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Interactive comment on "Regional-scale paleofluid system across the Tuscan Nappe – Umbria Marche Arcuate Ridge (northern Apennines) as revealed by mesostructural and isotopic analyses of stylolite-vein networks" *by* Nicolas Beaudoin et al.

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Anonymous Referee #1 Received and published: 7 June 2020 The authors present an interpretation of the paleofluid flow history across the Tucscan Nappe, constrained by a multiproxy study. They integrate detailed structural analysis of stylolites fracture networks with isotopic (O and C stable isotope, Sr isotopes, clumped carbonate isotopes) and some limited U-Pb dating of calcite veins, cements, and fault coatings. Using the dates from this study in concert with other timing and burial constrains, the authors reconstruct a âĹij12 my history of fluid flow events that are linked to deformation. They

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identify evidence for both closed fluid systems and the open system flow of hydrothermal fluids.

This is an interesting and comprehensive evaluation of the role and evolution of fluids during regional tectonic compression. The interpretations appear mostly supported by the data, the data is of good quality, and the methods thorough in most cases. The data are high quality and this is certainly appropriate for publication in Solid Earth, and will be of interest to structural geologists, geochemists, and those working on problems in regional tectonics. One of the big contributions is the careful linkage between deformation and closed versus open-system fluid-rock interaction.

However, the reviewed version requires moderate revisions to improve the impact of the paper. I outline the major issues here, and then provide some line-by-line comments below.

Writing: This paper needs a thorough technical edit paying particular attention to grammar, tense, subject-verb agreement, over-reliance on the passive voice, general clarity of sentences. Also, it still reads like it was prepared by multiple authors with different styles, and without careful review. In the line-by-line comments I point out many of the grammatical problems, but by no means are these comprehensive.

Author response: We agree the submitted version of the paper was prepared by several authors, and in spite of our efforts to make it seamless to read, results were below our expectation. The new version of the manuscript has been edited with much more care, following both's reviewers specific comments and going further to ensure internal consistency on multiple levels, like style, results report, and organization.

Organization: The presentation style of method-results, method -results, etc. is quite distracting to this reviewer. The authors state in the paper that this is intentional with the goal of improving clarity. However, in order to follow all of the different and related data sets, it is very distracting to switch gears to reading another methods summary. True, I could skip over, but I would rather have the option of reading a single methods section,

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and a single results section. Also, this has resulted in some of the methods sections actually containing results, so they are merging together in some places. This is a relatively complicated data set to understand as a reader, so the organization needs to be strong.

Author response: The previous organization was the results of a bad choice of organization, the new version now separate clearly the methods from the results, and also the interpretation from the discussion. We believe that the classic organization methods-results-interpretation-discussion make the manuscript easier and clearer to read.

Over-reliance on “isotopic jargon”: For clarity to non-experts and experts alike, it is important to use proper language when presenting and interpreting the isotopic results. For example, the stable isotope community prefers writing "δ18O values”. Avoid use C2 of depleted, enriched, heavy, and light. . .be specific. If using enriched or depleted, please be specific as to what is enriched with respect to what. Similarly, for the Sr - isotopes. . ..avoid the “radiogenic” term unless being specific – for example, rather than writing that a sample is less radiogenic than another, just provide the values.. Also, the term “signature” is really overused in this paper. Be careful with its use. A stable isotope delta value is not a signature. . .avoid “δ18O signature of X ‰$'$.$ItisOKtousephraseslike“meteoricisotopicsignature"$

Author response: The form of the geochemical part of the paper has been edited to avoid using jargon, the term signature has been kept only at two places in the manuscript, where it make sense as it refers to the fluid reservoir and not to measurements. The other occurences were replaced by values. The term radiogenic has been removed as well, and values were provided and compared as suggested.

Adding numeric ages to Geologic Ages: For those of us who do not work in the Miocene, referring to the Late Aquitanian and Messinian time lacks clarity. Please include the numeric ages as well. One, this helps the reader piece together the geologic

history of your study, and it teaches some of use more details of the time scale!

Author response: Thank you for this suggestion, we edited the text accordingly to add the absolute ages when we use a stage of the geological time scale.

Lack of adequate support/discussion for interpretations: The interpretation of the source fluids and degree of water-rock interaction are just stated. There is little discussion or justification and no examples from the literature. Please justify your interpretations. Also, the carbon isotope data is not discussed.

Author response: The fact we interpret the veins that show a d18O values higher than their host rock d18O values as witnessing an interaction between reservoir fluids and host rock is now extensively discussed in the manuscript. That interpretation also partly relies on the d13C values, that were not explicated in the previous version of the study, leading to confusion. Also, the wording “basinal contamination” we used in that section was unfortunate, we meant that the precipitating fluids where formation fluids, evolving after various degrees of interaction with host rock, likely related to migrations through the basin. The complete text is located lines 558-589, but the specific case of interpreting our data as related to the degree of water rock interaction is a classic interpretation proposed since Clayton et al., 1966. It is now discussed line 581-589 as follow: “Indeed, if considering an environment with limited connection between reservoirs and no implication of external fluids, i.e. where fluids are sourced locally from the marine carbonates, the fact that in the western part of the UMAR, the δ18O values of the veins are significantly more positive than the δ18O values of their host-rocks implies that fluids that precipitated were enriched in 18O isotope relative to the original formational fluid. Such a fractionation is usually interpreted as the result of rock dissolution during fluid migration (Clayton et al., 1966; Hitchon and Friedman, 1969). This is further supported by the δ18Ofluids values derived from Δ47CO2 measurements, that are higher in the Monte Subasio (8 to 16‰ VSMOW, Fig. 8) than in the rest of the UMAR (from 0 to 8‰ VSMOW, Fig. 8), witnessing a higher degree of reservoir fluid-rock interaction in the western part of the UMAR.”

U-Pb dating – this is outside of my expertise, but my read is that these veins only yielded limited information? Author response: Indeed, as we stated in the manuscript – and emphasizes more in the new version (line 462-464)- veins did not hold enough U, or were too rich in Pb, for the ratio to be favourable to return an absolute age. Only the faults had a U/Pb ratio high enough to return an age. The fact that veins are less favourable for U/Pb dating in the UMAR is out of the scope of this study, but we refer to a recent review paper (Roberts et al., 2020) where such observation (not limited to UMAR) is tentatively discussed. Clumped isotope data: The $\Delta 47$ results need to be added to Table 2 or 3, and presented in the results. Author response: Thank you for pointing that out, the analytical results of D47CO2 are now reported with uncertainty in table 3 and are presented in the text from line 438 to 443. The corresponding d18O and d13C values were reported in Table 2 and plotted on Fig. 6. We want to highlight that during the review time, we added 3 more samples analysed with D47 CO2 in the Monte Catria (2) and in the Monte Conero (1), extending the across strike and along strike representativity of our dataset. line by line 40-48: Paragraph needs strengthening. . .currently a 2 sentence paragraph with a really long second sentence. Suggest breaking this down for more impact. We rephrased this paragraph which was too hard to read indeed, it is now line 61-78.

53: comma before and Edited accordingly line 51

87: Define “LPS” here Done line 85

90 – 91: mixing tense: are and was in same sentence Edited line 87-89

100: This reviewer cautions the claim of “provides for the first time”. . .this is rarely true. We removed this statement

120-121: please provide numeric dates along with “Late Aquitanian”. . .etc. Also, should Late be capitalized? Edited accordingly, ‘late’ is not capitalized anymore and ages are provided all throughout the text (line 117)

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128: consider different and more active voice for “has been considered for long” We replaced by “UMAR was considered” (line 126)

144: Replace “Nowadays” with Currently; “undergoes” with “is experiencing” Edited accordingly lines 141-142

168 – 170: This reviewer finds this format difficult to follow. The manuscript has been reorganized.

179-180: This is actually a result, not a method. Thank you for pointing that out, this sentence is now in the result section (line 360)

186: need parentheses around sigma 1 Edited accordingly

197: How did you do the correction due to bedding dip – that is what program, or by hand. We edited the text to make this information available (line 189-194): “In order to capture the mesostructural and fluid flow evolution at the regional scale during layer-parallel shortening and folding, we gathered the statistically most representative fracture data by structure, regardless of the structural complexity in the individual folds, and corrected them from the local bedding dip using an opensource stereodiagram rotation program (Grohmann and Campanha, 2010) to discriminate between early and syn-folding features.”

212: Can be gathered? consider different word choice 221: New paragraph at “Finally” For these two remarks, we reorganized this result section relative to the structural approach, in order to make it clearer.

255: Perhaps a complicated equation like this should be a numbered one. OK, this is now equation (3)

288: Oxygen and Carbon should not be capitalized We corrected accordingly

293 – 303: need a method citation; specify dual inlet or continuous flow; probably not 105% or would crystallize. . .or did you measure density? How long were samples

equilibrated at 90C? The protocol is a very standard protocol but I am afraid there is no dedicated publication for it with this machine at the SUERC. However we did edit the text to add the fact it was a dual inlet trap, and the duration of the sample equilibration at 90°C (30 min for calcite and 45 min for dolomite). The solution of H3PO4 is 103%, derived from density measurement indeed. (lines 257-268)

306: avoid using "signature" when reported delta values Done here in everywhere in the text.

307: VPDB; report consistent precision (-5.28 and 0.40 or -5.3 and 0.4) – based on your methods these should be reported to one decimal. Done here in everywhere in the text.

309: Delta values, not isotopic signatures 313: VPDB Done here in everywhere in the text.

313, 314, 317: do not used "depleted". . . the delta values are lower or higher The new version does not use isotopic jargon such as depleted.

323-328: this method section seems a little incomplete compared to others. . .any citations on the method? What do you mean by "Mg-samples". How were samples dissolved and what kind of column chemistry was conducted to create solution that is loaded onto filaments? This section has been edited completely and is much more complete now (lines 270-281). The Mg-samples was a mistake. The specific dissolution process is reported as follow (line 273 onwards) "The samples were then dissolved in ca. 1 ml of calibrated 2.5M HCl in preparation for column chemistry, and centrifuged. Samples were pipetted onto quartz-glass columns containing 4mls of AG50x8 cation exchange resin. Matrix elements were washed off the column using 48 ml of calibrated 2.5M HCl and discarded. Sr was collected in 12 ml of 2.5M HCl and evaporated to dryness."

335: "less radiogenic" is jargon. . ..stick to the values and whether they are higher or

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lower than others. . .radiogenic can be used in a discussion when referring to a source rock or fluid, etc., but not when reporting the isotope ratios. Thank you, we do now stick to the values.

342: clumped isotope section lacks citations for the methods used We now cite (line 290) as follow: “The clumped isotopes laboratory methods at Imperial College follow the protocol of Dale et al. (2014) as adapted for the automated clumped isotope measurement system IBEX (Imperial Batch EXtraction) system (Cruset et al., 2016).”

352, 353: mixing past and present tense This part is consistent now, using past time (lines 292-294)

352: carbonate = calcite, dolomite, ? Carbonate is calcite, no dolomite was used for clumped D47CO2 measurements (line 292).

375: replace “can be” with are or were depending on what tense you want to stick with Done accordingly (line 313)

375: what are the errors on computed temperatures? The 1 standard error reported in the table 3 is computed taking the following errors into consideration: the error in D47, the uncertainty in the Davies and John 2019 regression, and (for fluid) the error in d18O measured and the uncertainty in the calibration. In other words, the errors are properly propagated to your final temperature or d18Ofluid values and are reflected in the uncertainties reported. I suggest you to refer to the Davies and John 2019 paper we cite for a more in depth discussion on the calibration itself.

377: which carbonate is this fractionation factor for? It is for calcite (line 315)

382: spell out 13 Done (but for 16) line 436

381: This results section is incomplete. The data is reported in table 3, but where are the actual clumped isotope data? I cannot find them in any of the materials, just the calculated temperatures. Please provide these. Also, the text only mentions the calculated Ãř180 value for the fluids, but do you want to also report in this text something

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about the oxygen vein isotope values? Perhaps this is covered prior to the methods for this section? This is an example of how the switching between methods and results is distracting to the reader. We did not report the D47CO2 results in the previous version, but they are now in the Table 3 and presented in the text line 438 onwards.

388: include the “equation of Kim et al” We apologize for that was a mistake in citation, it is actually a fractionation equation from Kim and O’Neil, 1997, wich reads as follow 1000 lnâĄą(α)=18.030$\times$10ˆ3/T-32.420. It is reported line 447. 403: calcite should not be capitalized Edited accordingly

405 – 409: The level of detail for this method of U-Pb dating is far briefer than your second method. Please provide equivalent levels of detail. Edited accordingly line 322-332

425: define “favorable U-Pb” levels The term favourable is not strictly bound to a numerical value of the ratio. It is usually accepted the ratio should be 100 at minimum, but this depends heavily on the absolute content of U and Pb. We do not mean to provide a debatable and ad-hoc value in this paper. Please refer to Roberts and al., 2020, for an in-depth explanation.

464/465: Are these the vein sets you said you were not going to discuss further on line 211? We apologize for the confusion, we edited the lines 365-366 (former line 211) and not refer to this vein sets anywhere further in the text.

470: same comment – is this repetitive from line 211 or different? We remove this sentence.

483: do not capitalize cardinal directions Edited accordingly

484: what do you mean by abnormal burial We rephrased for the sake of clarity (line 521-522): “revealed that most of this unit locally underwent more burial because it was underthrusted below the Ligurian Nappe”

509/510: poorly worded and repetitive sentence This part has been edited and re-

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worded for the sake of clarity (line 547 onwards) : “We can therefore estimate an average duration of folding in the western-central part of the UMAR of ∼3 Ma. Knowing the oldest record of post-orogenic extensional tectonics in the UMAR is mid-Pliocene (∼3 Ma) (Barchi, 2010), we can also estimate the duration of the LSFT to ∼2 Ma.”

529: calcite? twins Yes, it is now stated lines 566-569 : “Overall, most calcite grains from vein cements show thin twins (thickness < 5 ïĄm) and rectilinear, suggesting deformation at temperature below 170°C”

533: histories This part was rewritten for the sake of clarity and to make it more convincing (line 570-607)

536: Is this sentence complete? It starts with a lower case letter This part was rewritten for the sake of clarity and to make it more convincing (line 570-607)

537: So, this is an example of where you need to provide a discussion of why a δ18O value of 5 permil supports this interpretation. Just stating this as your interpretation is not good enough. This part was rewritten for the sake of clarity and to make it more convincing (line 570-607). We believe it is much clearer now that we don’t rely our interpretation only on the value of d18Ofluids but on an array of data including Sr and 13C as well.

542: same comment This part was rewritten for the sake of clarity and to make it more convincing (line 570-607). We believe it is much clearer now that we don’t rely our interpretation only on the value of d18Ofluids but on an array of data including Sr and 13C as well.

549: Sentence that starts with “That” does not make any sense. This part was rewritten for the sake of clarity

556 – 570: This paragraph is really problematic from various standpoints. First, the writing is poor – pay attention to grammar and subject-verb agreement. The use of signature is overused. The use of depleted must be changed. Be consistent with

VPDB and VSMOW. This part was rewritten for the sake of clarity and to make it more convincing (line 570-607) 564: “characterized by negative δ18O” – so the negative sign is simply an artifact of the reference standard VSMoW. Why is a “negative” value significant here? We agree “negative” is not the good wording, please refer to the new version of the paragraph (592-607).

559 – 562: this seems contradictory as presented. . .How do “very high signatures of the fluids” correspond to “very depleted signatures” of the cements. Where is the calculation that shows this? I am looking at Figure 8 for some help here, and it seems you are overgeneralizing. From 110 – 140 C, your plot suggests both meteoric and “basinal contamination”. . .cements from -17 to âĹij-3, and fluids from âĹij0 to 15 ‰ Again, this paragraph suffered from wording issues, thanks to your comments, we managed to make it more clearer and now avoid the use of jargon. Also, “basinal contamination” was not the good wording for “degree of reservoir fluid-rock interaction”. It was corrected here, in the whole text, and in the figures.

574 – 589: Again, pay attention to grammar. The prevalent usage of depleted, radiogenic, and signature need to be altered. Also, please provide discussion and citations for the claims that “very positive O isotope signatures” can be explained by your reasoning. This paragraph just needs reworking for clarification as it is really an integral part of your big interpretations. This paragraph was edited

590-594: This is a really long and confusing topic sentence. This paragraph was edited

594-595: consider using “difference in hydraulic head” rather than “water table height difference” Done accordingly line 627

650: omit “unparalleled detail” – this is subjective to the reader We removed that statement

658: where are the “C isotope signatures” discussed? The δ13C values are mentioned in the results and seemingly used in Figure 6, but what do they mean and how do they

support the interpretations. Also where are the $\Delta 47$ data? D13C is now discussed in the interpretation part relative to the fluid system, and a figure 6c has been added to present the d13C dataset, the D47 are now in the table 3 and described in the results section related to D47.

666-667: this last sentence is true of course, but many studies have shown this. Consider a more impactful final sentence that highlight what your study has provided. We modified this last sentence to make it more specific to this study: “Beyond regional implications, the promising combination of stylolite roughness inversion and burial history reconstruction, linked to reliable past geothermal gradient appears as a powerful tool to unravel coupled structural and fluid flow evolution in fold-and-thrust belts.”

Figures Fig 8: Justify the 0 ‰ division between meteoric and basinal in text and with citations. This is certainly not always the case. There are sedimentary basins with δ18O values that are both greater and less than 0 ‰ We agree, the ‘basinal’ is not a good word for what we wanted to say, we replaced with ‘’reservoir fluid-rock interaction”, as explained in the text lines 586-588.

Fig. 11. Please add numeric dates. Done

Table 2: Do not use signature in caption. These are delta values and sr isotope ratios. Why the change in carbon isotope precision in the table? We amended the wording and modified the precision to reflect the uncertainty consistently in every table and in the text

Table 3. See prior comments on using “signature” and please provide the $\Delta 47$ data + errors. Done.

Interactive comment on Solid Earth Discuss., https://doi.org/10.5194/se-2020-64, 2020.

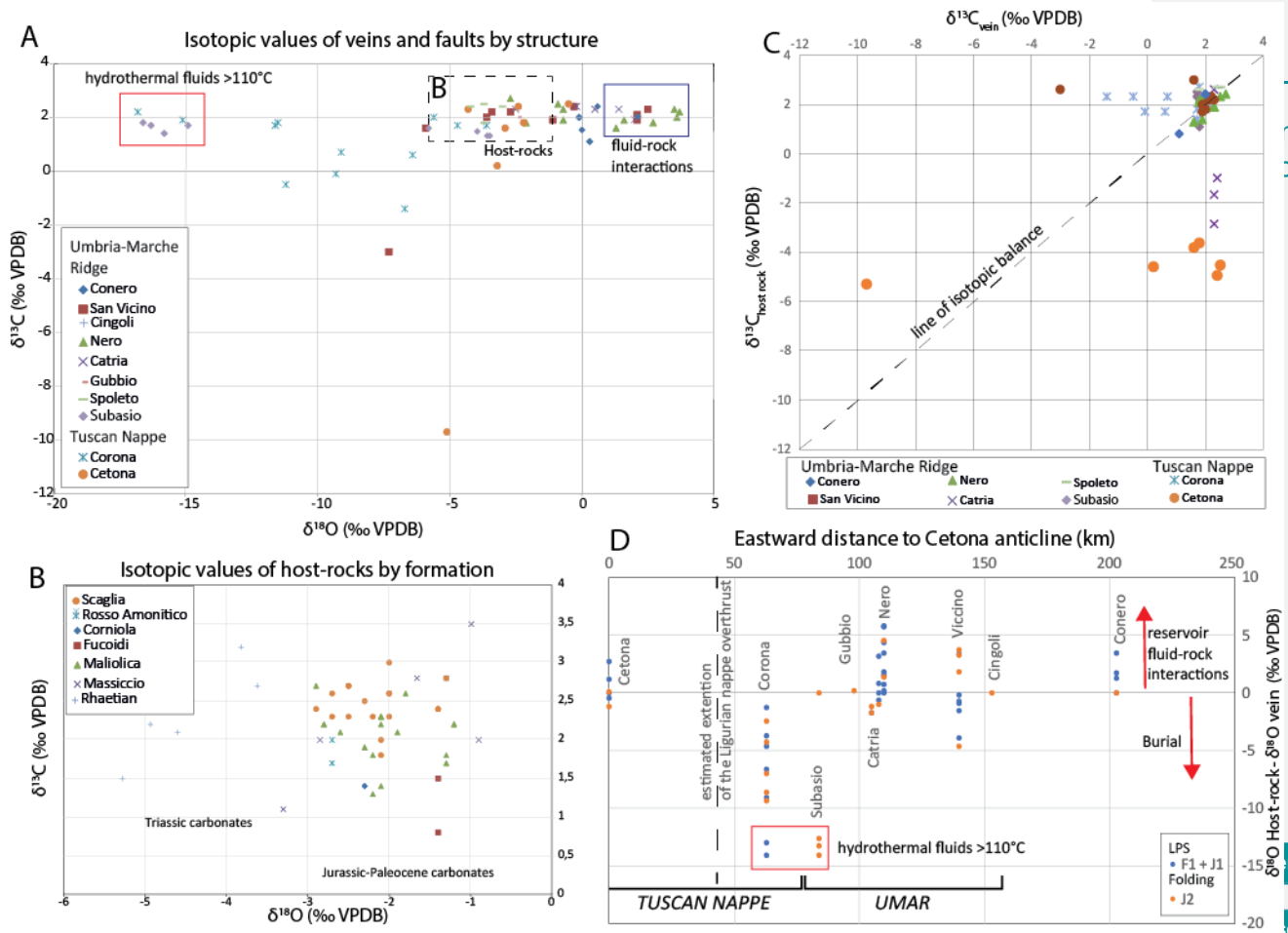

Fig. 1. Figure 6

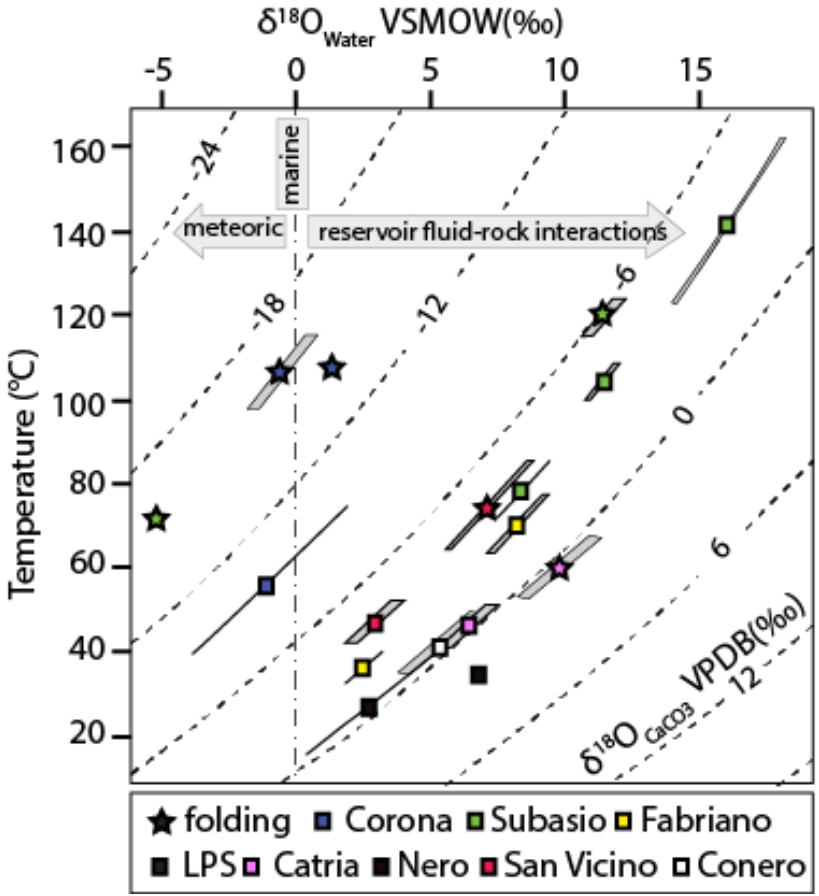

Fig. 2. Figure 8

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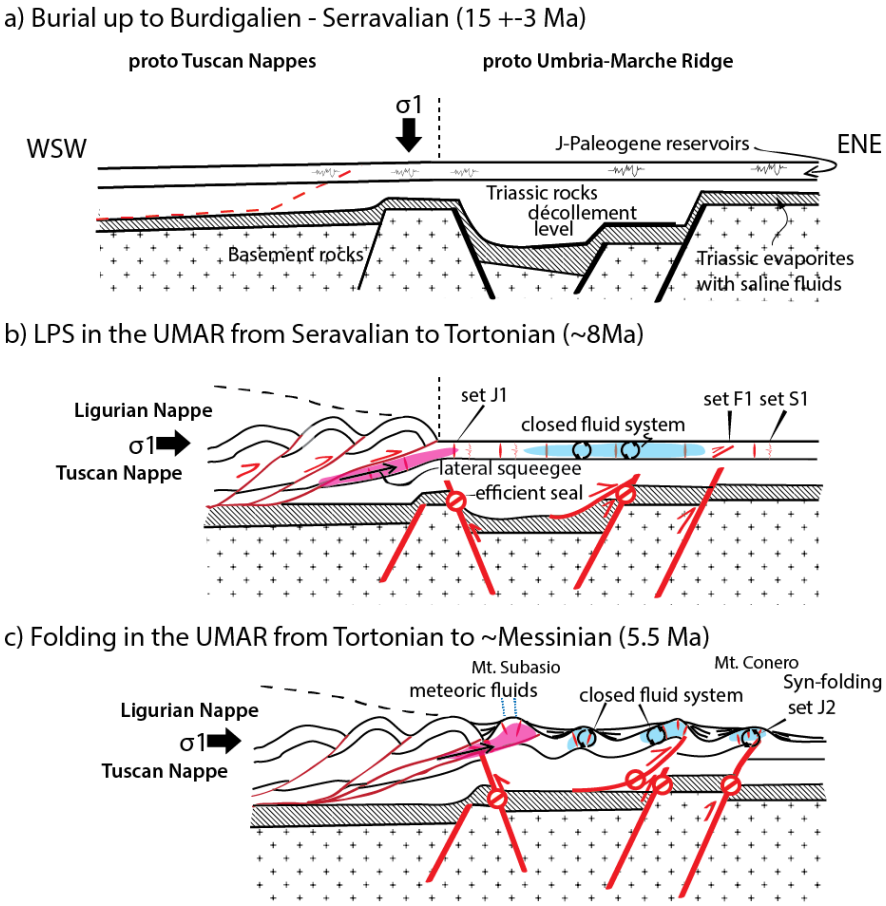

Fig. 3. Figure 11

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