Ms. Ref. No.: se-2020-81

Title: Structural control on fluid flow and shallow diagenesis: Insights from calcite cementation along deformation bands in porous sandstones

Journal: Solid Earth

Dear Editor,

We would like to submit our revised manuscript "Structural control on fluid flow and shallow diagenesis: Insights from calcite cementation along deformation bands in porous sandstones" by Leonardo Del Sole, Marco Antonellini, Roger Soliva, Gregory Ballas, Fabrizio Balsamo and Giulio Viola for consideration and eventual publication, as a research article, in the Special Issue in Solid Earth titled: "Faults, fractures, and fluid flow in the shallow crust".

The reviewers have done an invaluable job and put a lot of effort in improving our manuscript. We are grateful for their work.

We hope to have addressed all issues raised in the review.

All authors have approved the revised manuscript and agree with its submission to Solid Earth.

Looking forward for your feedback,

Kind regards,

Leonardo Del Sole, Marco Antonellini, Roger Soliva, Gregory Ballas, Fabrizio Balsamo and Giulio Viola

Response to Geoffrey Rawling (Reviewer #1) Comments

Ref: se-2020-81

Title: Structural control on fluid flow and shallow diagenesis: Insights from calcite cementation along deformation bands in porous sandstones

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Major comments		
Comment	Response author	
This is a well –written paper that summarizes incredibly detailed field observations of the relationship between deformation bands (DBs) and cementation. The figures are very well done. There are only a few comments on language and grammar.	We appreciate very much the comments of the reviewer and the help to improve our paper. Suggested edits have been implemented and they are tracked in the revised manuscript. Please, consider that the track-changes Word tool created some problems with line numbering and its jumping on the annotated manuscript. Line numbering of the "revised manuscript version with changes tracked" and "manuscript without tracked changes" may not coincide. The line numbering we use in this document (Author Response to Reviewer #1) refers to the revised manuscript with tracked change file.	
My main comments on this paper is that it needs restructuring for brevity and focus or change in emphasis. As it is the paper is a good discussion of two interesting field sites and a reasonable model for how the structures and cementation at these sites formed. However, as a paper in an international journal, I think it needs to be more broad.	Thank you for this comment. Following the comment of the reviewer, we moved some part of the field (former lines 180-185) and microstructural observations (former lines 315-324; 377-381; 389-392) to the Supplementary Material S1 We also moved the paragraph 7.1 to the Suppl. Mat. S1 as suggested by the Reviewer#2 and re-numbered the other paragraphs accordingly. We have created a Reference list in the Suppl. Mat. where we added the refs. that are cited only here and not in the main text.	
I think there needs to be some explicit statements in the introduction and conclusions about what new insights are provided by this study and how they are relevant to outstanding questions relating to the control of fluid flow by deformation bands. Are fundamental questions being answered? Are ideas proposed elsewhere given a more robust foundation? I think a focus on how the observations presented are relevant to, or support, proposed processes for cementation as discussed in section 7.3 would be good. But prior to all of this, there needs to be some discussion of what the outstanding questions are and why the reader should care about them.	-We think that in the introduction we explain the rationale of the paper (lines 74-104), what lacks in the existing literature (lines 133-154), and what is it the aim of this paper (lines 155-164). In the conclusions, and in particular in bullet points 2, 3, 6, 8 we sum up our insights. -We have reorganized and rephrased the Introduction and, hopefully, now it is more in line with what asked by the reviewer. -The discussions about how the observations support the mechanisms proposed in Section 7.2 are made in the Discussion section (7) and in particular in Sections 7.1 and 7.2. Our discussion is also supported by field, microstructural, and petrophysical data published in past works.	
I think these changes would give the paper much more focus and attract the readers interest immediately. The observations in the paper should be limited to those that are relevant to these questions and or are genuinely new. The maps and thin section figures are impressive and the	Ok, thanks for the comment. We have moved some field and microstructural observations, and Section 7.1 to the Supplementary Material S1 (see also response above in this file). We have reorganized and shortened other Sections as	

descriptions complete and accurate but I found	well (see tracked changes).
myself saying "What is new here? Is all this detail	W. 1
needed?" Many papers have contained such detailed	-We hope the paper is more to the point now.
observations of deformation bands and cements.	
What is essential to make the point?	
As explained below some of the conclusions are	Do you mean the discussion section?in the
vague. What data could help strengthen them?	Conclusions no recommendations were made. We
Recommendations are made that other workers	think you refer to comments on lines 733 and 740
should use the types of data presented here. How? A	(below in this file).
discussion of these two points would also strengthen	Please, refer to the responses below.
the paper in my opinion and give it a wider audience.	See also edit in the text (lines 1215-1217 and 1222-1224)
As an overall recommendation I suggest accept with	1221)
moderate to major revision. Perhaps resubmittal and	
another review is necessary if there are major	
changes.	
Specific Comments	
50. "Fluid flow mechanisms" I don't agree. The	Thanks for the comment.
next 20 plus lines describe numerous studies	Now the introduction has been rephrased. We
addressing the effects of dbs on fluid flow, so it	explicitly state what is known and which are the open
seems fairly well understood to me and heavily	questions this paper is trying to address (lines 92-
studied. And see the discussion and number of	164).
references listed in section 7.3. To justify the	
sentence in quotes I recommend stating clearly and	
explicitly exactly what is not currently understood	
and how the present study addresses and clarifies	
these problems.	Ol 1 1 1 1 1 1 20()
Figures 1 and 2. Clarify what is meant by DB	Ok, we have done that (lines 291 and 306). The azimuth data refers to the DBs strike and the ±
azimuth. Is this strike or dip direction? The azimuths range from +- 90 relative to what geographic	90° is relative to the north direction.
direction?	30 is relative to the north direction.
171. I would find it much clearer if you would use	We have added the mean orientations as suggested by
the average strike or dip direction to refer to the DBs	the reviewer (lines 354-355). We did the same for
rather than EESSWWNNWWE. Sorry, that's what it	Bollène (see response to comment just below).
looks like on the page! You have calculated the mean	However, we would like to keep the cardinal
orientations of the distributions in Figs 1d and 2d, so	directions.
you could use them in the text.	
244. Same comment as line 171. Reference to Figure	We have added the mean orientations as suggested by
11b here should probably be 6b?	the reviewer (lines 445-447). See also the response
	just above. The reviewer is right about the fig.
	reference. We changed it accordingly.
305. The microstructural observations that follow	Thank you for this comment.
here are exhaustive. To my mind all of these features	-Following the comment of the reviewer, we moved
have been described elsewhere in studies of DBs.	some part of the field (former lines 180-185) and
What is new here? What is relevant and essential to	microstructural observations (former lines 315-324;
the main points and arguments of the paper? If it is	377-381; 389-392) to the Supplementary Material S1.
not relevant then it can go in a supplement and or	W. 1
briefly summarized. It seems to me that many of the	-We have added a table in the Supplementary
microstructural observations could be replaced by	Material S3 where we summarize the petrophysical
permeability data and other hydrogeologic data by	data for two field sites along with their references We
these authors (from their other papers?) or	reference to it in the text (lines 867, 921, 940). We
summarized from the literature. Such data are much	have preferred to not add these data in the main text,
more relevant to the hydrogeological model	because those data have been already published, and
proposed in Sections 7.3 and 7.4.	so that the paper does not become longer than it already is.
591. Do you mean to say"decrease of hydraulic	Ok corrected (lines 944-945).
1 371. Do you mean to say decrease of hydraulic	OK COLLECTED (THICS 744-743).

and diviting for instances and a flavored site.	T
conductivity dominates over the flow velocity increase caused by porosity reduction"	
624. I don't think hypotheses is the right word here.	We thank the reviewer for this comment.
The field observations tend to confirm the theoretical	We rephrased the text (lines 984-986), however we
flow simulations and experiments etc. I think this	would like to stress the following points:
should be emphasized more in the paper overall and mentioned in the introduction. The three mechanisms	-As far as we know, the flow "slow down" has never been invoked as a possible cause for cement
described in this section have been invoked in other	precipitation in DBs.
field studies and/or examined in the laboratory, and	-Regarding the role of "reactive microfractures and
field observations in this study suggests that they are	fine-grained comminution products" on cement
all relevant and or viable as possible explanations for the cement distributions.	precipitation, we refer to several papers that propose or mention this model as relevant to the precipitation
	of cements around DBs (lines 952-964).
	-We do not say that we are hypothesizing a cement
	precipitation induced by solute-sieving. We suggest the applicability of this model to cement precipitation
	associated with DBs, whereas this model was
	proposed via experiment with an analog for fault
	gauge (Whitworth et al., 1999).
	Why should this be emphasized in the introduction?
	We think that this is a sort of conclusive statement. In
	the introduction we state our aims (lines 155-164)
634. it would be good to add a line or two	and the 3 mechanisms are widely discussed after. We have added a few lines in the methods where the
somewhere about basic interpretation of	controlling factors of CL characteristics (visual
cathodoluminescence colors for those who aren't	colors and intensity of emission) are summarized
familiar. 676. Add a reference to the measurements of DB	(lines 338-342). We have added the references as suggested by the
hydraulic properties, or better, add the data to the	reviewer (line 1098).
paper as suggested above.	-We have added a table in the Supplementary
	Material S3 where we summarize the petrophysical data for two field sites along with their references.
	We have preferred to not add these data in the main
	text, because those data have been already published,
	and so that the paper does not become longer than it
700. Can you expand on this? Are there any	already is. No, unfortunately we do not have enough
microstructural characteristics of the cement that	microstructural evidences to assess the "net" growth
would allow interpretation of its growth direction?	direction of the cement.
685 – 715. In general this discussion about the Bollene site seems reasonable but not definitive and	-Ok, we rephrased the discussion about Bollène in
rather underwhelming. E.g., Statements like "most	Section 7.3 (lines 1106-1181) to make the discussion more solid. However, we would like to point out that
likely" and "probably". Can you rework it to say	these are discussions and, here, we make (working)
what is known about the flow patterns and diagenesis	hypothesis and propose the most robust (from our
definitively versus not. What about the three mechanisms described in section 7.3. Which do you	point of view) mechanisms/model considering all the data available (our and from literature). "In geology
think are applicable here (and at the Italy site), or	there are rarely any absolute models" (cit. Charrach,
would that just be total speculation? What additional	2020 – JSG).
info would be necessary to better understand the	We discuss these machanisms as also design
flow patterns and how they are controlled by the DBs and the resulting cement diagenesis. Ie, what could	-We discuss these mechanisms, as also their applicability to both field sites, in Section 7.2 (former
be a future research direction here?	Sect. 7.3) (lines 937-980), and Section 7.3 (former
	Sect. 7.4) (lines 1031-1032; 1083-1085; 1094-1095;
	1164-1166). Certainly, in Bollène, the second and third mechanisms are not applicable since there is no

	spatial overlap (or it is rare) between DBs and cement. We state this also in the conclusions (bullet point 4).
	-About the future research direction that is a good point. We answered to that in the conclusions (bullet point 7). Flow simulations and cement precipitation modeling could be used to reconstruct paleo-fluid flow pathways; further explore micro-scale fluid flow and diagenetic mechanisms that drove preferential cement precipitation along DBs; and constrain the reaction kinetics. These tools will also be helpful to validate the mechanisms involved in cement precipitation along DBs proposed in this work.
726. I would say enhance rather than increase porosity reduction etc	Ok suggestion taken and implemented (line 1204).
733. How would you include this information in a fault seal analysis. Give an exampleit seems some sort of upscaling would need to be involved. E,g., Spatial density or proportion of cemented rock per unit area or length of fault? Something else?	Ok, we expanded on this point, and we added some references to studies in which DBs are incorporated into reservoir models and flow simulations (lines 1215-1218).
740. Again, give an example. If someone is working with seismic data to do a fault seal analysis or reservoir engineering study how does the present study help them predict where the reservoir compartments are arranged etc. Elaborate.	Ok, we have elaborated about how this study could be helpful during reservoir characterization (lines 1222-1224). However, we would like to stress the following points: It could be difficult with standard seismic to observe the network of DBs and the associated cement nodules because in most of cases these features are below seismic resolution. That is why a field (analog) study, such as that presented in this work, is necessary during reservoir characterization since it allows to: (i) define the geometry and orientation
	distribution of DBs, (ii) understand which sets of DBs are associated with cement; (iii) evaluate the cement distribution and how it is arranged with respect to the DBs; (iv) evaluate how the compartments are arranged. Such information should be then integrated with other data, such as the density and clustering of DBs, the volume of cement along DBs, the petrophysical properties. This information can be then incorporated in reservoir (flow) models employed for hydrocarbon production planning. Anyway, all the attributes listed above are somewhat implicit in the reservoir characterization workflow, so we would like to not repeat them in the text.
	-Through the text, we point out that DBs and related cements (SDH) are subseismic features (lines 27,93 1209,1224, 1274), and that the study of an outcrop analog can improve the characterization of these features and in general be useful for the characterization of a faulted sandstone reservoir (lines 1217-1224).
756. As noted above, I would say that the field observations support three mechanisms that have	The term "proposed" was substituted with "discussed" (Line 1250).

been proposed previously as relevant to the precipitation of cements around DBs. -However, as stated above in this file to the comment at line 624, we would like to stress the following points: -As far as we know, the flow "slow down" has never been invoked as a possible cause for cement precipitation in DBs. -Regarding the role of "reactive microfractures and fine-grained comminution products" on cement precipitation, we refer to several papers that propose or mention this model as relevant to the precipitation of cements around DBs (lines 952-964). -We do not say that we are hypothesizing a cement precipitation induced by solute-sieving. We suggest the applicability of this model to cement precipitation associated with DBs, whereas this model was proposed via experiment with an analog for fault gauge (Whitworth et al., 1999). 763. Comment at line 685 in the text, apparently I -As stated above in this file to the comment at lines missed this discussion in the text. Perhaps that 685-715, we discuss these mechanisms, as also their section can be rewritten to more clearly state this. applicability to both field sites, in Section 7.2 (former But then there should be some discussion as to why Sect. 7.3) (lines 937-980), and Section 7.3 (former the difference between the applicable mechanisms at Sect. 7.4) (lines 1031-1032; 1083-1085; 1094-1095; the two sites. Something about the host rocks, db 1164-1166). Certainly, in Bollène, the second and microstructures, regional geology, regional flow third mechanisms are not applicable since there is no patterns during cementation etc spatial overlap (or it is rare) between DBs and cement. We state this also in the conclusions (bullet point 4). -The second and third mechanisms are not applicable to the Bollène site simply because the cement do not spatially overlap the DBs (e.g. lines 969-971). -The difference in the cementation pattern between Loiano and Bollène could be related to several factors, such as the regional vs. local flow pattern and the hydrological conditions during cementation, to the fluid conditions and the rate of the process. To

> discuss the reason why this difference exists would be too speculative since, in this study, we did not

cover all possible controlling aspects.

Response to James Evans (Reviewer #2) Comments

Ref: se-2020-81

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Journal: Solid Earth

Major comments	
Comment	Response author
I fill in the specific review criteria below, after some detailed comments on the text. Overall this is a good contribution, with detailed observations of structures and cementation patterns. I suggest a slight recasting of the paper to the topic of the dbs and cementation, dropping a bit of the tectonic implications. I also have a few editorial changes that I will provide via written edits on the manuscript – sorry to go old school.	We appreciate very much the constructive comments and excellent suggestions of the reviewer that we think deeply improved the first version of our manuscript. Suggested edits have been implemented and they are tracked in the revised manuscript. Please, consider that the track-changes Word tool created some problems with line numbering and its jumping on the annotated manuscript. Line numbering of the "revised manuscript version with changes tracked" and "manuscript without tracked changes" may not coincide. The line numbering we use in this document (Author Response to Reviewer #2) refer to the revised manuscript with tracked change file. We have moved some of the main text to the Suppl. Mat. without altering the main message of the paper. This is because both reviewers asked for keeping the focus on the paper on the DBs and their control on fluid flow and diagenesis. See also responses below. Also the introduction has been rephrased, and now it
	is more focused on DBs and cementation.
Specific Comments	
Lines 15- 20 can be edited a bit; edits attached.	Ok suggestion taken and implemented (lines 15-19). The term "string mapping" has been kept (line 19). The field map in Loiano has been produced by building a network of strings on the outcrop surface, that was used as a reference frame for detailed mapping. We do not intend "scanline mapping".
Line 33 – Wilson and Goodwin (2006) discuss these sorts of processes, as does Parnell et al, (2004 – j sed research);	The reviewer is right. These papers address important issues regarding the hydraulic behavior of DBs and their role on diagenesis. They have been referenced later in the Introduction, when we focus on DBs, as also in the discussions. (Wilson et al. 2006: lines 90, 146, 930, 1163; Parnell et al., 2004: lines 135, 146). When you mention "Wilson and Goodwin, 2006", maybe you mean "Wilson et al., 2006". Am I right?
Lines 53 -55; Min et al., 2001, and Shipton et al., 2002 provide data on db fault permeabilities; Petrie et al, 2013 show alteration / mineralization/ cementation patterns in db faults	Shipton et al. (2002) and Petrie et al., (2014) were added as suggested by the reviewer (lines 98-99). We have a reference to Main et al. at line 143.
Lines 50-85 – could this be trimmed somewhat?	We have rephrased the introduction.

Line 170-175, Figures 3 and 4. It is a statistically stronger way to examine the data as vector data; decimating into histograms is ok, but better to determine mean vector of the poles to the dbs, with dispersion statistics.	Do you mean Figs. 1 and 2? Am I right? We thank the reviewer for his comment. We replaced the frequency histogram of DBs azimuth with azimuth frequency rose diagrams (Figs 1d and 2d). This representation is similar to the one shown in Fig.1 in Del Sole et al. (2020 – MPG). Here, the stereoplot reports the best-fit gaussian curves for each DB's population found by the software (Daisy3; Salvini, 2004) and calculated from the corresponding frequency distribution (histogram data). The values reported on the right side of the azimuth frequency rose diagrams (Figs. 1d and 2d) are the mean orientation (strike; N±90°) and the standard deviation (±sd) for each population.
186-187 – rephrase – cementation is a process, and you are describing here the distribution of zones,	Ok corrected (lines 369-370).
pods, etc., that reflect that cementation. Through the text, thee are sentences with phrases such as "more tabular", etc., but we don't always get what the more is relative to.	Ok, these sentences have been corrected. We hope the sentences are clear now. (lines 392-393 and Suppl. Mat. S1).
307-308. Figure 9 doesn't really report porosity data; the data are in Del Sole and Antonellini, 2019; and the porosity data are derived from microscopy, so it's a bit of an indirect measure.	Ok corrected (line 517). The reviewer is right, these data are in Del Sole and Antonellini (2019). We think, however, that this has already been specified in the caption of Fig.9 (line 583).
309 – oversized relative to what?	The term "oversize pores" indicates those (secondary) pores that are larger than the average pore size of primary porosity and also a larger diameter than that of adjacent grains (e.g. Schmidt et al., 1977 Bulletin of Canadian Petroleum Geology, 25(2), 271-290). E.g. oversized pores are due to dissolution of detrital grains (e.g. carbonate clast, feldspar).
428-431, Figure 12. On figures like this, usually the negative numbers decrease upwards along the y axisand I prefer the axes to be one the left and bottom like a normal graph - the origin will not be 0, 0 but that doesn't matter for delta values. And the text here can be tighted a bit, I think;	Thanks for this comment. We would like to keep the diagram of Fig. 12 as it is, following some of the most commonly used $\delta^{18}\text{O-}\delta^{13}\text{C}$ isotope diagram in literature (referenced in the manuscript: e.g. Hudson, 1977; Moore, 1989; Nelson and Smith, 1996; Pizzati et al., 2020). Regarding the diagram axis issue, we would like to keep them like this, since we are showing only the negative field/portion (-x, -y) of the diagram (references as above). The text in the legend was tightened as suggested by the reviewer.
Cement from the nodules of the Loiano samples have $\delta 13$ C values between -7.68 and -1.47 ‰ (V-PDB) and $\delta 18$ O values between -4.42 and -1.35 ‰ (V430 PDB) (Figure 12). The DBs-related nodules is characterized by isotope compositions between -5.41 and -1.47 ‰ (V-PDB) for $\delta 13$ C, and between -4.42 and -1.40 ‰ for $\delta 18$ O (V-PDB). The bedding-parallel nodules has isotope compositions between -7.68 and -5.94 ‰ (VPDB) for $\delta 13$ C, and between -2.09 and -1.35 ‰ (V-PDB) for $\delta 18$ O.	We have revisited and shortened the text according to the reviewer suggestions typed here in the comment (lines 663-667).
460-490 – I am not sure how much of this is needed. The focus of this paper is on the outcrop and microstructural observations and interpretations and	We did the edits suggested and moved the paragraph 7.1, along with the references therein, to the Suppl. Mat. S1 and re-numbered the other paragraphs in the

the regional tectonics do not seem to be the main	main text accordingly. We created a Reference list in
point	the Suppl. Mat. where we added the refs. that are
1	cited only here and not in the main text.
505 not clear what the meaning of the orange is here	Ok corrected. We hope it is clear now. (lines 788-
- do you mean orange cements? And orange color is	789).
redundant	,
510-515 – I am sorry – I got a little lost here with the	Thanks for this comment. Ok corrected. Now, the
terms like "likely preserved"; "suggest that cement	sentences you mention should be more solid (lines
dissolution" "suggesting that cementation	788-794).
postdate" There so many solid observations in this	ŕ
paper that I think you can state your interpreations	
more forcefully.	
519 and elsewhere – evidence is never plural	Ok corrected along all the manuscript (lines 374, 545,
evidences is not a word	706, 801, 842, 1030)
520. 800-1000 m	Ok suggestion taken and implemented (line 802)
530-535 - are these bed parallel nodules basically	If I understand well the reviewer point, yes. We think
related to diagenesis of some sort	that bedding-parallel nodules are related to cement
	precipitation from flow focused along bedding, and
	in particular they are related to flow within sand
	levels (lines 810-837). In this Section (now Sect. 7.1)
	we discuss their occurrence, morphology, and a
	possible relationship with sandstone grain size. In
	Sect. 7.3 we also discuss the formation of bedding-
	parallel nodules considering the data available from
540.500 TIL:	this study and from literature.
540-560 This is not very clearly written – please see	We implemented the suggested edits and rephrased
written edits on the text	the paragraph. We hope it is clear now. (lines 840-
570 715	857).
570-715 – need to break this into paragraphs;	The lines of this comment (570-715) refer to both
Shorten, and see edits. I suggest separating the facts,	Section 7.3 (now 7.2) and 7.4 (now 7.3). Considering the comments here at the left and the written edits on
and observations, and then discuss your interpretations; read through this section and	
eliminate all the clauses at the beginning of many of	the manuscript, we believe, instead, that the reviewer refers only to Section 7.4 (now 7.3).
the sentences; In this section, look for all the 'coulds'	refers only to section 7.4 (now 7.3).
in this section. My apologies – I think I am having	We accepted the edits suggested by the reviewer. We
COVID brain issues, but this section is pretty hard to	have broken this Section 7.3 in paragraphs,
read. I think it takes away from your work by not	reorganized and shortened the text. When possible
being a bit shorter, clearer, and organized.	the "coulds" were replaced trying to make the
comig a cit shorter, crearer, and organized.	discussion in this section more solid.
593 594 – Precipitation occurs when the reaction is	-We thank the reviewer for the comment, this is an
out of equilibrium. "slowing" flow could push fluids	interesting point.
to be closer to equilibrium with the host rocks, thus,	We added a possible explanation in text (lines 947-
less likely to precipitate	949). Below, we will discuss more about the reviewer
	point.
	-At lower flow velocities the precipitation reaction
	has more time to proceed before the fluid leaves the
	system. We added 2 references where the effect of
	flow hydrodynamics on kinetics of precipitation was
	studied.
	-We think that if fluids are enriched in constituents
	needed for calcite precipitation (Ca and bicarbonate),
	then the "equilibrium" you mention e.g. could just be
	reached through cement precipitation. We propose
	that a "slow down" of the flow could kinetically
	favor cement precipitation.
	-As argued by the reviewer, at low flow velocity, the

residence time could be long enough allowing the fluid to equilibrate with the host rock. In this case, the equilibrium between host rock and the percolating solution could be reached not far from the upstream side of the DB. This could support the asymmetric distribution of cement with respect to the DB, as observed in the field.

- -At higher flow velocity, there would be a higher and continuous supply of reagents, but the reaction would be disfavored. In fact, for most rock-forming minerals at ambient temperatures, chemical reactions at the solid surface are slow and thus rate limiting. If flow is fast, the reaction might not have time to occur. This is true if the fluid did not reach carbonate saturation (low saturation index).
- -In our case, it is also important to keep in mind, that the growth substrate is made mostly by quartz and feldspar, hence the mineralogy has a limited control over the process of mineral nucleation and growth [e.g. Pin and Singer, 2005, Geochimica et Cosmochimica Acta, 69(18), 4495–4504]. The precipitation of calcite over a silica substrate would need more time to occur when compared to a carbonate substratum (Stockman et al., 2014, Geochimica et Cosmochimica Acta, 135, 231–250).
- -Another simple reason that supports our hypothesis is that nodules preferably occur along DBs where the porosity and permeability are lower than the surroundings and where the net flow is slower. Accordingly, the host rock is higher in porosity and permeability; here, the net flow is faster and the cement is absent or poor. This possibliy mean that the flow velocity has a role in the precipitation process, or at least to its initiation (See refs in line 949).

What aspect(s) of this work / interpretation(s) address, or apply to, db faults-fluid flow questions in general?

- -Here, we bring some field evidence that show how DBs affect the flow pattern and control the distribution of diagenetic heterogeneities, i.e. nodules.
- -We also argue about different potential mechanisms that drove cement precipitation within and around the DBs (Section 7.2). Most of the past field-based works were focused on the occurrence and the distribution of the cement, whereas cementation mechanisms received less attention.
- -The mechanisms commonly employed to explain cementation within DBs (e.g. lines 141-147) are appliable and limited to specific conditions and need that the DB behaved as "conduits" (147-150). However, a lot of works demonstrate that commonly DBs reduce permeability and baffle the flow (lines 99-104).
- -We discuss some mechanisms that are pertinent also in late-stage diagenesis (post-DBs formation) and in saturated conditions (phreatic environment), and that

	are of more general validity in low-permeability DBs Conclusions (bullet point 6).
Suggest moderate revisions.	

Structural control on fluid flow and shallow diagenesis: Insights from calcite cementation along deformation bands in porous sandstones

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Abstract. Porous sandstones are important reservoirs for geofluids. Interaction therein between deformation and cementation during diagenesis is critical since both processes can strongly reduce rock porosity and permeability, deteriorating reservoir quality. Deformation bands (DBs) and structural-related diagenetic bodies, here named Structural and Diagenetic Heterogeneities (SDH), affect fluid flow at a range of scales and potentially lead to reservoir compartmentalization, influencing flow buffering and sealing during production of geofluids. We present two field-based studies from Loiano (Northern Apennines, Italy) and Bollène (Provence, France) that elucidate the structural control exerted by DBs on fluid flow and diagenesis recorded by calcite nodules associated with the bands. We relied on careful in situ observations through geo-photography, string mapping, and UAV aerial photography, integrated with optical, scanning electron and cathodoluminescence microscopy, and stable isotope (δ^{13} C and δ^{18} O) analysis of nodules cement. In both case studies, one or more sets of DBs precede and control selective cement precipitation. Cement texture and cathodoluminescence patterns, and their invariably negative δ^{13} C and δ^{18} O value ranges, suggest a meteoric environment for nodule formation. In Loiano, DBs acted as low-permeability barriers to fluid flow and promoted selective cement precipitation. In Bollène, clusters of DBs restricted fluid flow and focused diagenesis in parallel-to-band compartments. Our work shows that DBs control flow pattern within a porous sandstone reservoir and this, in turn affects how diagenetic heterogeneities are distributed within the porous rocks. This information is invaluable to assess the uncertainties in reservoir petrophysical properties especially where SDH are below seismic resolution. The localization of cement along DBs further enhance the flow buffering potential of these structural features.

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1 Introduction

Porous rocks, such as sandstones and carbonates, are important reservoirs for geofluids. Structural and diagenetic processes commonly affect the petrophysical properties and reservoir quality in these rocks. The importance of the interaction between deformation and deformational structures, fluid flow, and diagenetic processes has been emphasized only during the last two decades (e.g. see the recently coined term "structural diagenesis", Laubach et al., 2010; Mozley and Goodwin, 1995; Eichhubl et al., 2009; Balsamo et al., 2012; Philit et al., 2015; Antonellini et al., 2017, 2020; Del Sole et al., 2020). If deformation influences diagenesis and vice-versa, a feedback can eventually develop between these two processes. Early diagenesis influences the mechanical properties of rocks (Antonellini et al., 2020), and, in turn, their mechanical stratigraphy (Laubach et al., 2009; La Bruna et al., 2020). Structural and diagenetic heterogeneities (referred to as SDH from now on) can determine the texture as well as the petrophysical and mechanical properties of the rock volume hosting them (Antonellini and Aydin, 1994; Aydin, 2000; Faulkner et al., 2010; Bense et al., 2013; Pei et al., 2015; Del Sole et al., 2020). Cement precipitation in granular porous siliciclastic rocks leads to porosity loss and reduction in permeability (Tenthorey et al., 1998; Morad et al., 2010) and, in turn, overall reservoir quality deterioration (Ehrenberg, 1990; Morad et al., 2010). Carbonate cement is commonly concentrated within a few, specific horizons or nodules with various shapes and arrangements (Kantorowicz et al., 1987; Bjørkum and Walderhaug, 1990; Mozley and Davis, 1996) making porosity and permeability prediction more complex (Davis et al., 2006; Morad et al., 2010). Furthermore, cement increases the mechanical strength of the host rock (Dvorkin et al., 1991; Bernabé et al., 1992, Boutt et al., 2014) influencing fault-zone architecture and potential fault reactivation (Dewhurst and Jones, 2003; Flodin et al., 2003; Wilson et al., 2006; Williams et al., 2017; Philit et al., 2019; Pizzati et al., 2019).

Granular or porous sediments and sedimentary rocks commonly contain sub-seismic resolution strain localization features referred to as deformation bands, (Aydin, 1978; DBs from now on). The effect of DBs on fluid flow can significantly vary, Their overall different behavior depends on several factors, such as their permeability contrast relative to the host rock, their thickness, density, distribution, orientation, segmentation, and connectivity (Antonellini and Aydin, 1994; Gibson, 1998; Manzocchi et al., 1998; Sternlof et al., 2004; Shipton et al., 2005; Fossen and Bale, 2007; Torabi and Fossen 2009; Rotevatn et al., 2013; Soliva et al., 2016). In some cases, DBs appear to be conduits for fluids (Parry et al. 2004; Sample et al. 2006; Petrie et al., 2014; Busch et al., 2017). In most of cases, however, they are associated with a strong porosity and permeability reduction relative to the host rock (Antonellini and Aydin, 1994; Fisher and Knipe, 2001; Shipton et al., 2002; Sternlof et al., 2004; Balsamo and Storti, 2010; Ballas et al., 2015; Fossen et al., 2017; Del Sole and Antonellini, 2019) inducing permeability anisotropy and reservoir compartmentalization. This might impact negatively upon production from faulted siliciclastic systems (Edwards et al., 1993; Lewis and Couples, 1993; Leveille et al., 1997; Antonellini et al., 1999; Wilkins et al., 2019) and flow-based models and simulations (Sternlof et al. 2004; Rotevatn and Fossen, 2011; Fachri et al., 2013; Qu and Tveranger, 2016; Romano et al., 2020).

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Cements have been found in association with DBs. Localization of cement along these structural features, may significantly enhance porosity and permeability reduction caused by mechanical crushing and reorganization of grains, thus increasing their sealing or buffering potential (Edwards et al., 1993; Leveille et al., 1997; Fisher and Knipe, 1998; Parnell et al., 2004; Del Sole et al., 2020). Therefore, occurrence, distribution, and petrophysical properties of cement along DBs need to be properly characterized and implemented into reservoir quality models to predict porosity and permeability, and their heterogeneity (e.g. Morad et al., 2010).

Models for calcite cementation, besides, are fundamental for predicting sandstone and fault-rock properties such as porosity, permeability, compressibility, and seismic attributes. Diagenetic processes related to fluid-flow mechanisms and evolution within DBs remain poorly constrained. Different processes account for enhanced fluid flow within DBs, such as unsaturated flow relative to the host rock in arid to semiarid vadose zones, (Sigda et al., 1999; Sigda and Wilson, 2003), and transient dilation in the early stage of DB formation (e.g. Antonellini et al., 1994; Main et al., 2000), As well, these mechanisms have been employed to explain the occurrence of cement and other processes (e.g. cementation, hydrocarbon inclusion entrapment, removal of iron oxide coatings) in and around the band (Fowles and Burley, 1994; Labaume and Moretti, 2001; Ogilvie and Glover, 2001; Parnell et al., 2004; Parry et al., 2004; Sample et al., 2006; Wilson et al., 2006; Cavailhes et al., 2009; Balsamo et al., 2012; Lommatzsch et al., 2015). These mechanisms, however, appear to be limited to specific conditions (e.g. cement precipitation in the early stage of DB formation, or in vadose environments) and they assume that DBs behaved as fluid "conduits" in order to explain the occurrence of cement or other authigenic products within these structures. Nevertheless, a significant number of studies on DBs show that in most cases they are baffle or seals to fluid flow (see Ballas et al., 2015 for a review). Much less work has been addressed to elucidate the fluid flow and diagenetic mechanisms leading to selective cementation in association with low-permeability baffle/barrier DBs (Philit et al., 2015; Williams et al., 2015). Different mechanisms, then, need to be invoked to explain the occurrence of cement in association with DBs in a broader set of conditions.

The aim of our work is to elucidate the hydraulic behavior of DBs as well as fluid flow mechanisms and evolution, with regards to diagenetic processes, related to such structures. The novelty of our work is that by using a cross-disciplinary study integrating structural and diagenetic analysis, we constrain the interaction between DBs, fluid flow, and diagenesis. In particular, we assess the control exerted by DBs on flow pattern and diagenetic heterogeneities distribution, by characterizing the occurrence, and the spatial and microstructural relationship between DBs and cement nodules in two porous sandstone reservoir analogs. We examine two field sites in Italy and France where calcite cement nodules are spatially associated with DBs. The comparison between the two locations with different geological settings makes it possible to derive general conclusions, that can be extended to other cases where DBs and diagenetic processes interact. Our study allows also to evaluate the impact of both structural and structural-related diagenetic heterogeneities, on present-time fluid circulation, and on subsequent deformation.

2 Geological framework

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ha eliminato: A cross-disciplinary study integrating structural (DB characteristics) and diagenetic (cement characteristics) analysis is thus required to reliably constrain the combined structural and diagenetic evolution of the studied rock volumes (Laubach et al., 2010). The objective of this work is to investigate the interaction. [1]

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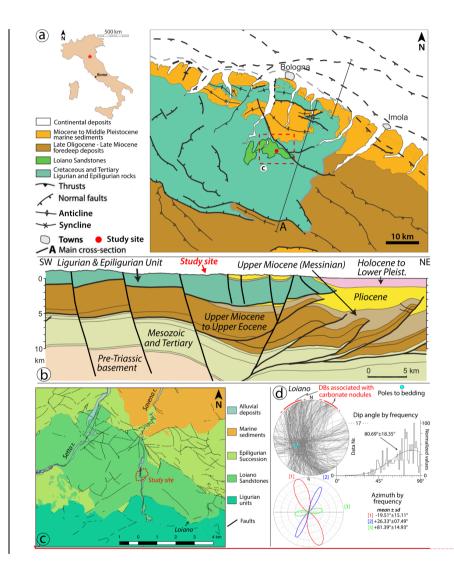
2.1 Loiano field site, Northern Apennines (Italy)

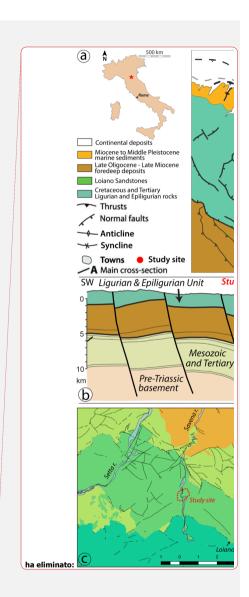
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The site of Loiano is in the Northern Apennines (Emilia-Romagna region, Italy), 20 kilometers to the south of the city of Bologna (Fig. 1a). The Northern Apennines are an orogenic wedge formed in response to the Upper Cretaceous-Eocene closure of the Ligurian-Piedmont ocean (Marroni et al., 2017) and the subsequent Oligocene-Miocene convergence and collision between the Adriatic Promontory and the Sardinia-Corsica Block, of African and European origin, respectively (Vai and Martini, 2001). Our work focused on the Loiano Sandstones of the Epiligurian Successions (Fig. 1a-c), the Middle Eocene to Middle Miocene siliciclastic infill of thrust-top, piggy-back basins discordant to the underlying Ligurian units, which migrated passively to the NE during the Apennines orogeny atop of the entre orogenic wedge. The 300-1000 m thick, Late Lutetian-Bartonian Loiano Sandstones are a fan-delta to proximal turbidite deposit (Papani, 1998). They are medium- to coarse-grained, poorly consolidated, immature arkosic sandstones and conglomerates deposited in a relatively small lenticular basin (a few tens of km in width and length; Fig. 1a, c). They are composed of 49 to 60% quartz and of 39–48% feldspar, the rest being rock fragments, detrital carbonate clasts, and minor accessories (Del Sole and Antonellini, 2019).

2.2 Bollène field site, Southeast Basin (Provence, France)

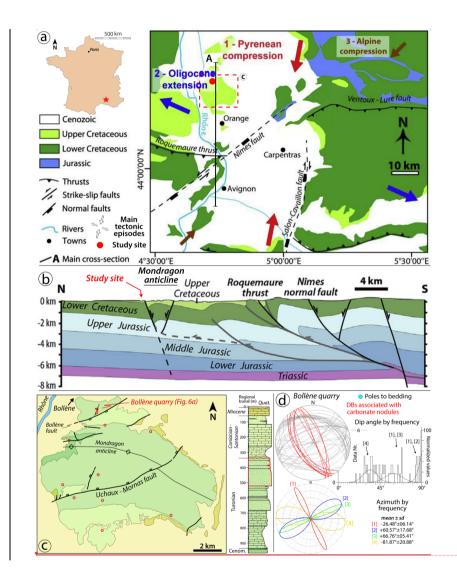
The site of Bollène is in the Southeast Basin of Provence (France), 15 kilometers to the north of the city of Orange (Fig. 2a). The Southeast Basin is a triangular region between the Massif Central to the north-west, the Alps to the east, and the Mediterranean Sea to the south. It is a Mesozoic cratonic basin on the edge of the Alpine orogen, approximately 200 km long and 100 to 150 km wide. Three main tectonic episodes affected the region (Arthaud and Séguret, 1981; Roure et al., 1992; Séranne et al., 1995; Champion et al., 2000): SSW-NNE Pyrenean contraction from Paleocene to Oligocene, NW-SE Gulf of Lion extension from the Oligocene to early Miocene (rifting), and, lastly, SW-NE Alpine contraction from Miocene to Quaternary (Fig. 2a). The site of Bollène is exposed in a quarry (Figs. 2c) located in Turonian sand (low cohesion sandstone), between 10 and 200 m thick in thickness and is situated north of the E-W Mondragon anticline (Fig. 2b, c). The Turonian sands at the Bollène quarry are laminated, fine to coarse grained with modal and bimodal grain size distributions; they formed in deltaic and aeolian environments. The host sands are not cemented. They are composed of 88 to 92% quartz, the rest being feldspar. The median grain diameter (D₅₀) is 0.31 mm, i.e. medium sand. Their porosities range from 20 to 43%, and the precise value at study site is 22.05% (Ballas et al., 2014).





225 Figure 1. (a) Schematic geologic map and (b) cross-section of the Northern Apennines near Bologna (Italy), modified from Picotti and Pazzaglia, 2008. (c) Geologic map of the study area and location of the studied outcrops (red dotted line). This map is constructed from data of the Regione Emilia-Romagna (http://www.regione.emilia-romagna.it/). Location of (c) is indicated by a red square in (a). (d) Lower-hemisphere equal-area projection indicates the orientation of the different sets of DBs (298 data points) and poles to bedding at the study site. DBs associated with carbonate nodules are highlighted by a red line. DBs azimuth (strike; N ± 90°) frequency rose diagram and dip angle (°) plotted against frequency. Best-fit Gaussian curves superimposed on the corresponding data histograms (frequency distributions). Gaussian peaks and related standard deviations (± sd) are indicated for each population.

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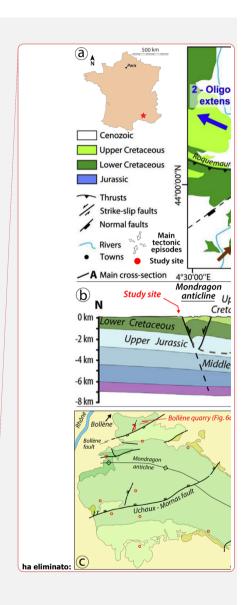


Figure 2. (a) Schematic geologic map and (b) cross-section of the South East Basin, Provence, France. The main tectonic episodes affecting the region are reported in (a). (c) Geologic map and stratigraphic column of the Bollène quarry. Location of map in (c) is indicated by a red square in (a), and red open circles indicate some of past studies locations (see Wibberley et al., 2007; Saillet and Wibberley, 2010; Ballas et al., 2012, 2013, 2014; Soliva et al., 2013; Philit et al., 2018). (a), (b), and stratigraphic column in (c) are modified from Philit et al., (2015, 2018). Geological map in (c) is modified from Ballas et al. (2012). (d) Lower-hemisphere equal-area projection indicates the orientation of the different sets of DBs (64 data points) at the study site. DBs associated with carbonate nodules are highlighted in red. Dotted lines indicate the main attitude of tabular carbonate nodules. DBs azimuth (strike; N ± 90°) frequency rose diagram and dip angle (°) plotted against frequency. Best-fit Gaussian curves superimposed on the corresponding data histograms (frequency distributions). Gaussian peaks, and related standard deviations (± sd), are indicated for each population. Number in square brackets [n] are the same as used in Fig. 6b to rank different sets of DBs.

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3 Methods

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3.1 Outcrops analysis

The geometry and distribution of DBs and nodules were documented by detailed field mapping at different scales for both sites. At the Loiano site, a map (370 m²) at the 1:25 scale (1 cm \approx 4 m) was made by standard topographic compass and tape mapping (Fig. 3). The Bollène quarry site pavement was mapped using a DJI PHANTOMTM drone. Photographs were taken at different altitude above the ground surface and were then used to build a 3D mesh and extract high-resolution orthophotos using Agisoft PhotoScan Metashape software (© Agisoft LLC). The high-resolution orthophoto mosaic (1 px \simeq 255 1-1.5 mm) was used for the detailed mapping of DBs and nodules. Furthermore, DBs and nodule patterns, as well as their characteristics and spatial relationships, were documented in the field on high-resolution photographs (15 megapixels), both in Loiano (Figs. 4 and 5) and Bollène (Figs. 7 and 8). Oriented samples were collected for thin section preparation, microstructural, and stable isotopes analysis. The orientation and dip of DBs were measured at each site and plotted in lower hemisphere equal area stereograms, rose diagrams, and frequency histograms (Figs. 1d and 2d) using the Daisy3 software (Salvini, 2004).

3.2 Microstructural analysis

Polished thin sections of host sandstones, DBs, and nodule samples were analyzed by natural-light optical microscopy, cold cathodoluminescence, and backscattered electron imagery using a JEOL JSM-5400, and a FEI Quanta FEG 200 environmental scanning-electron microscope (SEM). These microscopy techniques were used to examine the texture and microstructures of host rock and DBs, as well as the cement distribution and texture (Figs. 9, 10, and 11). In particular, cold cathodoluminescence (CL) analysis of carbonate cement in nodules was conducted with a CITL Cold cathodoluminescence 8200 Mk5-1 system (operated at 14-15kV beam energy and 250uA beam current) equipped with a standard petrographic microscope (Olympus BH41). CL was used to describe the cement-crystals properties (texture, fabric,

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luminescence) and the micron-scale spatial distribution and textural relationship among the cements, framework detrital grains, and the fractures (sensu lato). This information is used to (i) understand the interrelation between deformation, fluid flow, and diagenesis (e.g. cement precipitation); (ii) assess the relative timing of each process; (iii) describe porosity 275 evolution with time; and (iv) understand the mechanisms and the geochemical environment of cement precipitation when coupled with other tools (e.g. stable isotopes analyses). The CL features (color, brightness) of the carbonate minerals are controlled primarily by the relative abundances of Mn²⁺, REEs, and Fe²⁺. These differences, in turn, reflect specific physiochemical conditions of formation waters during mineral growth, including fluid chemistry (salinity), pH/Eh, temperature, pressure, ions activity, biological activity (e.g. Marshall, 1988; Barnaby and Rimstidt, 1989; Machel, 2000; Hiatt and Pufahl, 2014).

3.3 Stable isotope characterization

Stable carbon and oxygen isotope data from cements from within carbonate nodules were used to constrain the geochemical environment of precipitation and possible source of fluids. Powder samples for bulk rock carbon and oxygen stable isotopes analysis were ground with a dental drill from not weathered or altered sections of the nodules. A total of 46 sites were sampled from nodules in Loiano (n=30; Fig. 12a) and Bollène (n=16; Fig. 12b). Powders samples were analyzed with a Thermo Finnigan DELTA plus XP mass spectrometer coupled with a Thermo Finnigan Gas Bench II gas preparation and introduction system. δ^{13} C and δ^{18} O are referred to the international standard V-PDB (Vienna-Pee Dee Belemnite). Isotope determination analytical precision was 0.10% and 0.15% V-PDB for carbon and oxygen, respectively. The prediction uncertainty was c. 0.15% for carbon and c. 0.20% for the oxygen isotopes.

4 Deformation bands and cement: field observations

4.1 Loiano

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At the study site, bedding strikes NW-SE and dips at an average of 38° to the NE (Fig. 1d). Deformation bands cluster into three different trends striking N20°W (NNW-SSE), N26°E (NNE-SSW to NE-SW), and N81E° (ENE-WSW) (Fig. 1d). All DBs dip moderately to steeply mostly in the west and south quadrants (Fig. 1d). Deformation bands commonly occur with a positive relief and appear as whitish linear traces with minor undulations forming eye and ramp structures, where they branch and merge (Figs. 3 and 4). Already at the outcrop they exhibit a significant reduction in grain size and porosity in comparison to the surrounding host rocks (Fig. 4f). Deformation bands occur both as single features and as clusters or zone of bands, i.e. in narrow zones with variable thickness (0.8-60 cm) with sub-parallel DBs (up to 40). Single DBs accommodate minor offsets from a few millimeters up to 40 mm, whereas clusters can accommodate offsets up to 0.5 m (Fig. 4b, d). Deformation bands display a variety of apparent normal and strike-slip offsets (Fig. 3). Different sets of DBs ha eliminato: could be

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show ambiguous and conflicting crosscutting relationships. Field observations indicate that the NNW-SSE and NNE-SSW sets have mutual crosscutting relationships typical of faults forming synchronously (Fig. 3)

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The peculiar characteristic of the Loiano Sandstones is the occurrence of spatially heterogeneous carbonate cement in the form of isolated or multiple spheroids or irregular nodules and continuous tabular nodules (Figs. 4 and 5). The nodules weather out in positive relief, because they are more resistant to weathering than the weakly cemented host rock. Isolated nodules range in diameter (major horizontal axis) from 0.2 m to 3 m (Fig. 4c, d) whereas tabular concretions have a thickness ranging from 0.10 to 0.8 m and a long axis ranging from 3 up to 15 m in length (Fig. 5a). Generally, the nodule shape in Loiano is similar to that of an oblate spheroid, There is no evidence of spherical nodules or prolate spheroids. The volume of the carbonate nodules ranges from 0.001 m³ to > 10 m³. Nodules form about 20% of the exposed outcrop volume. Two types of nodules can be distinguished depending on whether they are associated with DBs or clusters (i.e. DBs-parallel 315 nodules; Figs. 3, 4, and 5a-c) or with bedding planes (i.e. bedding-parallel nodules; Figs. 3 and 5d, e). The former represent roughly 75% of the total nodules in the study area and are the main target of this work. The association between DBs and nodules occurs in the form of (i) parallelism and spatial overlap between DBs and nodules and (ii) confinement of the nodules by the DBs. In all cases, nodules are oriented with the major axis (elongation direction) parallel to the DBs and the minor-axis (i.e. thickness) perpendicular to them. Deformation band-parallel nodules are isolated ellipsoids (Fig. 4b, d), or, alternatively, continuous tabular objects (Figs. 4a and 5a). Nodules may be located along the DB (or zone of bands) trace (Figs. 4a, d and 5a, b), placed in between and confined by DBs (Figs. 4b, e, and 5c), or they may be asymmetrically placed on one side of the DBs (Figs. 4c and 9e). In some cases, nodules lie at the intersection of different DBs planes (Fig. 3). Some DBs are not spatially associated with nodules (Figs. 3 and 4b). Among the multiple sets of DBs, those mostly associated with carbonate nodules are the NNW-SSE and the NNE-SSW one. As a result, most nodules are elongated along these two structural directions (Figs. 1d and 3; see also Fig. 1b in Del Sole and Antonellini, 2019). The other sets are rarely associated with carbonate nodules. Nodules are never cut across by the DBs.

Bedding-parallel nodules are either isolated (Fig. 3), multiple but laterally discontinuous (Figs. 3 and 5d, e), or laterally continuous layers with a tabular geometry (Fig. 3; e.g. "nodular beds" in Del Sole et al., 2020). Nodular beds are continuous pervasively-cemented layers that extend along the bedding plane for several meters (up to 15 m in length) and a nearly constant thickness of c. 35-50 cm. Nodules along bedding planes are more rounded and with gentle boundaries (Fig. 5d, e) than those associated with DBs, which are, instead, more tabular and exhibit angular and sharp boundaries (Figs. 4 and 5a-c). In some cases, nodule geometry and elongation direction follow both bedding surfaces and DBs (Fig. 3). Nodules, despite being ubiquitous in the sandstone, are mostly observed within coarse levels with grain size equal or larger than medium sands (0.25-0.5 mm). We did not observe any nodules in sedimentary rocks with grain size finer than sand (siltstone and clay). Bedding-parallel nodules are commonly located in sandstone levels confined between clay/silty levels or finegrained-sand levels (Figs. 3 and 5d, e).

A set of joints and veins (Fig. 5a, b) were found exclusively within the carbonate nodules. They postdate DBs and nodules and do not propagate into the surrounding host sandstone.

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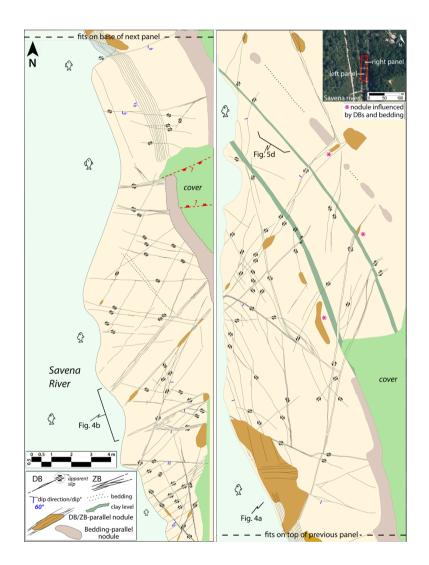




Figure 4. Relationships between nodules and DBs. Deformation bands occur either as single structures or organized in clusters (ZB). Nodules along DBs (or ZB) are isolated (b, d, e), or continuous with a tabular geometry (a). Nodules are located along the DB trace (a, b, d), or they are asymmetrically placed on a side of the DB (c). (e) Isolated nodule in between and confined by ZB. DBs are whiter than host rock, exhibit a positive relief, and a clear reduction in grain size and a lower porosity, both visible to the naked eye (f). The pen in (c, d) is 14 cm in length. The arrow-scale in (b, e) is 10 cm in length. The position of (a, b) is indicated in Fig. 3.

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Figure 5. (a-c) DB-parallel- and (d-e) bedding-parallel nodules. (a) Decametric-scale continuous nodule with a tabular geometry located along a zone of bands (ZB). NE-dipping layering is shown with dotted lines. The photo is about 10 meters in depth. (b) Close-up on (a) from a map-view. The lens-cover is 5.5 cm in diameter. (a, b) Late opening-fractures cut through the assemblage "DBs – nodule" and they do not propagate into the poorly consolidated host rock. (c) Isolated nodules placed in between and confined by ZB. (d, e) The bedding is

emphasized mostly by clay and silt horizons, sporadic well-defined thin levels of gravel, and the alignment of bedding-parallel nodules. (d) Black arrows point to multiple but laterally discontinuous bedding-parallel nodules. Here, a single DB (white line) crosses a bedding-parallel nodule without causing any offset. The position of (d) is indicated in Fig. 3. (e) Photomosaic showing a series of laterally-discontinuous nodules just below, above or in between several continuous impermeable clay-rich levels. The deformation pattern changes depending on the host rock properties (e.g. sorting degree, porosity \(\phi \), grain-size; see Supplement S1 for details). Cataclastic deformation is accompanied by clay smear (see inset) where DBs cut thin dark-colored clay levels.

4.2 Bollène

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At Bollène, DBs occurs as belonging to three different trends oriented (i) NW-SE to NNW-SSE (set 1: N26°W; Figs. 2d and 6b), (ii) NE-SW to ENE-WSW (set 2: N61°E and set 3: N67°E; Figs. 2d and 6b), and (iii) ESE-WNW (set 4: N82°W; Figs. 2d and 6b). Trend (i) can be divided in two subsets; one is characterized by normal offsets NW-SE conjugate bands, moderate dip angles (50-60°) to SW (Figs.7a and 8a, c), and just a few to NE; a second one is characterized by dominant dextral strike-slip kinematic bands with higher dip angles (70-90°), and a NNW-SSE trend (Figs. 6b and 7f). Trend (ii) can be divided in two sets; one set is characterized by dominantly left-lateral and minor right-lateral subvertical strikeslip conjugate bands striking NE-SW to ENE-WSW (set 2 in Fig. 6b; Fig. 7a-c); a second set is instead characterized by a set of conjugate DBs with moderate dips (~60°), NE-SW orientation (set 3 in Fig. 6b), and undetermined kinematic (likely normal-sense). Trend (iii) is composed of ESE-WNW conjugate bands, with reverse kinematics and low dip angles (30-40°). In the field, DBs appear as whitish linear traces with minor undulations and characteristic eye structures where they branch and merge (Figs. 6b and 7). In most cases, DBs weather out in positive relief. Frequently DBs occur in narrow zones (a few millimeters up to 5-15 cm in thickness). Field observations indicate that ESE-WNW DBs are crosscut by NE-SW strike-slip DBs (Fig. 6b). The latter also crosscut also the NW-SE/NNW-SSE set (Fig. 7a-c, f). Bedding is oriented NW-SE and dips gently (<10°) to the S (Fig. 2b, d). Bedding is difficult to recognize on the floor of the quarry, because of its low dip and the massive texture of the rock (Fig. 6b). The Turonian sandstones outcrop on the quarry floor. There are two lithotypes. The first one is represented by massive porous sands with DBs and localized carbonate cementation (see description below). The second one is characterized by a massive calcrete level with tabular geometry (see Supplement S2 for details).

The Turonian Sandstones in the Bollène quarry are characterized by a spatially heterogeneous cementation (Fig. 6b). These diagenetic heterogeneities occur as spherical and tabular nodules (Figs. 7 and 8). Spherical nodules are arranged as isolated bodies within the surrounding host rock (Figs. 7c, g and 8a, d, e) or aggregated in tabular clusters (Fig. 7a, d). Nodules weather out in positive relief. Spherical nodules range in diameter from a few millimeters (0.004-0.005 m) to a few tens of cms (0.2 m), whereas tabular ones have a thickness ranging from a few cms to 0.1 m and a long axis up to 5 m in length (Figs. 6b and 7a-c). Assessment of nodules lateral extension is hampered by the presence of vegetation and debris cover whereas subsurface extension cannot be measured, because of the limited vertical exposures of the outcrops. Hence, the values reported here are minimum values. In general, the nodule shape may be approximated by a sphere where length, width, and thickness are "equal" and by an oblate spheroid where length and width are larger than the nodule thickness.

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Carbonate nodule volume ranges from 10⁻⁷ (small spherical nodules) to > 2.5 m³ (tabular nodules assuming length = width = 5m, and thickness = 0.1m). In Bollène, the nodules are all spatially and geometrically associated with DBs (i.e. DBs-parallel nodules; Figs. 6b and 7). This association occurs in the form of (1) parallelism between DBs and nodules, (2) geometric congruence between the DBs trend and the nodule (or nodules cluster) shape, and (3) confinement of nodules in parallel-to-bands compartments. In all these cases, tabular nodules and clusters of spherical nodules are oriented with the major axis (elongation direction) parallel to the DBs and the minor-axis (i.e. thickness) perpendicular to them (Figs. 7a and 8a). Unlike what we have seen in Loiano, in Bollène nodules are in compartments among DBs. Carbonate nodules are associated with the NW-SE/NNW-SSE DBs set (Figs. 6b and 7a, f). Although this set is conjugate with bands dipping to the SW and to the NE, the tabular cement bodies dip only to the SW (Figs. 2d and 8a-c). No nodules are cut by the NW-SE bands. The NE-SW/ENE-WSW strike-slip bands cut through the NW-SE/NNW-SSE bands and the associated NW-SE-trending carbonate nodules (Figs. 7a-c, f). There is clear evidence of these crosscutting relationships both at the outcrop and at the micro-scale (see Sect. 5.2). For this reason, we focus on the NW-SE DBs and nodules in the remaining part of this study.



Figure 6. (a) Aerial photograph of the study site (© Google Earth). (b) Orthophoto that documents geometry and distribution of DBs and carbonate nodules in the Bollène quarry. Lower-hemisphere equal-area projection indicating the orientation of the cataclastic structures measured in (1) NW-SE/NNW-SSE normal and (dextral) strike-slip bands associated with tabular and spherical nodules; (2) NE-SW/ENE-WW strike-slip bands; (3) NE-SW bands with undetermined kinematics; (4) ESE-WNW reverse-sense bands.

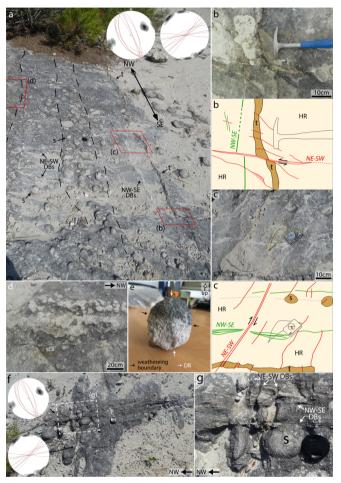
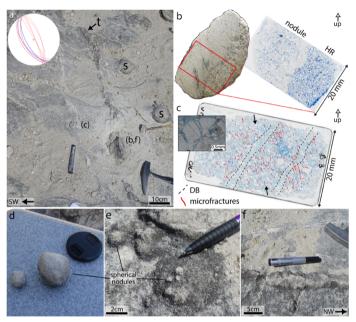


Figure 7. Calcite cement occurs in the form of isolated (a, c, g) or clusters (a, d) of (S) spherical nodules and continuous (t) tabular nodules (a-c). Nodules are arranged in compartments parallel to clusters of NW-SE normal bands (a-c) and to NNW-SSE dextral strike440 slip bands (f, g). NE-SW/ENE-WSW strike-slip bands displace both the NW-SE bands and their associated nodules (a-c, f). (e) Spherical nodule (about 5 cm in diameter) in spatial superposition with a NW-SE DB that does not displace the cement. Lens-cover in (a, f) has a 5.5 cm diameter. The figures (a-d, f, g) are in map-view. The position of (a, f) is indicated in Fig. 6b. Hammer length in (b) is 30.5 cm.



445 Figure 8. Typical relationships between nodules and DBs. (a) Continuous tabular nodule (t) and isolated spherical nodules (S) aligned parallel to the NW-SE normal-sense bands dipping SW (~55°; red lines in the inset stereoplot). The tabular bodies dip to the SW parallel to the bands (blue lines in the stereoplot in the inset). The position of (a) is indicated in Fig. 6b. (b) Hand specimen and polished thin sections impregnated with blue-dyed resin of a tabular nodule in (a). (c) Polished thin sections impregnated with blue-dyed showing two sub-parallel NW-SE normal-sense bands dipping SW. Mapping of microfractures developed at grain contacts consistent with Hertzian contacts (e.g. Eichhubl et al., 2010; Soliva et al., 2013) endorses the normal kinematic of these bands (see Supplement S1 for details). "Up" refers to the topography. Close-up on spherical (d-e) and tabular (f) nodules from the field. Pen-marker length in (a, f) is about 13.5 cm. Lens-cover in (d) has a 5.5 cm diameter.

5 Deformation bands and cement: textural and microstructural characteristics

5.1 Loiano

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Host rock total porosity (minus-cement ϕ) is between 20-26% (Fig. 9; Del Sole and Antonellini, 2019). Porosity is predominantly intergranular, whereas intragranular (e.g. pores within bioclasts) and "oversize" pores are due to dissolution

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of detrital grains (Figs. 9 and 10). Deformation band total porosity (minus-cement ϕ) is lower by an order of magnitude (below 5%) than the host rock porosity (Fig. 9d). In the nodules, the host rock porosity is almost completely filled by cement (Fig. 10), so that the remnant porosity (voids) is low (down to 1.3%) (Fig. 9a, c). The presence of cement within the DBs enhances the porosity reduction caused by grain crushing and compaction (Fig. 9d). The microstructure of the DBs is characterized by reduced of grain size, porosity and pore size than in the host rock (Fig. 10i-1). Within the DBs a few coarse grains are surrounded by a fine-grained matrix.

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Despite the different effects of mechanical and chemical compaction and minor authigenic alterations (refer to Supplement S1 for details), the major diagenetic components of the Loiano Sandstone are calcite cements. These cements fill mainly intergranular, and at lesser extent intragranular (intraskeletal) pore spaces, intragranular fractures, and they encase the framework grains and all other diagenetic features. Bedding-parallel nodules (Fig. 10a-h) are characterized by a mosaic texture of blocky sparite to poikilotopic bright-orange to orange-CL calcite cement. Crystal-size is typically 40-100 µm and up to 300 µm (Fig. 10g, h). This cement phase is the most widespread one and it is almost everywhere uniform in terms of texture and CL-pattern, if not for some minor dark-CL sub-zones (Fig. 10g, h). A minor calcite cement phase is associated with detrital carbonates (bioclasts) and it shows a bright-orange CL (Fig. 10c-d). It occurs as pore-lining formed by elongate and sharp rhombohedral shape calcite (dogtooth) that outlines the outer rim of the bioclasts (Fig. 10c) and drusy mosaic calcite that fills intraskeletal pores, outline bioclasts, and fills intragranular fractures in bioclasts (Fig. 10d). This subordinate phase was observed only in bedding-parallel nodules. Pore-lining cement around bioclasts is present only where there was pore-space (now filled), whereas it is absent where other grains are in contact with the bioclast. All cement phases described above (intergranular, intraskeletal, and pore-lining) encase compacted grains, and cements are undeformed still preserving the original shape. Pore-filling cement in DBs-parallel nodules (Fig. 10i-n) show a similar texture and CL-pattern to that described for the main intragranular cement phase in the bedding-parallel nodules (Fig. 10a-h). The main features that differentiate DB-parallel nodules from bedding-parallel ones are the finer crystal size of calcite within DBs, (Fig. 10i-l) and the absence of a bright-orange CL cement phase described in association to bioclasts in bedding-parallel nodules (Fig. 10c, d). Some bright-orange CL cement was observed only in detrital form (crushed) within the DB (Fig. 10k). The pore filling in DBs is fine-grained sparite; no evidence was found of crushed calcite crystals belonging to the dominant calcite phase. The finer fraction within the DBs is a matrix made up of comminuted angular and fine-grained clasts (flakes) of feldspar and in a smaller degree quartz, encased by the cement (Fig. 10j-l). Similarly, the cement fills the microfractures that cut through coarser grains and it encase the fine-grained clasts that are present within these fractures. Although, these microfractures are frequent in the host rock sectors in proximity to the DB (Fig. 10i), they were observed also in bedding-parallel nodules (Fig. 10a, b). Host rock volumes within DBs-parallel nodules are still characterized by blocky sparite cement with some minor dark-CL growth sub zones (Fig. 10i, m, n), similarly to what was observed in bedding-parallel nodules.

To evaluate any sign of dissolution in nodules, we carefully checked cement crystals morphologies adjacent to poorly- or non-cemented host rock sectors at the edges of nodules. Here, cement crystals boundaries are regular and sharp (Fig. 10m, n).

ha eliminato: Grains in the DBs are fractured and characterized by angular shapes, whereas the host rock consists of more rounded and nearly undisturbed medium- to coarse-grained sand grains (Figs. 9b-d and 10). However, some intragranular fractures are present at grainto-grain contacts (Fig. 10a-b). These microfractures are common in the boundary zone of the DBs (Fig. 10i). Microfractures in larger grains are often filled by fine-grained clasts. Detrital calcite clasts and bioclasts are often fractured or affected by pressure solution at contact points with other framework grains (Fig. 10b-d). Elongated detrital mica grains (mostly biotite) are bent between other grains and they tend to be preferentially aligned parallel to the bedding (Fig. 10c). In some cases, where framework grains are in contact, they show straight-elongate planar to slightly undulated grain to grain contacts (Fig. 10b) that are also roughly parallel to the bedding. Locally, we observed partial dissolution of feldspar with formation of authigenic calcite (Fig. 10e). Minor calcite cement occurs also as syntaxial overgrowths around fossil shells and detrital carbonate grains (Fig. 10f). ..

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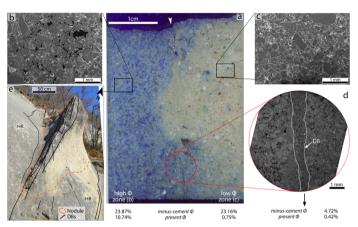


Figure 9. Host rock (HR) and DBs porosity and relationships between cement and DBs in Loiano Sandstones. (a) Polished thin sections impregnated with blue-dyed resin. The section shows a DB (arrow) separating two host rock sectors: in the right-hand side there is extensive calcite cementation whereas on the left-hand side cementation is poor. (b, c) Secondary electrons and (d) backscattered electrons SEM images from different sectors of the section (a). Porosity (\$\phi\$) estimations data in (a-d) from Del Sole and Antonellini (2019). (e) Field example where a nodule is asymmetrically placed on a side of the DBs, similarly to what is observed in (a). See text for further details.

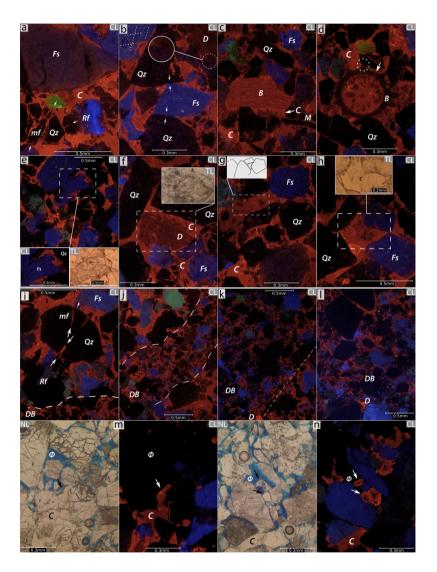


Figure 10. Natural- and CL-light photomicrographs showing the microstructure, and cement textures in (a-h) bedding-parallel and (i-n) DBs-parallel nodules. (a-b, d) Microfractures forms at grain contacts due to stress concentration at contact points. (i) Microfractures are common in the host rock areas close to the DB. (b) Feldspars break mainly by cleavage-controlled intragranular fractures (white dotted line). Some framework grains show planar to slightly undulated framework grain-to-grain contacts. Detrital carbonate clasts and (c-d) bioclasts are partially dissolved at grain contacts. (c) Some detrital grains are corroded and coated or partially replaced by cement. (f)
 Syntaxial overgrowth cement on a detrital carbonate clast (D). Bright-CL (c) circumgranular pore-lining (dogtooth texture) and (d) intraskeletal (drusy mosaic) calcite cement was observed only in bedding-parallel nodules. The main cement phase is characterized by bright-orange to orange-CL calcite cement that fills intergranular porosity and intragranular fractures both in (a, b, e-h) bedding-parallel nodules and (i-n) DB-parallel ones. (g-h, m-n) Host rock volumes in nodules are characterized by blocky sparite to poikilotopic calcite cement with minor dark-CL sub-zones, whereas (j-l) the cement in DBs is fine-grained sparite. (m-n) At nodules edges, cement crystal rims are regular and sharp suggesting absent or negligible dissolution. Bright grains in (k, l) are detrital calcite (D). Qz - quartz; Fs - feldspar; M - mica; Rf - rock fragment; B - bioclast; φ - pore space; C - calcite cement; TL - transmitted light. See text and Supplementary Material (S1) for further details.

5.2 Bollène

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The host sands at Bollène are weakly cemented, with the exception of localized carbonate cementation described above. Host rock grains are mostly rounded and Jack a fabric (Fig. 11a, f). Here, we describe the microstructure of NW-SE/NNW-SSE normal-sense and strike-slip bands, and NE-SW/ENE-WSE strike-slip bands sets. The most recognizable features that characterize both DBs sets are the reduction of grain size, porosity, and a tighter packing relative to the host rock (Fig. 11). NE-SW strike-slip bands (Fig. 11i-l) have a higher degree of grain comminution, porosity reduction, and tighter packing when compared to NW-SE bands (Figs. 8c and 11g-h). Most grains within the bands are fractured and angular. Despite the strong comminution, a few rounded large survivor quartz grains are preserved in the DBs matrix (Fig. 11g, h, k). Fine angular grains that are mostly comminuted feldspars fragments and secondarily quartz and minor oxides make up the matrix. We observed also fine particles of crushed calcite cement among the matrix grains within NE-SW bands (Fig. 11k, 1). In some cases, the grains in the host rock areas in proximity to the DB are encased by relatively undeformed carbonate cement (Fig. 11i, j). Some grains in the host rock are corroded and partially replaced or coated by calcite cement (Fig. 11c).

The main cement in spherical and tabular nodules is a poikilotopic calcite that infills intergranular pores (Fig. 11a-e). Most of the cement is non-luminescent (dark luminescence) under CL (Fig. 11c, d) but a few crystals show partial overgrowths with bright-orange CL color (Fig. 11e). When the crystal has a heterogeneous CL-pattern, the non-luminescing zones are mainly in the crystal core whereas the luminescing sub-zones are mostly at the crystal edges (Fig. 11e). A very thin film (up to c. 10µ thick or less) of bright-orange CL calcite cement commonly coats the detrital grains (Fig. 11c), and it is visible also under natural-light (Fig. 11b). In the nodules, some of the intragranular microfractures at contact points are filled by cement (Fig. 11a); a few are not (Figs. 11b). The cements described above (pore-filling and grain-coating) are relatively

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ha eliminato: A few intragranular fractures break framework grains at the contact-point among two or more grains (Fig. 11a, b), and they are more frequent approaching the DB (Fig. 11g, h, j). These microfractures, in fact, are a common feature in the host rock sectors in proximity to the DB and they are preferentially oriented with respect (ranging from ca. 30° to 50°) to the force chain around DB (Fig. 8c). Despite the grains being fractured in the host rock sectors close to the DB, and the reduction in grain size is limited. ...

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undeformed (i.e. no microfractures, no twin-lamellae) and still preserving the original shape, except where the NE-SE/ENE-WSW strike-slip bands crosscut the cement nodules. At the crosscutting site, indeed, and more specifically in the host rock sectors in proximity to the NE-SW/ENE-WSW bands, we observe intragranular fractures at contact points and the onset of cement comminution between quartz clasts (Fig. 11i, j). Fine particles of crushed detrital calcite cement are found among the cataclastic matrix grains within NE-SW/ENE-WSW strike-slip bands where they interact with nodules (Fig. 11k, l). At the microscale, no preferential or significant calcite cementation was observed in association with the NW-SE bands. The association between cements and these latter bands was observed only at the mesoscale (see Sect. 4.2).

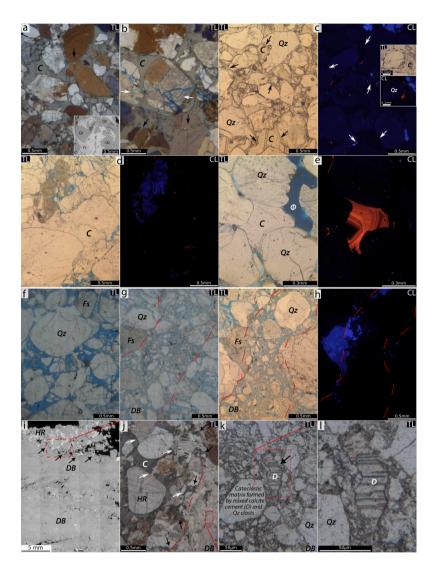


Figure 11. Natural- and CL-light photomicrographs showing the internal texture and microstructure of (a-e) spherical and tabular nodules and (f-l) DBs. (a, b, f) Host rock grains are mostly rounded and nearly undisturbed. Some microfractures break framework grains at contact points. In nodules, (a) some of the microfractures are filled; (b) a few are not. (g, h) Microfractures are more frequent approaching the DB and (j) they are preferentially oriented with respect to the band (white arrows). Cement fills intergranular pore-space and intragranular fractures. (c-e) The major diagenetic component is poikilotopic spar cement with dominant dark-luminescence and (e) minor bright-orange CL growth sub-zones. (c) A very thin film of bright-orange CL calcite cement often coats detrital grains. Minor diagenetic alterations are corroded detrital grains that are partially replaced by calcite cement; see inset in (c). (g, h) NW-SE bands and (i, l) NE-SW strike-slip bands show a similar pattern, but NE-SW bands feature a high degree of grain comminution and porosity reduction. (i, j) NE-SW strike-slip bands crosscut cement nodules; intragranular fractures (white arrows) and incipient stage of cement comminution (black arrows) between quartz clasts in the host rock sectors in proximity these bands. (k, l) Fine particles of crushed detrital calcite cement (D) are found among the matrix grains at the crosscutting site. The inset in (a) is a backscattered electrons SEM image. Qz - quartz; Fs - feldspar; \(\phi - \) pore space; C - calcite cement; TL - transmitted light. See Supplementary Material (S1) for details.

6 Cement stable isotopes geochemistry

600 **6.1 Loiano**

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Cement from the nodules of the Loiano samples has δ^{13} C values between -7.68 and -1.47 % (V-PDB) and δ^{18} O values between -4.42 and -1.35 % (V-PDB) (Fig. 12a). The cement from DBs-related nodules is characterized by isotope compositions between -5.41 and -1.47 % (V-PDB) for δ^{13} C, and between -4.42 and -1.40 % for δ^{18} O (V-PDB). The cement from bedding-parallel nodules has isotope compositions between -7.68 and -5.94 % (V-PDB) for δ^{13} C, and between -2.09 and -1.35 % (V-PDB) for δ^{18} O. Both cement groups (DBs-parallel and bedding-parallel nodules) have a relatively narrow range of oxygen isotopic composition featuring a near-vertical alignment in the δ^{18} O- δ^{13} C cross-plot. DBs-parallel nodules show a slightly wider span of δ^{18} O composition when compared to bedding-parallel nodules. However, carbon isotopic composition shows a wide range of variability, both when considering the total isotopic composition data and when considering the cement groups data.

610 6.2 Bollène

Stable isotope analysis of the Bollène samples also defines two groups of data in the δ^{18} O- δ^{13} C space (Fig. 12b). The cement group referring to the DBs-related nodules has δ^{13} C values between -7.73 m and -4.68 % (V-PDB) and δ^{18} O values between -7.70 and -5.88 % (V-PDB). The other group is from cement sampled in a calcrete level observed within the same Turonian sandstone few meters above the studied outcrop (see Sect. 4.2 and the Supplement S2 for details), and it is characterized by isotope compositions between -2.54 and -2.39 % (V-PDB) for δ^{13} C, and between -6.58 and -6.32 % (V-PDB) for δ^{18} O. Both cement groups have a relatively similar δ^{18} O signature and a relatively narrow range of δ^{18} O composition varying only between -7.70 and -5.88 % (V-PDB). In a similar way, cement sampled from the calcrete has a

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630 narrow range of δ¹³C composition and show the heavier δ¹³C values in the data set. However, δ¹³C composition of DBs_related nodules has a wider variability range and is the most depleted in the data set.

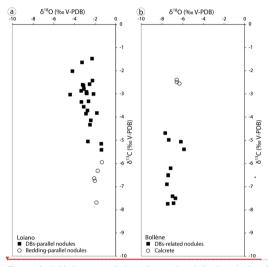


Figure 12. Stable isotopes analysis results. (a) Cumulative isotopic data characterizing the DBs-parallel nodules (black full-dots) and bedding-parallel ones (empty-dots) inside the Loiano Sandstones. (b) Isotopic data from the DBs-related nodules (black full-dots) and cement sampled in the calcrete (empty-dots) in Bollène quarry (see the Supplement \$\frac{\sigma}{2}\$ for details).

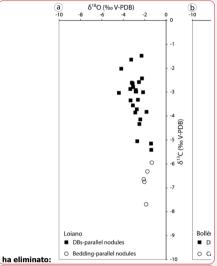
7 Discussion

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In the following, we compare the two field sites highlighting their similarities and differences concerning the interaction between deformation, fluid flow, and diagenesis. We discuss the influence of DBs on fluid flow, their role in enhancing diagenesis and localizing diagenetic products (nodules). Finally, we propose an explanation for the geochemical environment within which fluids were sourced and precipitated the nodule cement. We then explore the implications of structural diagenetic heterogeneities (SHD) upon subsurface fluid flow and reservoir characterization.

7.1 Cement distribution and its relationship with deformation bands

The distinctive feature of the *Loiano Sandstones* is a spatially heterogeneous cementation in the form of nodules. Field evidence indicates that DB formation predates calcite cementation. All nodules are spatially related to DBs (Figs. 3 and



ha eliminato: 7.1 Deformation band characteristics

In both study areas, the key, common structural element are the DBs. In Loiano, geometric compatibility between DBs strike (Fig. 2d) and large-scale normal faults in this sector of the Northern Apennines (Fig. 2a, c; Antonellini and Mollema, 2002; Picotti et al., 2009) indicates that they might be coeval. For instance, our study outcrops are close to a high-angle normal fault striking nearly N-S and dipping W (Del Sole et al., 2020). However, the presence of multiple sets of DBs, with different trends (Fig. 2d), kinematics, and ambiguous crosscutting relationships (Fig. 3) suggests that the Loiano Sandstones recorded multiple tectonic phases (Cibin et al., 2001; Antonellini and Mollema, 2002) from the Eocene onwards. A clear sequence of deformation events has not yet been defined. In Loiano, the inhomogeneous mesoscale pattern and geometry of DBs along the exposed sandstone sequence is related to variations in host rock properties, such as sorting, porosity, and grain-size (Fig. 5e), Low porosity and/or poorly sorted coarse-grained host sandstones promote localized deformation commonly with a single straight-trace DB accommodating all displacement. High porosity and/or well-sorted fine-grained sandstones feature, instead, a more distributed deformation with several anastomosing DB segments, where each segment accommodates part of the total displacement. Others host rock properties steering the overall DB characteristics are mineralogy, lithification, and grain roundness (Antonellini and Mollema, 2002; Fossen et al., 2017; Del Sole and Antonellini, 2019). In the Bollène quarry, structural features include diachronous and differently oriented DBs and occur only in the unconsolidated Turonian sands (Fig. 2c). Crosscutting relationships between different sets point out that ESE-WNW reverse DBs set should be the

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5a-c) except for those that are situated along bedding planes (~25% of the total nodules; Figs. 3 and 5d, e). In contrast, not all DBs are associated with nodules. A clear correspondence always exists between shape and elongation direction of the nodules and the DBs direction. This pattern is observed also from aerial photographs (Del Sole and Antonellini, 2019). Localized cement along these structural features itself is an indication that deformation preceded cement precipitation (e.g. Eichhubl et al., 2004). If the sandstones were completely cemented at first, and then completely removed except from the DBs, the cement in the DB's matrix would most likely have been preserved in orange reddish hues (oxidation residues); but nothing like that was observed. Moreover, cement morphologies adjacent to the porosity at nodules edges imply that cement dissolution has not occurred (Fig. 10m, n), thus excluding that nodules, both those parallel to bedding and those parallel to 755 DBs, are relicts from an overall dissolution process. No DBs crosscut the cement, at least for those sets that are spatially related to nodules (NNW-SSE to NE-SW) indicating that cementation postdate DBs development. The precipitation of cement and (the consequent) lower porosity would favor the formation of joints over DBs in the sandstone (Flodin et al., 2003; Aydin et al., 2006; Fig. 5a, b). The presence of pore-filling cement would increase the strength of the sandstone (Del Sole et al., 2020), preventing rotation and sliding of particles, increase rock cohesion (Bernabé et al., 1992) and grain contact area, thus yielding a uniform contact stress distribution and higher stiffness (Dvorkin et al., 1991). Extensive cement, then, would inhibit DBs development. We can affirm, hence, that cement overprints the deformation bands.

Results from microstructural observations show that intergranular cement in the nodules encloses the grains both within host rock and DBs, and it overprints burial-related mechanical and chemical compaction features (Fig. 10a-h). These evidence, point out that the formation of authigenic cements occurred after significant compaction (Cibin et al., 1993; Milliken et al., 1998). Estimated burial depths referred to the top of the Loiano Sandstones are 800-1000 m (Cibin et al., 1993) and 700-1200 m (McBride et al., 1995). Transgranular microfractures at grain contacts are due to stress concentration at contact points and they are interpreted as load-bearing structures within the granular framework (e.g. Antonellini et al., 1994; Eichhubl et al., 2010; Soliva et al., 2013). In DBs-parallel nodules samples the cement that fills the transgranular fractures is in continuity (i.e. same textural and CL characteristics) with the pore-filling cement outside the fractures. The presence of undeformed cement within structural-related features such as microfractures and crushed grains (Fig. 10i-l), both within and outside the DBs, proves that cement precipitation occurred after (at least after the early stages of) deformation.

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The bands are the main controlling factor on the location, geometry, and elongation direction of DBs-parallel nodules. The occurrence and location of bedding-parallel nodules is controlled by grain-size and contrast in grain-size within the host rock. Although bedding-parallel nodules are found in all sands, they are more common within coarse-grained levels (≥ medium sands; i.e. size range: 0.25-0.5 mm). There are no nodules in sediments below the sand range or in layers with permeability below 100 mD (Del Sole et al., 2020). Moreover, bedding-parallel nodules are often restricted to sand level in contact above and/or below with clay/silty levels (Fig. 5d, e). Hence, grain size, and permeability variations are the most important factors controlling diagenetic and nodules formation in Loiano. The grain size and permeability variations as dominant control on nodules development in porous media is also reported by other authors (Mozley and Davis, 1996; Davis et al., 2006; Cavazza et al., 2009; Balsamo et al., 2012). In general, bedding-parallel nodules show a more rounded

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morphology when compared to DBs-related nodules. The former nodule type owns its smooth morphology to a homogeneous and isotropic weathering; the sharp and squared shapes of DB-s parallel nodules is probably due to the anisotropy introduced by the DBs in the host rock that influences the cementation. The interplay between band strength and erosion may also be influent on nodule shape.

In the Bollène quarry, all calcite nodules occur in association with the DBs, and in particular with the NW-SE/NNW-SSE set (Fig. 6b). At this site, we observe complex relationships among multiple deformational and diagenetic events. Timing of bands and nodules is inferred from crosscutting relationships. There is no evidence of low-angle ESE-WNW reverse-sense DBs crosscutting the cement nodules, whereas NE-SW to ENE-WSW trending strike-slip DBs offset the reverse-sense bands, the NW-SE bands, and the NW-SE-trending cement nodules (Figs. 6b and 7). The localization and parallelism between DBs and cement is similar in the two field sites, with the exception that NW-SE-trending nodules and DBs in Bollène are not superposed. Here, DBs are always overprinted by cement but the spatial overlap between DBs and 810 nodules (Fig. 7e) is unusual. Nodules occur in compartments that are spatially confined by DBs zones. Tabular nodules and clusters of spherical nodules are oriented with the major axis parallel to the NW-SE DBs (Figs. 6b and 7a). The NW-SE bands do not crosscut the cement, therefore, calcite cementation occurred between the NW-SE bands formation (Pyrenean contraction or Oligocene-Miocene extension?) and the NE-SW strike-slip bands (Miocene-Quaternary age Alpine shortening?). Please refer to Supplementary Material (S1) for details on how DBs relate to the tectonics of the area. Microstructural observations show that the dominant phase of intergranular calcite cement encloses the grains within the nodules and it overprints only a proportion of the transgranular microfractures at grains contact points. All microfractures in the nodules are filled by a cement that is in continuity, same texture and CL characteristics, with the pore-filling cement outside the grain. Unfilled microfractures (Fig. 11b), were not connected to the poral network and they were potentially quickly isolated by the calcite mineral growing in the pore space. It is less likely that they formed after cement precipitation, 820 otherwise the cement would have been broken.

7.2 Role of deformation bands on fluid flow and diagenesis

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The localized diagenesis observed in form of nodules at Loiano and Bollène provides evidence for the effect of structural heterogeneities, such as DBs, on fluid flow in porous sandstones (Eichhubl et al., 2004, 2009; Balsamo et al., 2012; Philit et al., 2015; Del Sole and Antonellini, 2019; Pizzati et al., 2019; Del Sole et al., 2020). The petrophysical properties (porosity, permeability, capillary entry pressure) of DBs influence fluid flow and localize diagenesis and cement precipitation.

A marked grain-surface roughening and reduction of grain-size, porosity, and pore-size characterize the DBs presented in this work. In *Loiano*, the combined effect of cataclasis and compaction in the DBs causes porosity reduction by one order of magnitude, permeability reduction by three orders of magnitude, and advective velocity reduction by 2 orders of magnitude with respect to the host rock (Del Sole and Antonellini, 2019; Supplement S3). Similarly, DBs in the *Bollène*

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860 quarry have lower permeability (up to 3 orders of magnitude) and porosity (up to 50%) (Ballas et al., 2014; Supplement S3) when compared to the host rock. Cataclastic DBs negatively affect flow tortuosity in reservoirs and produce capillary barriers that severely baffle the flow at the reservoir scale and limit cross flow between host rock compartments (Harper and Mofta, 1985; Edwards et al., 1993; Lewis and Couples, 1993; Antonellini and Aydin, 1994; Leveille et al., 1997; Gibson, 1998; Antonellini et al., 1999, 2014; Sternlof et al., 2004; Rotevatn and Fossen, 2011; Ballas et al., 2012; Medici et al., 2019; 865 Romano et al., 2020). Smaller pores within bands result in higher capillary forces than in the host rock. This may cause higher water saturation within the bands with respect to the host rock (Tueckmantel et al., 2012; Liu and Sun, 2020), Higher degree of flow tortuosity (reduction in pore interconnectivity) and lower porosity and permeability within the bands may increase the fluid retention time regardless of the water-saturation conditions (Antonellini et al., 1999; Sigda and Wilson, 2003; Wilson et al., 2006). Recently, Romano et al. (2020) documented with single and multiphase core flooding experiments, that cataclastic bands can strongly influence the fluid velocity field. Other authors (Taylor and Pollard, 2000; Eichhubl et al., 2004) recognized that a slower rate of solute transport relative to the fluid within the bands causes the formation and local perturbation of diagenetic alteration fronts. In light of these considerations and the temporal and spatial relationships between bands and cements obtained from field and microstructural observations, we propose a model for selective cement precipitation associated with DBs. In our model we assume a reservoir in saturated condition (see also Sect.

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We propose that the presence of the bands in *Loiano* and *Bollène* slowed down the fluid flow. This happens because the bands have lower permeability and transmissibility, a higher degree of tortuosity (i.e. lower pore size) and reduced section area available for flow (i.e. lower porosity) with respect to the host rock (Ballas et al., 2014; Del Sole and Antonellini, 2019; Del Sole et al., 2020; see also Supplement S3). In *Loiano*, the "slow down" effect would be more pronounced when considering the normal-to-DB flow than the parallel-to-DB one given that normal-to-DB permeabilities are lower (1 order of magnitude in average) when compared to parallel-to-DB ones (Del Sole et al., 2020). Cataclasis has competing effects on advective flow velocity; it causes (i) an increase of flow velocity linked to the porosity reduction and (ii) a decrease of the hydraulic conductivity (if the hydraulic gradient does not change). The decrease of hydraulic conductivity (3 orders of magnitude; Del Sole and Antonellini, 2019) dominates over the flow velocity increase caused by porosity reduction (1 order of magnitude; Del Sole and Antonellini, 2019). As a result, there is a net decrease in advective flow velocity in the DBs. A reduction in flow velocity (i.e. slower flow path in the DB with respect to the host rock) might increase the residence time of the fluid migrating through the reactive material (see next paragraph), enabling precipitation to take place (Bott, 1995; Walker and Sheikholeslami, 2003). This "slow down", alone, could represent one of the first trigger to promote preferential cement precipitation within the band or in its proximity as observed in the field.

A second mechanism responsible for cement nucleation in association with DBs would be the presence of highly reactive crushed and pervasive fractured siliciclastic grains within the cataclastic DBs (e.g. Lander et al., 2009; Williams et al., 2015). The comminuted material of the DBs owns a large amount of reactive surface area (nucleation spots) and very tiny pores spaces among the crushed grains. With these conditions, cement precipitation requires less free energy to occur

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(Wollast, 1971; Berner, 1980) whereas greater cement abundances (e.g. Walderhaug, 2000) and faster rates of cement emplacement (Lander et al., 2008; Williams et al., 2015) are promoted. This mechanism has already been proposed to explain the presence of cement within the bands pore space and contrast in the degree of cementation between the bands and the surrounding rock (Antonellini et al., 1994; Knipe et al., 1997; Fisher and Knipe, 1998; Milliken et al., 2005; Philit et al., 2015; Del Sole and Antonellini, 2019; Pizzati et al., 2019). This mechanism may be relevant for *Loiano* where the calcite cement fills small pore spaces among fresh quartz and feldspar surfaces created during fracturing. This process can explain why in most cases DBs are more cemented than the surrounding host rock. The low-porosity angular fine-grained cataclastic matrix within the bands offers a lower energy barrier for cement nucleation (Wollast, 1971; Berner, 1980), so that it is not necessary for fluids or brines to reach carbonate saturation for cement precipitation at grain contacts (De Yoreo and Vekilov, 2003). On the contrary, this process was less relevant in the *Bollène quarry* where the bands are not cemented by carbonate and the cementation is localized in compartments between zones of bands rather than within them.

A third mechanism could have worked in conjunction with the presence of more reactive fine-grained comminution products to promote cementation in the DBs in *Loiano*. According to their experiments on analog fault gouge, Whitworth et al. (1999) suggested a membrane behavior for faults in sandstones during cross-fault flow and solute-sieving-aided calcite precipitation. A membrane effect and solute-sieving by faults may locally increase the concentrations of components needed for calcite cementation (e.g. Ca and bicarbonate) and induce precipitation. The DBs could have acted as a semipermeable membrane in baffling chemically reactive flow and favor cement precipitation. This process may explain a higher concentration of cement along the DBs in nodules, and the asymmetric distribution of cement on one side of DBs (upstream side; Figs. 4c, e and 9a, e). An analogous mechanism was proposed by other authors to explain the occurrence of preferred and asymmetric distribution of the authigenic alterations (carbonate and clay cements, Eichhubl, 2001; hematite bleaching, Eichhubl et al., 2004) on the upstream side of DBs in sandstones.

Other factors that may have locally favored (the initiation of) calcite cement precipitation, are the growth of cement on detrital grains (*Loiano*, Fig. 10e; *Bollène*, Fig. 11c) and the presence of broken detrital carbonate clasts (e.g. shell fragments) that act as a "seed" (cement nucleation sites) (e.g. Bjørkum and Walderhaug, 1990). The latter case was observed in *Loiano*, mainly in bedding-parallel nodules (Fig. 9c, d). The mechanisms discussed above explain how and why cement precipitation would occur within the band and in its proximity, as observed on-site. Our field observations confirm the theoretical and flow simulations as well as the analog experiments which demonstrated that DBs can negatively affect the fluid flow in porous sandstones (e.g. Rotevatn and Fossen, 2011; Antonellini et al., 2014; Romano et al., 2020) and enhance cement precipitation (e.g. Lander et al., 2009; Williams et al., 2015).

7.3 Structural diagenesis scenario for carbonate nodules formation

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We will integrate the petrographic observations and stable isotopes characterization of cements with the meso-scale spatial organization and the micro-scale textural relationships between nodules and DBs to discuss the geochemical conditions and potential fluid sources that controlled the formation of carbonate nodules in the studied areas.

In Loiano, the first calcite cement to precipitate is the intraskeletal and pore-lining cement associated with bioclasts in bedding-parallel nodules (Fig. 9c-d). The cement fabric and textures, circumgranular dogtooth and void-filling drusy mosaic, and the dominant bright-orange CL of calcite associated with bioclasts could suggests a meteoric phreatic environment with reducing conditions (low pO₂) (Longman, 1980; Moore, 1989; Hiatt and Pufhal, 2014; Adams and Diamond, 2017). Drusy calcite spars can result from replacement of aragonite in bioclasts that occur in meteoric environments (Flügel, 2013). The second, more pervasive phase of cementation, consists of the intragranular cement observed in all the nodules. The mosaic of blocky sparite with coarse crystals and homogeneous distribution, point to meteoric phreatic conditions (Longman, 1980; Flügel, 2013; Adams and Diamond, 2017). In contrast, the dominant bright cathodoluminescence response suggests an environment with reducing (low pO₂) geochemical conditions. Cement zonation could be triggered by the shifting from more reducing (bright CL) to more oxidizing (dark-CL) conditions and vice versa (Barnaby and Rimstidt, 1989) due to water table fluctuations (Li et al., 2017). The intergranular cement pattern is analogous in DBs-parallel nodules and bedding-parallel nodules meaning they probably formed in a similar meteoric phreatic environment. Phreatic meteoric conditions for the nodules formation point to a shallow diagenesis, and it is consistent with the shallow burial depths estimated for the Loiano Sandstones (see Sect. 7.1).

The negative, depleted $\delta^{13}C$ and $\delta^{18}O$ values found in both types of nodules (Fig. 12a) are consistent with a meteoric environment of precipitation (Nelson and Smith, 1996). DBs-parallel and bedding-parallel nodules show a similar composition for $\delta^{18}O$, however bedding-parallel nodules have more depleted $\delta^{13}C$ values. This <u>unight</u> reflect a higher contribution of organic carbon from soil-derived CO₂ (Hudson, 1977), <u>possibly indicating that bedding-parallel nodules</u> formed in shallower conditions with respect to DBs-parallel nodules. Another explanation <u>is</u> that the two types of nodules were formed by different episodes of water income with different (external) environmental conditions. The difference in isotopic composition between these two types of nodules, indeed, suggests different cement precipitation timing and water compositions as proposed by McBride et al. (1995) and Milliken et al. (1998).

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Cementation pattern can be used to infer the paleo-fluid flow direction at the time of calcite precipitation (Mozley and Goodwin, 1995; Mozley and Davis, 1996; Cavazza et al., 2009; Eichhubl et al., 2009; Balsamo et al., 2012). Bedding-parallel nodules organization within the local rock sequence supports a phreatic condition for these nodules. Clay horizons are considered sealing features at least at short-time scales, so that the formation of bedding-parallel nodules in sand levels below and/or confined in between clay levels let us infer that fluid circulation was not occurring in the vadose zone. Bedding-parallel nodules, then, could have formed by lateral fluid circulation in saturated conditions (Fig. 13a). The occurrence of preferential cementation in coarser sediments is more macroscopic evidence for cementation in phreatic environment, due to higher saturated permeability and larger solute flux (Mozley and Davis, 1996). DBs-parallel nodules, however, indicate that local fluid circulation was mostly driven by these structural heterogeneities. The different spatial

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arrangements between DBs and nodules in Loiano make the paleo-fluid flow direction reconstruction complex. The asymmetric distribution of cement in some nodules associated with DBs can be also explained by lateral fluid circulation (Fig. 13a), and the accumulation of cement would result on the upstream side of the DBs (Fig. 4c, 9, and 13a). In other cases, cement is roughly symmetrical with respect to the bands, or it is placed in the zones where conjugate bands intersect (Figs. 4b, 5c, and 13a). The most likely interpretation is that both lateral flow in saturated conditions and "direct" meteoric infiltration from the surface, and percolation through the rock succession, contributed to the formation of nodules in Loiano (Fig. 13a).

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The calcite source (i.e. diffusive supply of Ca²⁺ and HCO³⁻), possibly derives from the infiltration of CaCO₃saturated meteoric fluids carrying soil-derived CO₂ (Hudson, 1977; Nelson and Smith, 1996), and/or it is autochthonous deriving from detrital carbonate grains in the sandstone layers or intra-formational deriving from shale beds and calcite-rich clays layers (McBride et al., 1995; Milliken et al., 1998). In both the scenarios, calcite precipitates where fluid flow slows down in proximity to zones of DBs (DBs-parallel nodules) and low conductivity layers (bedding-parallel nodules). McBride 010 et al. (1995) suggest that calcite precipitation along faults (DBs) in Loiano was induced by the mixing of locally derived formation water with meteoric water introduced along the faults or by a loss (exsolution) of CO2 along the fault zones. These mechanisms, however, assume that DBs were conductive to fluid flow. This hypothesis disagrees with our measurements of the DBs hydraulic behavior (Del Sole and Antonellini, 2019; Del Sole et al., 2020). More likely, carbonate DBs cementation resulted by CO₂-saturated groundwater (Fig. 13a). We cannot exclude the role of active normal faults in the area (Picotti and Pazzaglia, 2008; Picotti et al., 2009; Fig. 2a), that might have had a control on regional subsurface fluid circulation. These faults could have cut through top/bottom seals and driven fluid migration from top/underneath aquifers (Fig. 13a). Episodic fault activity can also favor (episodic) horizontal fluid migration along layering at the time of faulting, and possibly explains the occurrence of nodules (Fig. 13a) and their different isotopic signature (Fig. 12a). From our observations, we can say that the selective cementation process in the Loiano Sandstones depends on "regional" hydrological factors (e.g. topographic gradient, bedding, faults?) coupled, locally, to the presence of DBs.

In the Bollène quarry, the relative timing of DBs formation and cementation in the Turonian Sandstones is complex to unravel. Carbonate cementation occurred in between distinct deformation phases with multiple DBs formation (see Sect. 7.1). The dominant dark cathodoluminescence pattern and homogeneous distributed poikilotopic spar texture suggest an oxidizing (high pO₂) meteoric phreatic environment (Longman, 1980; Moore, 1989; Flügel, 2013; Hiatt and Pufhal, 2014). 025 The zonation is induced by unsteady geochemical conditions, and the bright-orange CL growth sub-zones could be related to stages with more reducing conditions (Barnaby and Rimstidt, 1989; Hiatt and Pufhal, 2014). The invariably negative, depleted δ^{13} C and δ^{18} O values of nodules in Bollène are consistent with a meteoric environment in a continental setting (Nelson and Smith, 1996). Maximum burial depth of the Turonian sandstone was estimated, through stratigraphic constrains, to be 400 ± 100 meters (Ballas et al., 2013; Soliva et al., 2013). This data supports the shallow conditions for nodules diagenesis in Bollène. The phreatic environment is more probable given that in vadose conditions we should have observed meniscus cements, and because massive calcrete such as observed in the study area generally form in groundwater

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environment (e.g. Alonso-Zarza, 2003). In the vadose zone, besides, DBs would enhance unsaturated flow relative to the host rock (Sigda et al., 1999; Wilson et al., 2006; Cavailhes et al., 2009; Balsamo et al., 2012).

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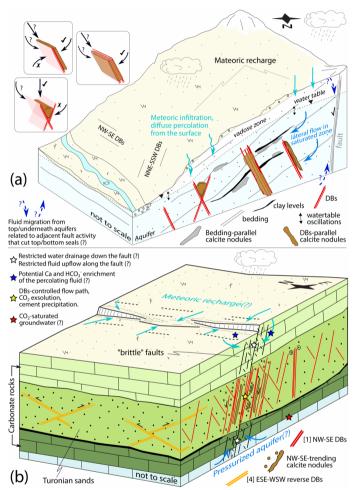
Field evidence suggest that clusters of low permeability DBs in Bollène impeded cross-fault flow since no cement was found in superposition with the DBs. The presence of nodules in between the DBs clusters implicates that the DBs forced the fluid flow and localized the diagenesis in parallel-to-bands compartments. This evidence and the fact that nodules are homogenous along their elongation direction discredit the hypothesis of lateral flow. The cement could have been originated from a (i) downward fluid flow directly from infiltration of meteoric waters, or (ii) an upward flow of basinal fluid (pressurized aquifer) along fractures and faults pathways in the carbonate rocks (Fig. 13b). In both cases, the water flow was potentially driven from the vertical continuity of DBs clusters, that have acted as the propagation features of faults in overlying (i) or underlying (ii) series and aquifers (Fig. 13b). This scenario might explain why the cement is found only in association with the NW-SE DBs. In both cases (i) and (ii), the constituent necessary for the precipitation of cement in nodules (i.e. Ca and bicarbonate) would come from the surrounding carbonates. Above the Turonian sandstones there are several carbonate layers in the Upper Turonian and Santonian interval (Fig. 2c; Ferry, 1997), whereas below there are 070 carbonates belonging to the Jurassic and Cretaceous series (Fig. 2b, c; Debrand-Passard et al., 1984). In the first case (i) continental meteoric waters saturated with meteoric carbon dioxide have dissolved the necessary constituents along their path through the rock succession toward the high-porosity Turonian Sandstones. The water percolation through the soil favored fluids acidification. Similar depleted δ^{18} O values between nodules and cement from the calcrete level (Fig. 12b), support the (i) hypothesis, and they may have originated from similar surficial cement source from downward water flow in 1075 association with variations of bicarbonate concentration and/or pH in the water table. In the second (ii) hypothesis nodule cement resulted from CO2 exsolution during the upward flow of basinal brine or CO2-saturated groundwater in a pressurized aquifer.

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Figure 13. Generalized conceptual model for calcite nodules precipitation in the two study areas: (a) Loiano and (b) Bollène. See text (Sect. 7.) for details. The inset sketches in (a) show possible paleo-fluid flow direction at the time of calcite precipitation for different "DBs-nodule" configurations.

7.4 Implications for subsurface fluid flow, reservoir characterization, and resources development

Models for calcite cementation are of fundamental importance for predicting sandstone and fault-rock properties such as porosity, permeability, compressibility, and seismic attributes. In Loiano, zone of DBs has acted as fluid flow baffles. First, they slowed the fluid flow and localized cement precipitation, acting as areas of preferential cementation in otherwise excellent porosity sandstones. The resulting diagenetic products enhance porosity and permeability reduction 100 caused by cataclasis, further affecting subsequent fluid circulation. The presence of structural-related cement in the form of concretions i) strengthens the rock volume, ii) degrade porosity and permeability increasing the buffering effect or sealing capacity of zone of DBs, and iii) impart mechanical and petrophysical anisotropy to the host rock (Del Sole et al., 2020). We think that it is important to consider the possibility of concretions to form in association with faults within siliciclastic reservoirs, especially where these structures (DBs) are below seismic resolution (e.g. Del Sole et al., 2020). It is also critical to understand structural diagenesis heterogeneities (SHD) spatial organization, extension, continuity, density, their hydraulic role in terms of fluid flow circulation as well as their mechanical influence on the host rock. This information should be included in a robust reservoir characterization and, in general, it is beneficial during geofluids exploration and energy appraisal, resources development strategies (groundwater, geothermal, hydrocarbon), well production, reservoir simulation modeling, geomechanical evaluation of a drilling site, and other environmental and industrial operations (e.g. waste fluid 110 disposal; groundwater contaminants; geologic CO2 sequestration; Enhanced Oil Recovery [EOR]). The incorporation of this information into aquifer/reservoir (flow) models requires implicit representation of the SDH network and the upscaling of its (structural and petrophysical) properties (e.g. Fachri et al., 2013; Antonellini et al., 2014). When the cementation is heterogeneous, such as in the examples presented in our work, it could be difficult to model and predict, especially when data are spatially discontinuous (e.g. wells). In these cases, outcrop-based studies allow continuous and more reliable reconstruction of the cement distribution. The characterization of SDH network distribution (e.g. Del Sole et al., 2020) allows to predict where (i.e. location and volumes) and how (i.e. spatial organization) the reservoir compartments are arranged and how the fluid circulation can be affected. The kind of study that we present here might be helpful to extract those statistical parameters necessary to implement reservoir studies that account for heterogeneity in petrophysical properties and their association with seismic/subseismic structural heterogeneities.

8 Conclusions

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In this contribution, we <u>present</u> two examples of structural control exerted by deformation bands on fluid flow and diagenesis recorded by calcite nodules strictly associated with deformation bands. The objective of this research was to constrain the <u>role</u> of deformation bands in <u>affecting the flow pattern</u> and in localizing cement precipitation in porous sandstones, as well as to elucidate the mechanisms involved in these processes. The major results of our study can be summarized as follows:

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(1) In both <u>study sites</u>, one or more sets of DBs precede, and control selective calcite cement precipitation in the form of nodules. The <u>later</u> localization of cementation along these structural features results in a complex and spatially heterogenous cementation pattern (SDH).

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- (2) Selective cementation of nodules associated with DBs indicates interaction between deformation structures, fluid flow, and chemical processes. The volumetrically significant presence of cement (10-25% of the exposed outcrops volume) indicates that fluid flow and mass transport have been strongly affected by the presence of low permeability DBs.
- 145 (3) Three main processes are discussed to explain selective carbonate cementation associated with low permeability DBs. (i)

 The DBs slow down the advection velocity and promote cement precipitation in the low velocity zone. (ii) Solutesieving across the DB (membrane effect) promotes Ca and bicarbonate concentration increase on the upstream side. (iii)

 The high concentration of nucleation sites on the fine-grained comminution products with increased reactive surface
 area of the pore-grain interface in the DB triggers cement precipitation and fast growth rates. Our hypotheses are
 supported by field and microstructural observations and petrophysical data.
 - (4) In Loiano, mechanisms (i) through (iii) of bullet (3) likely contributed to selective cement precipitation within the bands and in their proximities, and asymmetric cement distribution with respect to the bands. In Bollène no clear superposition among bands and cement was observed and only the first mechanism (i) applies. Here, the clusters of bands acted as hydraulic barriers to cross-flow, thus compartmentalizing the fluid circulation and localizing diagenesis in volumes arranged parallel to the bands.
 - (5) In both areas, cement texture and cathodoluminescence patterns, and their invariably negative, depleted δ¹³C and δ¹⁸O values suggest a shallow meteoric environment for nodules formation,
 - (6) In a framework of late-stage diagenesis (post-DBs formation) and saturated conditions (meteoric phreatic environment), the processes commonly employed to explain focused fluid flow and preferential cement precipitation associated with DBs, such as "transient dilation" and "capillary suction" (see Sect. 1), appear to be not pertinent, In Bollène and Loiano the DBs buffered and compartmentalized the fluid flow and localized the diagenesis.
 - (7) Further analyses, such as flow simulations and cement precipitation modeling, are deemed necessary to further explore micro-scale fluid flow and diagenetic mechanisms that drove preferential calcite cement precipitation along DBs in porous sandstones.
- 165 (8) DBs control flow pattern and affect how diagenetic heterogeneities are distributed within a porous sandstone. The association of diagenetic cementation with DBs further increases the flow buffering potential of these structural features.

 It also creates SDH that impart a mechanical and petrophysical anisotropy to the host rock volume and can seriously affect the subsurface fluid circulation in porous sandstones. These features should be considered during reservoir characterization especially where SDH are below seismic resolution.
- 170 Data availability. Most of the data produced and used to write the paper are contained in it. More detailed information will be made available on request by contacting the corresponding author.

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Author contribution. MA and LDS conceived the paper. LDS collected and processed field and laboratory data, provided their interpretations, drew the figures and wrote the manuscript, and did the revisions. RS and GB contributed to field work in Bollène study site and to cathodoluminescence data interpretation. MA, FB, and GV participated to field work in Loiano study site. All authors actively participated in discussing the results and drawing the conclusions, and critically revised the

Competing interest. The authors declare that they have no conflict of interest.

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