by bed-bed-perpendicular stylolites (arrows). Cc) Distinct transition (dashed line) between dolomitized and undolomitized Calcare Massiccio limestone in the footwall damage zone.

Fig. 5. Field photograph (Aa) and a simplified sketch (Bb) in field site d showing of a dolomitic pocket (grey color) within the folded Calcare Massiccio (grey color) and their its relation with bed-bed-parallel stylolites within the Calcare Massiccio Formation (hammer is 40 cm long). Note C1 is the only calcite cement here.

Fig. 6. <u>Undolomitized and dolomitized Calcare Massiccio Formation in field site d: Aa)</u>
Transmitted light image showing a micritic peloid rimmed by the fibrous cements (FC) which are <u>followed overgrown</u> by the mosaic cements (MC). <u>Bb</u>) Transmitted light image showing mosaic cements (MC) in a peloidal limestone over-printed by high amplitude <u>bed-bed-parallel</u>

stylolites (dotted white line). Note the core of some of the peloids is partially cemented as well. Cc, Dd) Respectively, transmitted light and corresponding cathodoluminescence image of FC and MC cements. Ec) Transmitted light photomicrograph showing D1 crystals (arrows) rimming lining a fracture which is cemented by CV1C1. The fracture is in turn affected by a bed-bed-parallel stylolite. Ff) Cathodoluminescence image showing D1 scattered in the host rock and riming the fracture. Gg, Hh) Respectively, transmitted light and corresponding cathodoluminescence image showing part of a bed-bed-parallel stylolite (dotted white line) overprinting D1 and D2 crystals.

Fig. 7. Aa, Bb) Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image showing the zoned rhombs of D2 with the remnants of D1 preserved in their cloudy core sampled from dolomitized Calcare Massiccio Formation in field site d. The pore space is occluded by D4. Cc, Dd) D3 cementing angular breccia fragments of the Bugarone Formation in the damage zone of the Montagna dei Fiori Fault in the Corano Quarry site. Note the breccia is overprinted by a fault-fault-parallel bed-bed-perpendicular stylolite. Ec, Ff) Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image showing the euhedral to subhedral crystals of D3 entirely replacing the matrix and also present as cement developing a bright subzone and rim sampled from dolomitized Corniola Formation in Osso-caprino road. Gg, Hh) D3 with a saddle crystal outline (SD) postdating calcite cements (MC) and a zoned D2 crystal. The saddle morphology is outlined by a dotted white line.

Fig. Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image of dolomite types: Aa, Bb) The cross-cutting relationship between D3 and D4 sampled from dolomitized Corniola Formation in Osso-caprino road. Note the presence of D3 within the core of dolomite crystals overgrown by D4. Cc, Dd) Successions of dolomite types sampled from dolomitized Calcare Massiccio Formation in field site f. Note the green CL color of D4 crystals. Typically, luminescent dolomites are known to show yellow, orange to red colors (Machel et al., 1991). Green luminescence in carbonates including dolomite have been attributed by a number of researchers to the incorporation of three valent rare earth elements (REE) such as Dy3+ and U3+ as luminescence activators within their crystal lattice (Luczaj and Goldstein, 2000). Another possibility is the emplacement of Mn<sup>2+</sup>, with yellow

luminescence, in Ca<sup>2+</sup> sites with blue luminescence in the dolomite crystal lattice instead of preferential incorporation in the Mg<sup>2+</sup> site (Sommer, 1972b; Amieux, 1982; Walker et al., 1989; Habermann et al., 1999). Accordingly, non-stoichiometric, Ca-rich and poorly ordered dolomites may favor Mn<sup>+2</sup> incorporation into their Ca<sup>2+</sup> site. Ee, Ff) Vuggy porosity rimmed by D4 (green CL). Note the porosity is filled with fine dolomite rhombs including traces of D2 in their core and D4 overgrowths.

Fig. 9. Photomicrographs showing respectively, transmitted light and corresponding cathodoluminescence image of D4 and D5 in relation to stylolites and fracturing: Aa, Bb) D4, exploiting a bed-bed-parallel stylolite that crossed-cuts D1 and D2 sampled from dolomitized Calcare Massiccio Formation in field site d. Cc, Dd) A sub-horizontal fracture cemented by D4 sampled from dolomitized Corniola Formation in field site f. Ee, Ff) D5 microveins (arrows) intersecting all the predating dolomite types in the footwall brecciated zone of the Montagna dei Fiori Fault-, sampled from dolomitized Calcare Massiccio Formation in Castel Manfrino site.

Fig. 10. Field photographs showing the major calcite vein settings observed in Montagna dei Fiori: Aa) Cross-sectional view of bed normal Calcite vein 1 (CV1C1) abutting bed-bed-parallel stylolites in folded beds of the Calcare Massiccio Formation. Bb) Plan view of the Calcite vein 2 (CV2C2) intensely affecting the deformed Scaglia (Rossa) Formation. Cc, Dd) Cross-sectional view of the Scaglia Formation, intensely affected by pressure solution seams of tectonic origin crossed-over by populations of bed-perpendicular Calcite veins (CV3C3) in en echelon extensional arrays.

Fig. 11. Aa) Cathodoluminescence and transmitted light (in set) image showing blocky to elongated crystals of CV1C1 with zoned CL pattern in the Corano Quarry site. Bb) Transmitted light image showing intensely twinned CV1C1 crystals overprinted by euhedral to subhedral crystals of D3 in the Corano Quarry site. Photomicrographs of respectively, transmitted light and corresponding cathodoluminescence image: Cc, Dd) CV2C2 in the Scaglia Formation abutted by a bed-bed-perpendicular stylolite (indicated by white arrows and dashed line) in the Corano Quarry site. The crystals display blocky to fibrous morphologies, deformation twinning, and a similar orange luminescence pattern comparable withsimilar to the adjacent host rock. Ee, Ff)

CV3C3 cementing the breccia fragments in the damage zone of the Montagna dei Fiori Fault. The crystals are blocky and show faint deformation twinning. They are brown-orange with distinct darker luminescence sector zones. Gg, Hh) CV4C4 present as a cement within a polygonal pore space rimmed by dolomite, sampled from dolomitized Calcare Massiccio Formation in field site f. Note the blocky crystals, absence of deformation twinning and distinct concentric luminescence zonation pattern. CV4C4 is corroded and followed by a late telogenetic calcite.

Fig. 12. A, B) Overview of the  $\delta^{13}$ C and  $\delta^{18}$ O values of dolomites (Aa) host rocks from Montagna dei Fiori as well as calcite veins (Bb). The stable isotope value of Lower Jurassic marine limestones based on Veizer et al. (1999) is indicated by a dashed rectangle in subset B. The  $\delta^{18}$ O values of the marine dolomites are considered to be 3-4‰ V-PDB higher than those of marine limestones (Land, 1980; Major et al., 1992; Horita, 2014). Cc) Cross-plot of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and corresponding  $\delta^{18}$ O values of host rocks, dolomites and calcite veins compared with Lower Jurassic marine carbonates  ${}^{87}$ Sr/ ${}^{86}$ Sr (dashed rectangle) framework reported by McArthur et al. (2012).

Fig. 13. Overview of microthermometry analysis of primary inclusions in Montagna dei Fiori: Aa) Frequency distribution of the Tm<sub>ice</sub> (°C) in dolomite phasestypes. Bb) Frequency distribution of the Th (°C) in dolomite phasestypes. Cc) Salinity (eq. wt. % NaCl) versus Th (°C) of dolomite and calcite phases. Dd) Isotopic fractionation diagram from Land (1983) used to determine the isotopic composition (% V-SMOW) of parental fluids in equilibrium with dolomites in Montagna dei Fiori.

Fig. 14. A) Generalized paragenesis of diagenetic phases in relation to deformational stages and burial history of the Calcare Massiccio Formation in the Montagna dei Fiori Anticline. The deformational stages are from Storti et al. (2018), and the burial curve is based on Ronchi et al. (2003). The burial curve was made based on paleo-depth, paleo-temperatures, sedimentation rate and paleo-heat flow.

Fig. 15. Sketch showing the successive fault-related diagenetic phases, of most importantly dolomitization, recorded in the carbonate succession exposed at the core of the Montagna dei Fiori Anticline (not scaled). Different diagenetic phases are indicated with different colors. Aa) The first dolomitization event is pre-orogenic (syn-rift), triggered from the fluids channelized along Jurassic ~ E-W and ~ N-S striking extensional faults. This event occurred during burial compaction and development of bed-bed-parallel stylolites (BS). It is represented by scattered dolomite rhombs (D1) followed by calcite cementation (CVICI). The dolomitization continued with precipitation of larger crystals of D2. **Bb**) Second dolomitization event: syn-orogenic (early folding/ faulting) dolomitization from fluids that migrated from more internal regions of the thrust belt and were channelized along the basal detachment level into the fold core. This dolomitization event presents matrix replacive and cements displaying infrequent saddle outlines (SD) in pore spaces, within bed-bed-parallel veins and shear fractures. These dolostones postdate compaction but are affected by bed-bed-perpendicular stylolites (TS) generated by horizontal to sub-horizontal layer layer-parallel shortening related to the growth of the Montagna dei Fiori Anticline. Cc) Extensional collapse of the anticline and development of the Montagna dei Fiori Fault, followed by buttressing of the Scaglia against Calcare Massiccio and Corniola Formations during positive inversion induced by continuing underthrusting at depth. Precipitation of D5 in micro-veins and cements in breccia zones, followed by late stage calcite cementation in the Montagna dei Fiori Fault damage zone (CV2C2, CV3C3 and CV4C4).

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	Stable isotopes		Sr isotopes	Fluid inclusion microthermometry		
	$\delta^{13}$ C	$\delta^{18}O$	<sup>87</sup> Sr/ <sup>86</sup> Sr	Th (°C)	Salinity	n
Calcare Massiccio Fm.	+2.4 to +3.1	-1.6 to 0.0	0.70766	-	-	
Corniola Fm.	+2.0 to +2.5	-3.1 to -1.4	0.70725	-	-	
Scaglia Fm.	+1.0 to +3.1	-2.2 to -1.0	0.70784-0.70791	-	-	
D1	+2.5	-1.9	0.70789	≤ 40-50	3.5 to 11.3	<u>27</u>
CV1	+1.6 to +2.1	-4.7 to -2.7	0.70773	-	-	Ξ
D2	-	-	-	$ \leq 40-50 \text{ to} $	7.9 to 20.5	<u>37</u>
D3	+2.0 to +2.6	-2.8 to -1.9	0.70859-0.70964	70 to 73	9.2 to 16.9	9
D4	+2.4 to +2.5	-3.0 to -2.5	0.70790	79 to 105	12.8 to 18.6	<u>7</u>
CV2	+1.2 to +3.1	-1.7 to -1.6	0.70779 - 0.70787	-	-	
CV3	+0.5 to +2.4	-2.2 to 0.0	-	≤ 40 <b>-</b> 50	4.5 to 9.7	9
CV4	+3.8 to +4.9	-9.4 to -9.1	-	≤ 40-50	0.17 to 3.0	<u>19</u>

Table. 1

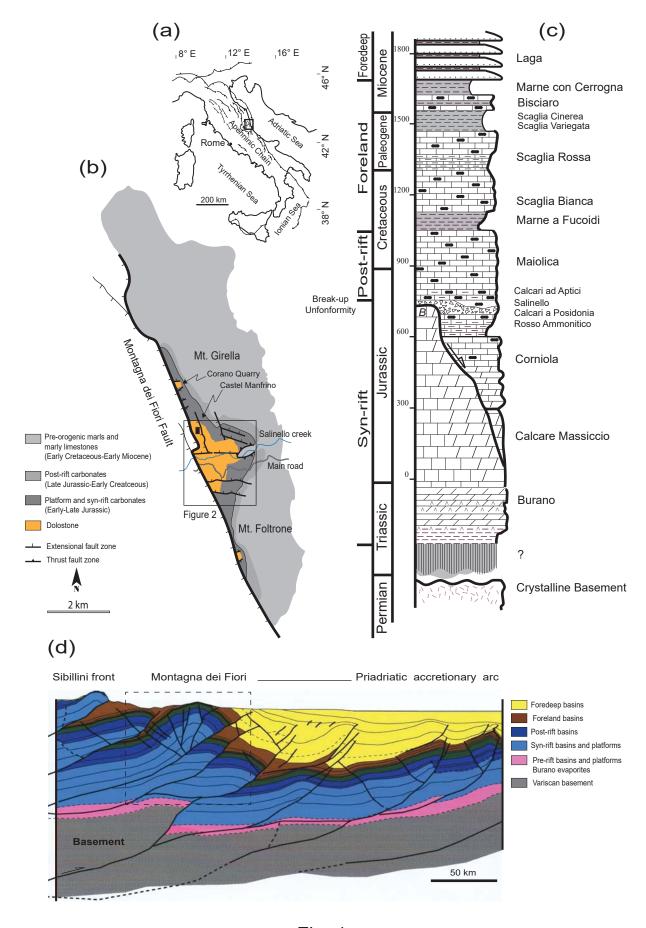


Fig. 1

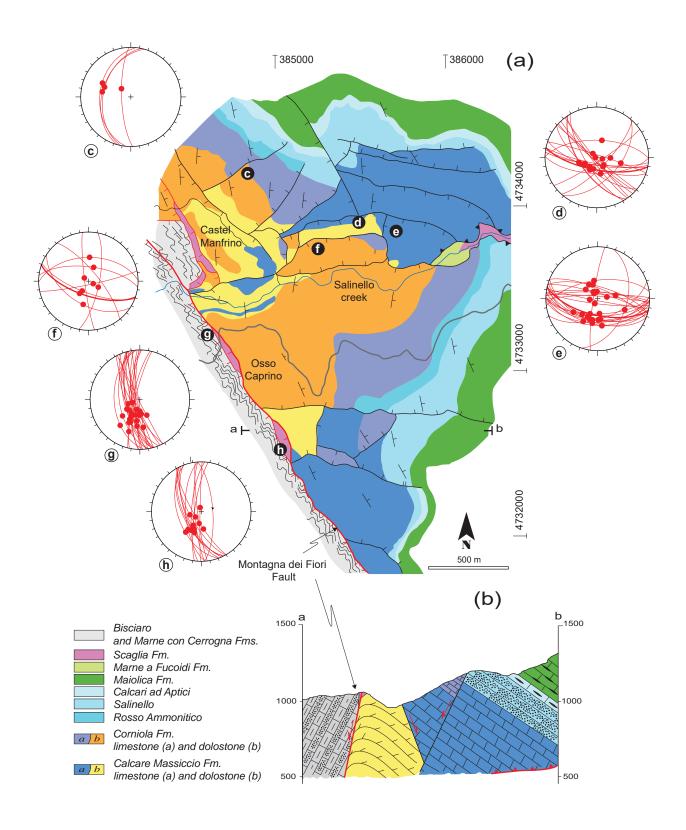


Fig. 2

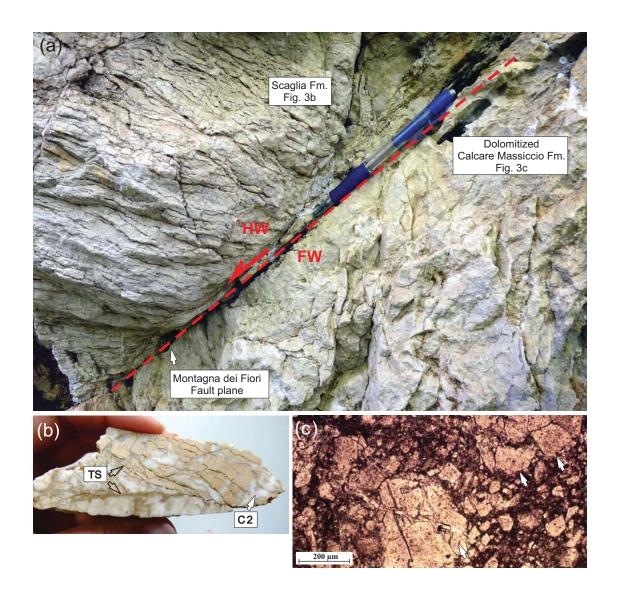


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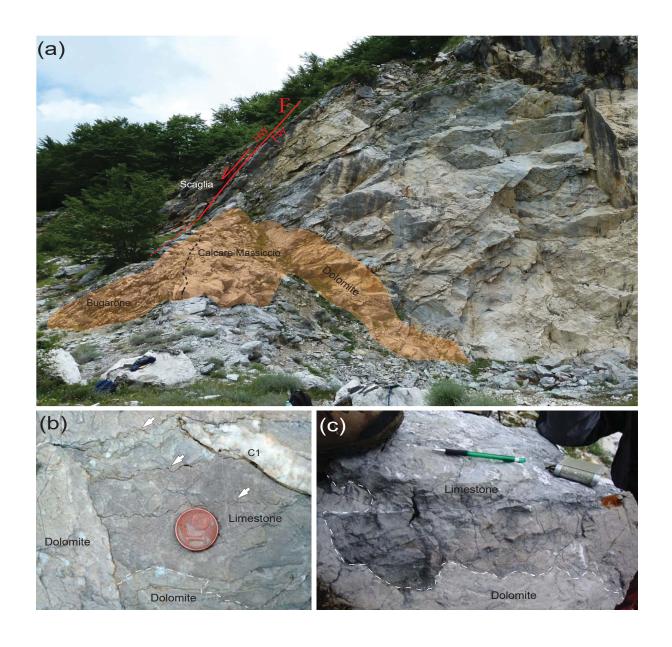


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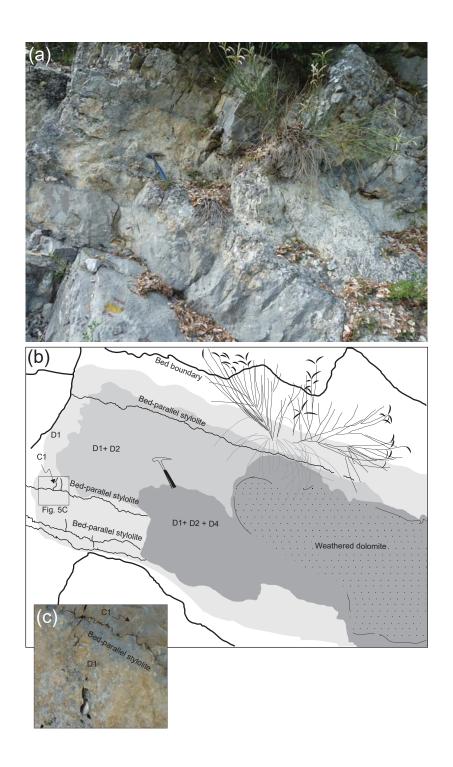


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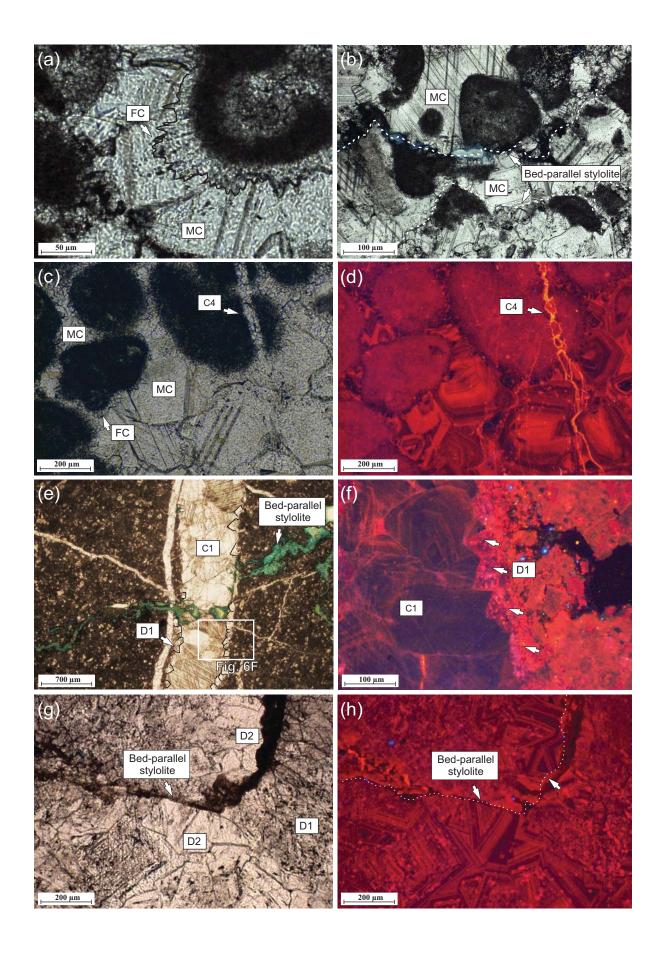


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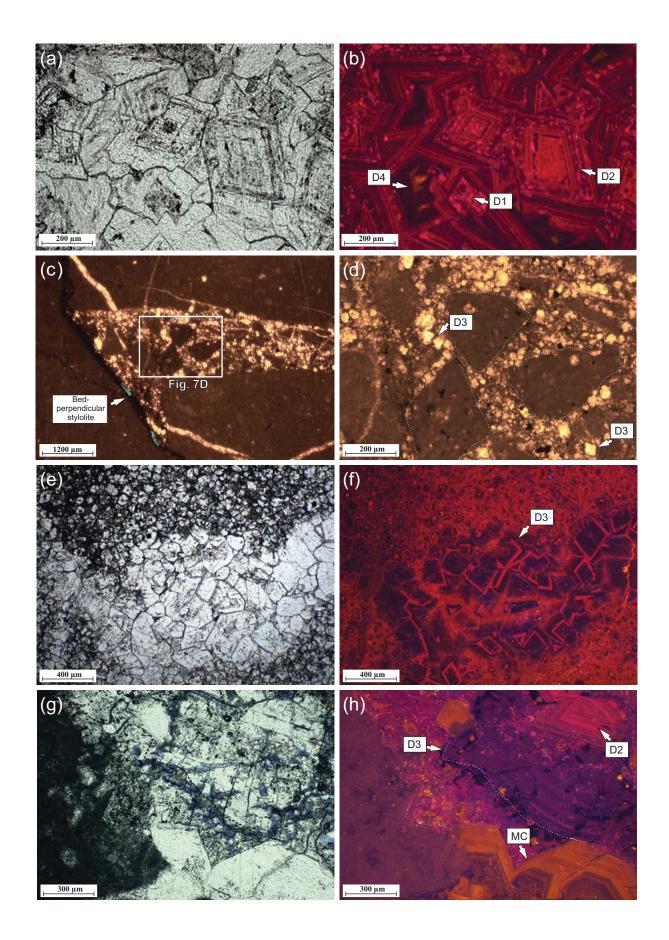


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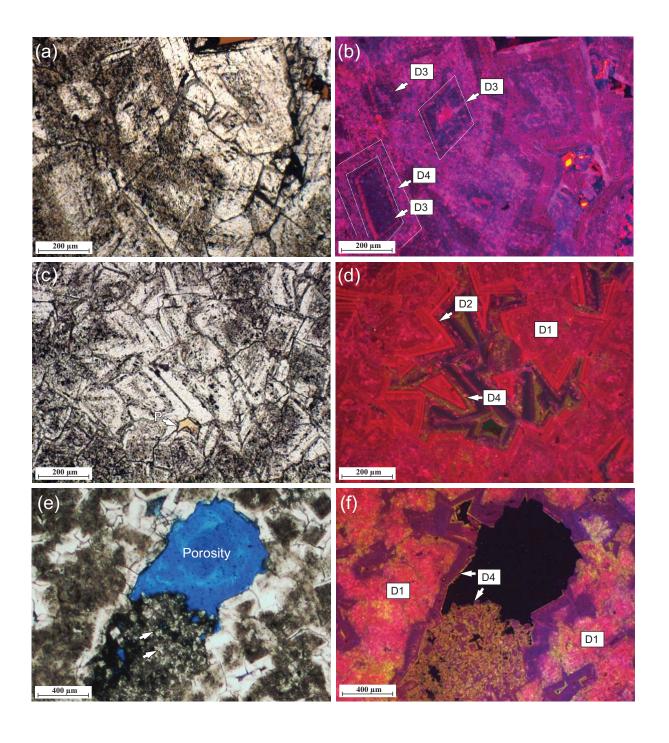


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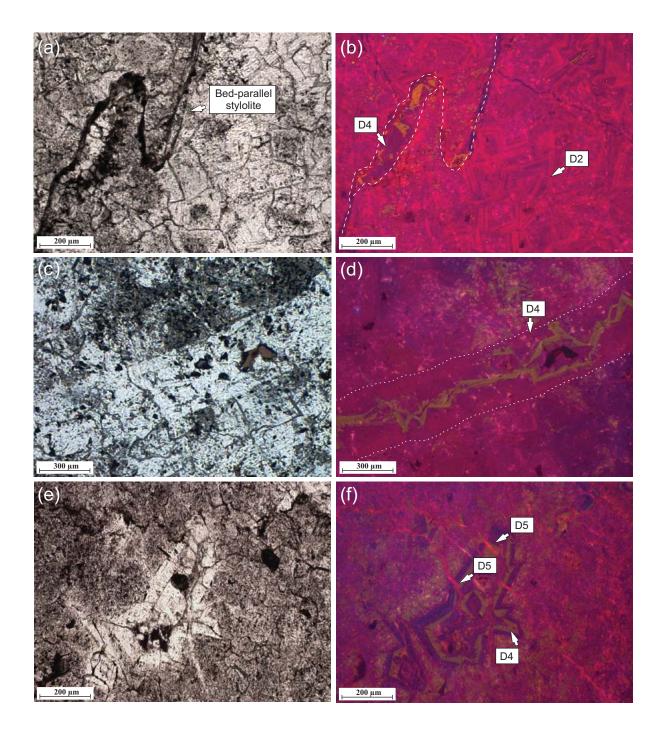


Fig. 9

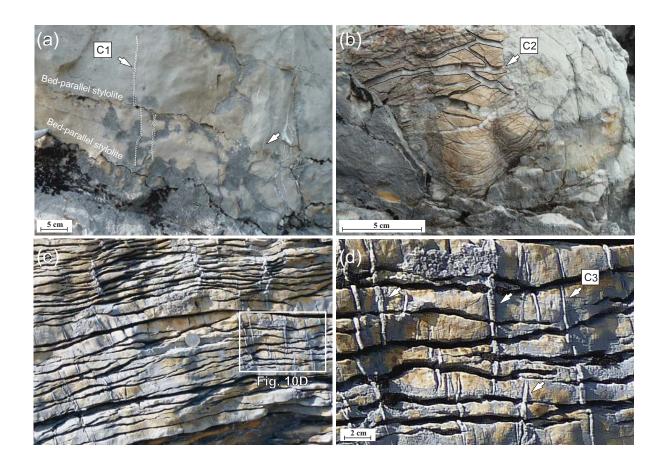


Fig. 10

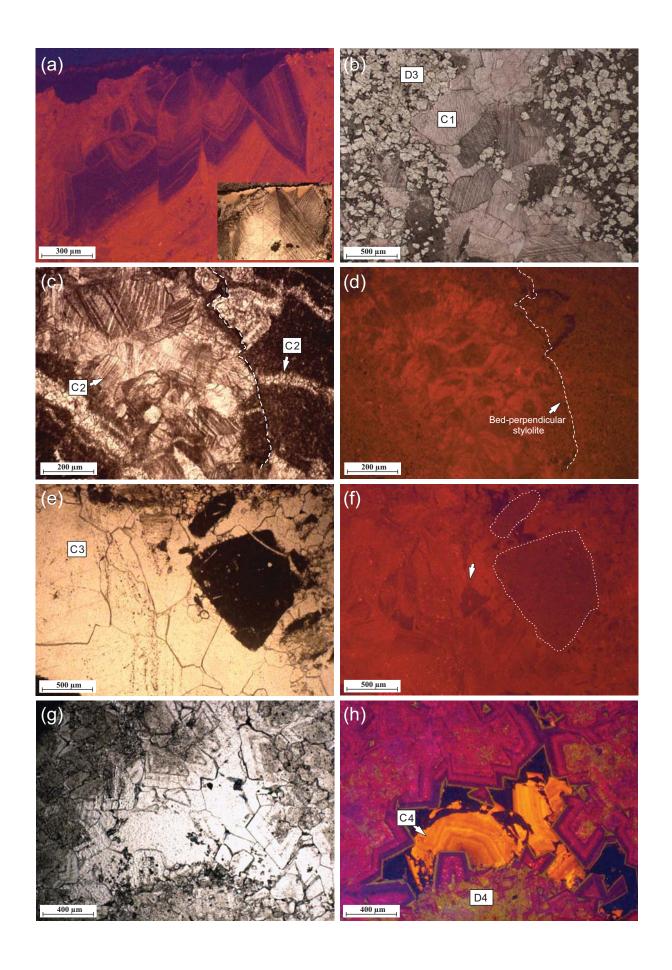


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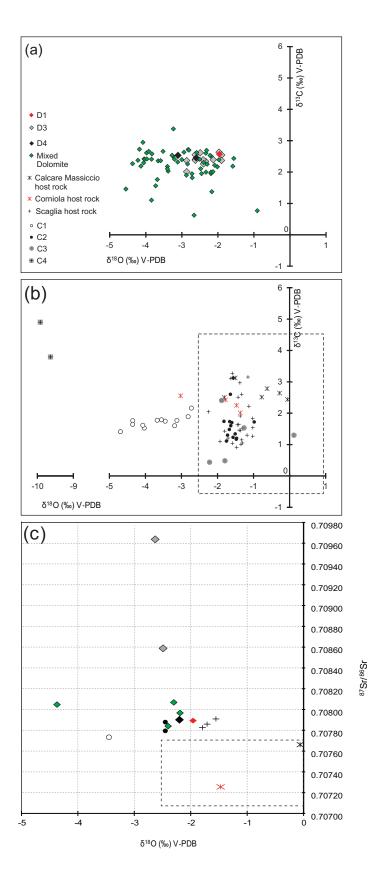


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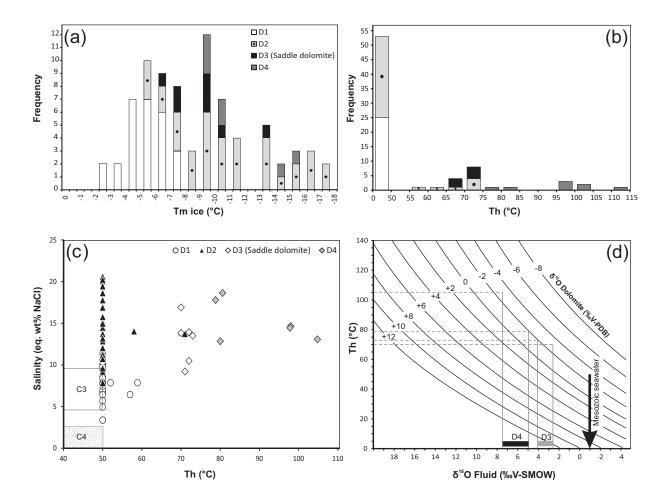


Fig. 13

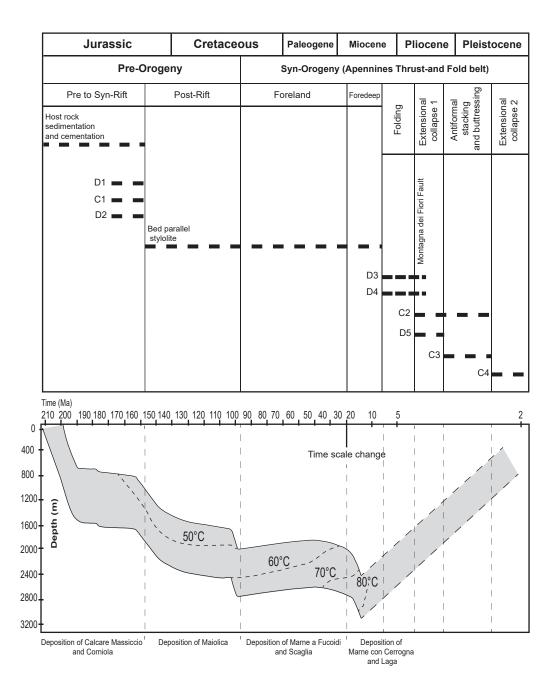


Fig. 14

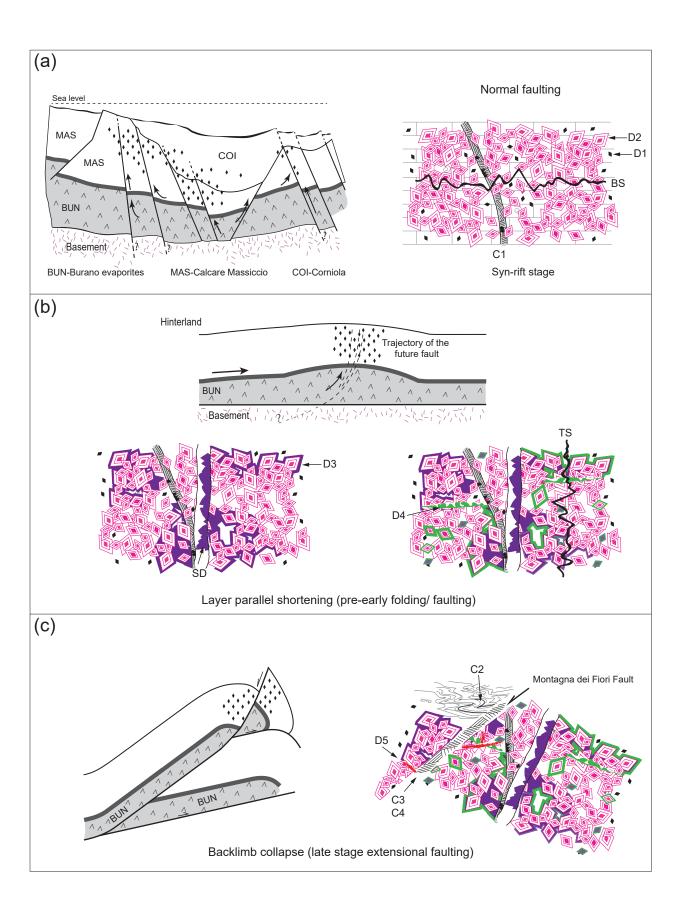


Fig. 15