Dear Editor,

Please find enclosed our revised manuscript "Precipitation of dolomite from seawater on a Carnian coastal plain (Dolomites, northern Italy): evidence from carbonate petrography and Sr-isotopes" for your consideration as publication in *Solid Earth*.

The reviewer's suggestions allowed us to improve the manuscript significantly and we are thankful for their efforts. We have already responded in a general way as part of the open discussion. Here we provide specific responses to each comment. The indicated line numbers refer to the clean version of the manuscript.

All data from the former Tables 3-6 were uploaded to the Pangaea online repository under the access number PDI-20535. The data report awaits confirmation by the administrator.

We hope you will find the responses and the changes in the annotated manuscript satisfactory.

Sincerely yours,

Patrick Meister

Referee #1 (Chris Romanek)

This manuscript was very well written and it was a pleasure to read. In fact, there were very few places where improvements could be suggested. The summary information provided in the introduction was appropriate and insightful, and the methodology and analytical procedures were explained in a straightforward way. The investigators presented convincing petrographic and geochemical evidence that supports their interpretation for the depositional environment of the Travenanzes dolomites. The Sr isotope data are remarkably consistent with Triassic seawater throughout the length of the section and they only show hints of a continental signature with the most aggressive leaching procedures. The stable O-isotope data are consistent with a marine signature and the C-isotopes demonstrate the incorporation of oxidized organic matter in texturally distinct samples. Overall, the data appear to be straightforward and easy to interpret.

We are thankful to the Reviewer for his patience to look through our manuscript again, and we are pleased about the encouraging assessment given here. Thereby we would like to highlight that Reviewer Romanek states that "the methods are explained in a straightforward way" and he does in no way suggest that the manuscript is too long or that the methods should be cut down. This seems therefore to be a particular opinion of the anonymous Reviewer 2.

The sequential extraction work (e.g., Table 6) for the Sr-isotope work could be presented better so the reader can understand why various procedures and reagents (e.g., NaCl, AcOH, HCl) were being used. The TIC/TOC results could be integrated in more substantial ways, e.g., perhaps TOC could be related to the development of dolomite nodules during microbial sulfate reduction."

In this point, we agree with both reviewers. Table 6 has now been uploaded to the Pangaea data repository, and we provide a better overview of the leaching procedure by showing the results graphically, as a new Figure 10.

It should be noted that only clay samples were analysed for TIC and TOC, for the purpose to select the sample with the lowest carbonate content. Also these data are now available from the Pangaea repository.

Several aspects of the present manuscript, that were identified in my previous review, still remain: 1) a general lack of engagement with the bulk elemental data (i.e., Table 5), 2) although 39 samples were collected in this study, it appears only a handful of these are presented in the manuscript for analysis, and 3) the manuscript does not substantially engage the potential for microbial origins although the subject is broached in general ways.

- 1.) It should be noted that the sole purpose of selecting three dolomite samples and two clay samples for elemental analysis was to test extraction efficiency. It was never intended to provide a full elemental analysis of dolomites through the section. An in-depth discussion in the sedimentological context would immediately raise the criticism that the sample selection was incomplete. Table 5 is also in the repository.
- 2.) Several samples of the 39 hand specimens collected in the field were claystone or a mixture of dolomite and clay. Upon petrographic inspection 11 samples were microdrilled to analyse the most pure aphanotopic dolomite.
- 3.) The reviewer suggests that we discuss the microbial dolomite formation. This matter is currently rather controversially debated. Our manuscript does not provide much new insight on any microbial influence, nor is our interpretation affected by it. Therefore we prefer not to engage in an elongate discussion on this matter. We agree, however, that the microbial dolomite hypothesis should be briefly mentioned. A short section was added in the discussion (line 720).

Nevertheless, and as stated in my previous review, "... my overall impression is that this manuscript provides a plausible interpretation for the origin of Travenanzes dolomites. This contribution provides an incremental step, albeit a small one, in our general understanding of dolomite formation and more specifically dolomite formation along the Tethyan margin and I feel it is acceptable for publication ...", although slight modifications are warranted that can be supervised by the associate editor.

With the reviewer's conclusive statement that our study "provides an incremental step, albeit a small one, in our general understanding of dolomite formation" we do not entirely agree. Our study provides more insight into the depositional environment and mechanism in an ancient system. Our work is, hence, of importance from a palaeo-environmental point of view, which should be valued for a geologically oriented journal as *Solid Earth*.

Anonymous Referee #2

I have read through the paper by Reider and others entitled: "Precipitation of dolomite from seawater on a Carnian coastal 1 plain (Dolomites, northern Italy): evidence from carbonate petrography and Sr-isotopes". I find the paper to be an interesting contribution to our understanding of the processes that led to the formation of primary dolomite in the sedimentary rock record and the authors use some innovative methods to prove a primary origin for the dolomite.

We are thankful to this reviewer for providing extensive comments throughout the manuscript, and for providing annotations in the manuscript. We agree with most suggestions, which we included in the revision. Below we explain how each point was addressed, or, in a few cases, why we disagree with the Reviewer's comment.

However, my main criticism about the paper is that it is too long in its current state, and should be shortened. Examples of text that needs to be edited or cut out altogether include:

- The authors spend approximately 4 pages describing their methods, which could be cut down to at least half that length by referring to similar methods in other papers and describing their methods in less detail.

We found a way to shorten the section by including the description of elemental and TOC/TIC analyses as part of the Sr-isotope analytics. Elemental and TOC analyses were only performed to test extraction efficiency of the sequential extraction for Sr-isotopes. Also the results section was considerably shortened and tables were moved to the Pangaea data repository.

- Related to the previous example, the paper contains data (e.g., %TOC, some of the elemental data, etc.) that seems unnecessary to the overall study. I would recommend that the authors carefully go through their manuscript and remove any data that is not deemed essential to their manuscript.

Done. TOC data were only measured in the clay minerals and are not discussed in the discussion. Both TOC and elemental data are now deposited in the Pangaea repository.

The inclusion of 6 tables seems excessive. The number of tables should be reduced to one or two, with the extra tables relegated to a "Supplemental Materials" section.

Done. Table 1 is provided as supplemental material. Table 2 is shown as an inset in Fig. 7. Tables 3 through 6 are now deposited in the Pangaea data repository.

- It is not clear to me why the authors include analyses of the Germanic Keuper dolomites (lines 359-371) in this paper.

The sentence in line 185 in the introduction was rephrased to clarify the purpose of analysing Keuper dolomites: "To demonstrate contrasting origin of ionic solutions, Srisotope values were compared to values from dolomites from the Germanic Keuper, that are of clear continental origin, and to values in modern dolomites showing marine and/or continental influence."

I am not an expert on Sr geochemistry, but it's not clear to me why the authors spend so much time discussing sequential extractions (lines 425-472). It seems to me that this text could be reduced.

The sequential extraction is absolutely critical to provide Sr-isotope data from pure uncontaminated dolomite, in particular if they are embedded in so much clay. The authors do not know of any other study, where the extraction procedure was so rigorously tested. This method must be described in detail here and cannot be shortened. In accordance with Reviewer 1, we provide a graphical representation of the leaching results, which should provide more clarity to the reader.

Lines 622-638 also seems unnecessary to the paper, as the authors explain one anomalous value from one sample. This value could be explained away in just a few words.

The first sentence of the section was rephrased (line 619). This discussion is not only about one outlier but about the influences that can provide more radiogenic values in general. This section should not be removed.

- Lines 639 – 662: This text seems more pertinent to a geochemical methods paper and does not seem to be needed here. The discussion concerning the origin of Sr is interesting, but again, does not seem pertinent to the paper.

We refer the Reviewer to the goal of the study in the introduction: "... to determine if ionic solutions conducive to dolomite formation were derived from seawater or from continental runoff."

Hence, the discussion of the origin of Sr is central to this study and cannot be removed.

Overall, the authors should spend time editing and rewriting the sections dealing with Sr isotopes and the origin of Sr in the dolomite in order to make them shorter, but should still use the Sr isotope results in their paper (these results could be included in the text from lines 757-763). This section is interesting, but much of it seems tangential to the current paper, and should be removed and incorporated into a separate paper.

See comment above.

A second major criticism of the paper is the use of the the term "non-actualistic" when describing the conditions that led to the precipitation of the dolomites. "Non-actualistic" refers to periods when environmental conditions were so different from today that there is no modern analogue. For example, the occurrence of epeiric seas, or the resurgence of microbial carbonates following several mass extinctions. The conditions cited to have led to the growth of the dolomites only require minor modifications to modern models of dolomite precipitation (i.e., the occurrence of clay-rich aquitards preventing the input of meteoric waters), and so the authors should use different terminology here.

We believe the term "non-actualistic" is still correct. First, thick successions of fine-grained, fabric-preserving dolomite as the Triassic Travenanzes and Dolomia Principale do not form today – it is indeed an unusual facies. Second, "non-actualistic" (also: "non-uniformitarian") not only implies extreme events rare in Earth history but more generally should include situations where processes were similar, but boundary conditions were different from today. Accordingly, a process may have been different in duration, scale, or rate from any modern analogue. Dolomite formation is a very good example where delicate changes in boundary conditions could have made the difference. There are many aspects about the Triassic Tethys that imply non-actualism, such as a different sealevel and area of epeiric platforms, Tethys seawater chemistry, atmospheric pCO₂, climate, all of which may have influenced the formation of dolomite. Hence, the present as the key to the past only partially works under these circumstances and must be used with caution.

Overall, I recommend that the paper be accepted with major revisions, and that the editors work with the authors to cut down on the amount of text.

We tried our best to improve the manuscript, and we incorporated most suggestions by the reviewer, except for shortening the discussion on the origin of ionic solutions, which is central to this study.

Specific comments:

Mud clasts vs. mudclasts: The authors use both spellings throughout the manuscript. The authors should separate the 2 words so that it reads "mud clasts".

Done

Line 28: The use of the word non-actualistic is typically associated with unusual facies or intervals in Earth History. While the model proposed by the authors is certainly unusual, I would avoid using the term non-actualistic and instead perhaps state that there is no modern analogue for a similar system.

See discussion above.

Line 43: Competing theories of what? I assume dolomite formation, but the authors need to be specific.

It should say "dolomite formation" (was added to the sentence).

Lines 56-58: I would draw the attention of the authors to a recent paper published in Geology by Li et al. that documents the widespread precipitation of primary dolomite around the Permian – Triassic boundary.

We are thankful for this reference, which was included.

Lines 61-62: What are the signatures indicative of a burial diagenetic overprint? The authors need to be specific.

Rephrased to: "... show oxygen isotope signatures of diagenetic overprint at burial temperature"

Lines 68-70: This text is vague, and the authors need to explain what the dolomite phases are that are documented by Frisia and Wenk (1993) so the reader can better establish that these are burial diagenetic features.

Further explanation is provided with reference to the recent publication (Meister and Frisia, 2019). See line 70.

Lines 88, 99 and 782: The authors use the term "Carnian platform", which is incorrect, as "Carnian" is a time term and a platform is a physical object. I would change the text to "Carnian-aged" and also add a modifier to state where the platform was. So, "Carnian-aged western Tethyan platform".

Done

Lines 102-103: What is the evidence for seasonally wet conditions? The authors state in the abstract that the seasonally wet conditions make these dolomites special (nonactualistic in their terms), and so they need to provide evidence of the seasonally wet conditions.

The sentence was reorganized to clarify that the large amount of distal riverine silicilastic input, and the presence of vertic paleosols suggesting vertical movements of the water table implies at least seasonally humid conditions. See lines 105-107.

Line 103: Which facies? Dolomite or clay? Or is this the entire sequence? It should say "facies association".

Line 104: Use of the term "extended" is confusing. Do the authors mean laterally extensive? Extensive over time? Both?

Yes it should be "extended in space". The sentence was re-organized to clarify this point.

Lines 104 and 107-109: Use of the term "a Germanic Keuper facies" is confusing. It's not clear to me if the authors are discussing a general facies type or a formational name, especially in lines 107-109 where they discuss paleogeographic separation between the Travenanzes Fm and the Germanic Keuper facies. Overall, the text in lines 107-109 is confusing and needs to be rewritten.

The reviewer is right that the Germanic Keuper is a palaeogeographic region and not a facies. We are trying to distinguish between the palaeogeographic regions of the Germanic Basin and the Alpine Tethys region. However, the continental facies association found in Germanic appears to reach far beyond just the Germanic Basin. We can see red clays with intercalated dolomites in both an endorheic setting (playa lake – alluvial plain facies association) or in a

setting linked to the Tethyan sea (coastal lake – dirty sabkha facies association). The lithological evidence is scarce (except in the few beds showing marine fossils). Sr isotopes can help us to distinguish the two facies associations.

Line 111: One facies zone is the Germanic Keuper facies. What is the other facies zone? If it is the Travenanzes Fm, then the authors need to word this differently, since it is confusing to compare facies to formations. This can be solved by referring to "dolomitic facies of the Travenanzes Fm", for example.

Yes, we agree. See comment above.

Lines 114: I would replace "carbonate" with "dolomite" since the authors are attempting to prove that the dolomite is primary in origin, and use of the term "carbonate" here is not specific enough.

Done (just to be cautious, we add in brackets "or a precursor carbonate phase")

Lines 148-149: It's not clear to me why the authors interpret the Travenanzes Fm as having been deposited on a very flat surface based on the lithologies that make up the unit. The authors need to provide stronger evidence.

This becomes obvious from the stratigraphic context. Gattolin et al. (2013/15) show very clearly the stratigraphic relationships where the deep basins are filled up and sealed by the laterally extensive clay depositis of the Travenanzes Fm. The palaeogeography has been established by Breda and Preto (2011) showing the interfingering with alluvial fans and marine carbonates over tens of kilometres. The sentence was rephrased (line 157).

Line 190: Are there units that go with "...a spot size 5.0..."?

There is no unit for the spot size. "5" is just the number of the spot size chosen.

Lines 237-238: The authors need to provide units for their detection limits.

The unit is µmol/g for all measurements, as indicated in the same sentence (line 260).

Line 292: Approximately how thick are the tempestite beds?

Ca. 20-cm-thick.

Line 293: I think the authors mean to state "megalodont teeth".

It should say "megalodont bivalves"

Lines 319-322: The ooids appear to have been micritized to me, based on the photo. Is this the case? If so, this needs to be mentioned in the description. If not, then the authors need a better photo.

The ooids show concentric, micritic layers. I think it is not possible to say whether they were micritized or originally micritic. In fact, ooids are often micritic.

Line 328: The authors need to be more specific in terms of what the measurements are measuring. Diameter? Thickness?

It should be "diameter"

Line 329: "Pale" is not a color, it is a shade of color. The authors need to add a color after the word "pale".

It should say "pale grey"

Line 362: I'm not sure if the peloids are a rare type of allochem, or if subunits made up mostly of peloids are rare. Please clarify.

It should say that there are only a few peloids in the thin section. Both onlites and peloidal grainstone occur as part of a distal shoal facies in the Weser Fm. (Seegis). See line 363.

Line 436: I'm not sure what it meant by "It".

The pure celestine. The whole section was reorganized.

Lines 479-481: The authors state that the mud was unlithified, but also note the presence of rip-up clasts made of the same mud. The authors need to account for this difference, since rip-ups require at least semi-lithification to form.

The rip-up clasts often show ductile deformation and are well rounded. They were clearly unlithified. Most likely the cohesive mud was sticking together (probably with a consistency like cottage cheese). Some clasts show brittle deformation: those ones may be semi-lithified.

Line 484: I'm not sure what the authors mean by "this type". Microfacies, perhaps? Yes, it should be the homogeneous aphanotopic dolomite described here, we explicited it.

Lines 491-492: The authors should include a reference at the end of this sentence.

This was suggested by Breda and Preto (2011). The reference was added.

Lines 492-493: This sentence seems out of place here since this is a discussion of processes within a possible ephemeral lake, and the previous text is trying to establish the larger depositional setting. In addition, I'm not sure that this text is necessary, since the mud is homogenous in composition, so stating that waves are responsible for homogenizing the mud is pure speculation without other evidence of wave action, like ripple marks.

The sentence explains why the sediment is homogenous, as opposed to laminated with separate clay and carbonate mud couplets observed in the laminated facies. The homogenization is explained by mixing upon wave action, which is commonly observed in shallow ephemeral lakes (e.g. Deep Springs Lake, Coorong Lakes, Lake Neusiedl, etc.). No bed forms, such as ripple marks, are formed because the dolomite is in the clay size fraction and transported in suspension. To better embed the sentence in the context of the section, the following sentence was added: "..., which is often observed in ephemeral lake settings, explaining the formation of homogeneous dolomite beds."

Lines 511-513: I'm confused. Are the authors stating that the ooids are marine in origin, or lacustrine (like the ooids found at the Great Salt Lake). The authors need to be more clear as to what they believe the origin of the ooids are, and if lacustrine, provide modern examples, since ooids are rare in that setting.

Marine fossils that occur in the same bed point to a marine origin in this case. The sentence is not important and was removed.

Line 530: "in situ" should be in italics.

Done

Lines 538-539: If the sediment is being plastically deformed, it must be at least partially lithified.

Lithified means that it is actually cemented by a mineral phase. If this is the case, the sediment can only break discretely and can no longer show plastic deformation. As we see plastic deformation, the sediment must be unlithified but cohesive.

Lines 543-544: The authors need to cite a reference at the end of this sentence: "What is atypical for a modern sabkha is the large amount of detrital input."

"Detrital input" is perhaps misleading because actual sabkhas may receive Aeolian input. What we mean is the large amounts of clay, which is derived from river flooding (Breda and Preto, 2011), which requires at least episodically humid conditions. This matter is already discussed in the introduction and is again addressed later in the discussion. For this reason we shall not engage further in this matter here. "detrital" was changed to "clay", and in brackets we add "(see discussion below)".

Line 544: The authors need to cite a reference to support their contention that the Carnian was seasonally wet.

Perhaps not the Carnian overall, but the depositional environment experienced episodic, most probably seasonal, fluvial input. This is well established by the regional facies reconstruction by Breda and Preto (2011), and probably represents the tail (the last pulses) of the Carnian Pluvial Episode.

Line 554: The authors need to cite a reference that red color represents seasonally arid conditions in clays.

A reference to Sheldon (2005), and a discussion as to why drainage was reduced, was added in line 547.

Line 556: I think the authors mean "after burial", not "after sedimentation".

Sentence rephrased to: "... internal brecciation, which must have occurred after sedimentation". Then in the next sentence we say that internation brecciation is also typical in calcretes, hence not "after burial".

Lines 679-680: This sentence is confusing, and needs to be rewritten. It could probably be shortened to just a few words and added to the end of the previous sentence.

Sentence rephrased.

Lines 691-696: These temperature ranges seem high, and therefore a reference to the temperature range of modern sabhkhas is needed. In addition, the authors also need to consider the effect of evaporation on oxygen isotope values and therefore temperature estimates from those values.

A reference to Hsü and Schneider (1973) was added.

The effect of evaporation on the oxygen isotope values of the water is already taken into account (see line 692) with reference to McKenzie et al. (1980) and McKenzie (1981).

Lines 697-699: Why is this important?

The trend in d¹⁸O is observed. We only provide possible explanations here. It is a matter of ongoing investigation; we cannot say more at the moment.

Line 700: Why do the oxygen isotopes indicate a primary signature as opposed to a secondary signature?

The reviewer is correct that this is somewhat overstated. While the matter of temperature is being further investigated, we moderate the wording to: "... the oxygen isotope data do not imply any post-depositional overprint."

Line 712-715: I'm not sure how these nodules relate to the cement rims surrounding the dolomicrite grains. I do agree with the formation mechanism for the nodules, but the authors need to add references to support their proposed formation mechanism.

This is just a mass balance. If unlithified mud becomes lithified after sedimentation or during burial, the aphanotopic cement filling the interstitial space between the micro-scale crystals incorporates the isotopic composition of the surrounding interstitial fluid. The dissolved inorganic carbon most likely carries a more negative d¹³C value, due to decomposition of organic matter. As said, this is a simple consequence of mass balance.

Line 768: What kind of isotopes?

Sr-isotope values.

Figure 1: âAc Change "positive areas" to "highlands" or "topographic highs". âAc The authors need to define the following abbreviations in the figure caption: Drau., Mr, Wa, Kr, Be, Fr and Ly. âAc I don't see any Continental/Lacustrine areas on the map, but the symbol for this facies is provided on the key.

Done.

Figure 3: âAc 3A need to focus in on the homogenous dolomite bed, as it is currently difficult to see as the view is too far out to allow any details to be properly discerned. âAc The calcitic vertisol in 3b needs to be labelled. âAc Gypsum nodules and crack fills need to be more clearly labelled in 3d. âAc The view on 3f needs to be closer to allow the soft sediment deformation, and, in particular, the isoclinal fold, to be more clearly seen.

Fig. 3A shows the large-scale bedding relationship of homogeneous dolomite beds. The image size was further increased. For the description of the aphanitic microstructure we refer to the subsequent section. In 3b, the vertisol was graphically indicated. Gypsum in 3d was labelled with "Gy". Fig. 3f was zoomed in to better show the isoclinal fold.

Figure 4: âAc The authors need to more clearly distinguish the mud clasts, as well as the coarser grained and finer grained layers in 4b. âAc The authors need to add arrows to 4d to point out the pseudomorphs. âAc The ooids in 4e appear to be micritized to me. This may be a reflection of the size/resolution of the photo. I would recommend that the authors show a close-up view of the ooids. âAc The feature labelled with a "P" in 4f is supposed to be a peloid, but it's not clear to me what the "P" is referring to on the photo. âAc The authors need to include boxes in 4g that shows the areas depicted in 4h and 4i. âAc

Done. Fig. 4d is full of pseudomorphs, so arrows are only pointing out examples.

Ooids are micritic. This is already explained in the text "... consist of microcrystalline dolomite and lack a radial structure". They most likely are recrystallized because dolomitic ooids are, not to our knowledge, observed in modern environments. The replacement must have been mimetic, i.e. replicating the micritic structure down to the micron size. This needs further examination by SEM in future studies.

Figures 8 and 9: The captions need to be more detailed for all plots in both figures. What is the significance of each plot for the study?

Further explanations were added.

Figure 10: What is the significance of the circled areas on the figure? This needs to be explained in the figure caption.

Circled datapoints are clay samples or samples of nodules containing clay. Information was added in the figure caption.

Figure 11: The authors need to note in the caption that Coorong Lagoon and Deep Springs Lake are modern dolomite deposits. Also, there is no mention of the Abu Dhabi sabkha in the caption, and it needs to be added to the caption.

Figure caption was re-organized accordingly.

Table 1: âAc I am unfamiliar with the term "laminate". The authors need to be more specific as to what this is. âAc This text at the bottom of the table is confusing and needs to be rewritten: "*Needs to be further subdivided into peloids, intraclasts, flat pebbles and clast of brittle deformation" I'm especially confused by the term "clast of brittle deformation".

It should say "laminite" (not laminate). This refers to the classical "Loferites" or "algal laminites", except in this case they may not be algal (or microbial). The table was changed to a neutral terminology: "laminated dolomite". The Table will be provided as online supplemental material (Table S1).

Table 2: I think the authors mean "Height" and not "Depth" as they refer to "Height" elsewhere.

Yes, "height" is correct. The table is now incorporated as inset in Fig. 7.

Table 4: âAc Again, I think the authors mean "megalodont teeth". âAc It's not clear to me what the authors mean by "top", "bottom" or "part". âAc

It should say "*Megalodon* bivalves". "top" and "bottom" refers to the position within the thin section. This is of no meaning for the interpretation and was therefore removed. The data are now available from the Pangaea repository.

Please also note the supplement to this comment:

We are extremely thankful to Reviewer 2 for very nicely revising grammar and style of our manuscript.

Precipitation of dolomite from seawater on a Carnian coastal plain (Dolomites, northern 1 Italy): evidence from carbonate petrography and Sr-isotopes 2 Maximilian Rieder¹, Wencke Wegner², Monika Horschinegg², Stefanie Klackl¹, Nereo Preto³, 3 Patrick 24-4-2019 Gelöscht: Stephanie Anna Breda³, Susanne Gier¹, Urs Klötzli², Stefano M. Bernasconi⁴, Gernot Arp⁵, Patrick 4 Meister1 5 6 Department of Geodynamics and Sedimentology, University of Vienna, Althanstr. 14, 1090 Vienna, Austria 7 ² Department of Lithospheric Research, University of Vienna, Althanstr. 14, 1090 Vienna, Austria ³ Department of Geosciences, University of Padova, Via Gradenigo 6, 35131 Padova, Italy 8 9 ⁴ Geological Institute, ETH Zürich, Sonneggstr. 5, 8092 Zürich, Switzerland 10 ⁵ Geoscience Centre, University of Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany Correspondence to: Patrick Meister (patrick.meister@univie.ac.at) 11 Formatiert: Schriftart: Kursiv 12 Abstract. The geochemical conditions conducive to dolomite formation in shallow evaporitic 13 environments along the Triassic Tethyan margin are still poorly understood. Large parts of the 14 Gelöscht: Most 15 Triassic dolomites in the Austroalpine and the Southern Alpine realm are affected by late diagenetic or hydrothermal overprinting, but recent studies from the Carnian Travenanzes 16 Formation (Southern Alps) provide evidence of primary dolomite. Here a petrographic and 17 Patrick 13-5-201 Gelöscht: ine geochemical study of dolomites intercalated in a 100-m-thick Carnian sequence of distal 18 Patrick 23-4-2019 17:47 Gelöscht: the alluvial plain deposits is presented to gain better insight into the conditions and processes of 19 20 dolomite formation. The dolomites occur as 10- to 50-cm-thick homogenous beds, mm-scale 21 laminated beds, and nodules associated with palaeosols. The dolomite is nearly stoichiometric 22 with slightly attenuated ordering reflections. Sedimentary structures indicate that the initial Patrick 28-4-2019 15:29 Gelöscht: cprimary dolomite or precursor phase consisted largely of unlithified mud. Strontium isotope 23 24 ratios (87Sr/86Sr) of homogeneous and laminated dolomites reflect Triassic seawater, suggesting precipitation in evaporating seawater in a coastal ephemeral lake or sabkha 25 system. However, the setting differed from modern sabkha or coastal ephemeral lake systems 26 27 by being exposed to seasonally wet conditions with significant siliciclastic input and the Gelöscht: a

mechanism to pump large volumes of Mg-rich water through porous rock (Machel, 2004),

and is not always a viable process. There is evidence that Jarge amounts of dolomite could

have formed under near-surface conditions (penecontemporaneous dolomite) at certain times

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inhibition of significant lateral groundwater flow by impermeable clay deposits, and thus the 34 Patrick 23-4-2019 17 Gelöscht: through ancient Tethyan margin represents a non-actualistic system in which primary dolomite 35 Patrick 23-4-2019 17:5 Gelöscht: representing 36 formed. Patrick 28-4-2019 16:30 Gelöscht: along the ancient Tethyan margin 37 Keywords Dolomite, Sr-isotopes, sabkha, coastal plain, peritidal platform, Travenanzes 38 Patrick 13-5-2019 0 Gelöscht: alluvial Formation, ephemeral lake, authigenic carbonate. 39 40 41 1 Introduction 42 The formation of dolomite [CaMg(CO₃)₂] under Earth surface conditions in modern and 43 ancient environments is still a major unsolved problem in sedimentary geology. Dolomite 44 45 does not precipitate from modern open ocean water, apparently because its nucleation and Patrick 23-4-2019 17:42 Gelöscht: . growth is inhibited by a high kinetic barrier. For the same reason, the precipitation of 46 Patrick 23-4-2019 17:43 Gelöscht: its dolomite under laboratory conditions has also been difficult (cf. Land, 1998), and therefore 47 the factors that may have influenced dolomite formation throughout Earth history also remain 48 Gelöscht: , giving rise to a significant part of 49 poorly constrained. Van Tuyl (1916) discussed several competing theories for dolomite the sedimentary record, formation, one of which was the chemical theory, whereby dolomite is a primary precipitate, 50 forming as the result of prevailing conditions within the depositional environment. In contrast, 51 Gelöscht: hence, 52 stable isotope and fluid inclusion data often indicate that massive dolomites formed due to Patrick 23-4-2019 Gelöscht: a replacement of precursor calcium carbonate during burial diagenesis, i.e., at higher 53 Patrick 23-4-2019 17:46 Gelöscht: the conditions temperatures and under conditions decoupled from the ancient depositional environment. 54 Chilingar (1965) suggested that the portion of dolomite in carbonates increases with 55 geological age, implying replacement during burial. However, burial dolomitization requires a 56 Patrick 23-4-2019 17:41 Gelöscht: a

Gelöscht: ing

Patrick 23-4-2019 17:40

Gelöscht: at certain times in Earth's history,

in Earth's history, and several studies linked the abundance of dolomite to secular variation in

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seawater chemistry, with primary dolomite preferentially forming during times of "calcite 75 seas" (Given and Wilkinson, 1987; Warren, 2000; Burns et al., 2000). 76 77 In contrast, penecontemporaneous dolomite formation seems to have prevailed in the Tethyan realm during the Triassic (Meister et al., 2013, and references therein; Li et al., 78 2018), in an "aragonite sea", while elsewhere dolomite was not particularly abundant (cf. 79 Given and Wilkinson, 1987). In Norian shallow water dolomites of the Dolomia Principale, 80 Iannace and Frisia (1994) measured oxygen isotope values as positive as +3.5%, suggesting 81 formation at Earth surface temperatures, whereas dolomites from overlying Lower Jurassic 82 83 units typically show oxygen isotope signatures of diagenetic overprint at burial temperature. Frisia et al. (1994) interpreted these dolomites to be an early diagenetic replacement of 84 precursor carbonate. In a recent study, Preto et al. (2015) suggested that the dolomites of the 85 Carnian Travenanzes Formation (Fm.) in the Venetian Alps are primary precipitates, i.e. they 86 87 precipitated directly from solution in the sedimentary environment and not by the replacement of a precursor phase during burial. This interpretation is based on high-resolution 88 transmission electron microscope (HR-TEM) analysis, which revealed that single micron-89 90 scale dolomite crystals consist of grains with incoherent crystallographic orientation at the few-nanometre scale (cf. Meister and Frisia, 2019). The nanocrystal structures were not 91 replaced by any of the dolomite phases described by Frisia and Wenk (1993) in Late Triassic 92 93 dolomites of the Southern Alps; instead they are similar to dislocation-ridden Mg-rich phases 94 observed in dolomite from modern sabkhas and are interpreted as primary in origin (Frisia and Wenk, 1993). This finding is intriguing, not only because it is consistent with primary 95 96 dolomite formation proposed by Van Tuyl (1916) and observed in many modern environments (e.g., Sabkha of Abu Dhabi: Illing, 1965; Wenk et al., 1993; unlithified 97 dolomite is also mentioned in Bontognali et al., 2010; and Court et al., 2017; Deep Springs 98 Lake, California: Jones, 1965; Clayton et al., 1968; Meister et al., 2011; Coorong Lakes: Von 99

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der Borch, 1976, Rosen et al., 1989, Warren et al., 1990; Brejo do Espinho, Brazil; Sánchez-Román et al., 2009; Lake Acigöl, Turkey: Balci et al., 2016; Lake Neusiedl, Austria: Neuhuber et al., 2015; Lake Van: McCormack et al., 2018), but it also provides a window into ancient primary dolomite formation pathways. This finding is also consistent with recent experiments by Rodriguez-Blanco et al. (2015), demonstrating a nano-crystalline pathway of dolomite nucleation and growth. Critically, nanometre size nuclei show a different surface energy landscape compared to macroscopic crystals, allowing for potentially lower energy barriers, perhaps modified by organic matter, microbial effects, clay minerals or particular water chemistry, and thus, promoting the spontaneous precipitation of dolomite.

The interpretation of primary dolomite in the Travenanzes Fm. needs further validation by nano- and atomic scale analyses and further petrographic and geochemical investigations to establish the sedimentary and geochemical conditions in the depositional environment, an extended mud plain that occurred along the western Tethys margin during the Carnian. In particular, the origin of ionic solutions conducive to dolomite formation is still unclear. Comparison with modern environments shows that ionic solutions may either be seawater-derived, as shown for the sabkhas along the Persian Gulf coast, where several hydrological mechanisms were discussed (Adams and Rhodes, 1960; Hsü and Siegenthaler, 1969; McKenzie et al., 1980, McKenzie, 1981; see Machel, 2004, for an overview; cf. also Teal et al., 2000), or derived from continental groundwater, as shown for the coastal ephemeral lakes of the Coorong area (Australia; Alderman and Skinner, 1957; Von der Borch et al., 1976, Rosen et al., 1989; Warren et al., 1990). While both types of fluid become concentrated during evaporation and are, perhaps, modified by the precipitation of carbonates and evaporites, it remains unclear which source prevailed during deposition of the Travenanzes Formation.

Dolomites occur in the Travenanzes Fm. as intercalated beds in a 100-m-thick sequence of red and green clay. The environment hence differed from modern analogues (e.g. sabkhas) in

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formation,

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that it contained large amounts of clay derived from riverine input and deposited on a distal alluvial plain, implying seasonally wet conditions. This facies association shows, except for the horizons containing marine fossils, striking similarity to the Germanic Keuper, which represents an entirely continental playa lake system, and also exhibits intercalations of primary dolomite in red clay (Reinhardt and Ricken, 2000). The Keuper facies association extended over much larger areas than just the Germanic basin during the Carnian. Although the Travenanzes Fm. is clearly located, palaeogeographically, in the Tethyan depositional region (Breda and Preto, 2011), its facies separation from the Germanic Keuper may not be precisely coincident with palaeogeographic features, such as the Vindelician high zone. We suggest that the composition and origin of ionic solutions conducive to primary dolomite formation, from either continental water or seawater, is also an indication of separation between the two palaeogeographic domains.

Here we provide a detailed investigation of dolomites of the Travenanzes Fm. to reconstruct the processes and factors conducive to dolomite formation. We specifically searched for sedimentary structures indicating that the initial authigenic dolomite (or a precursor carbonate phase) was unlithified, as would be expected if it spontaneously precipitated from the shallow water bodies of ephemeral lakes or tidal ponds. Radiogenic Sr isotope ratios (87Sr/86Sr) were measured in the dolomites and compared with the established Triassic seawater Sr-isotope curve (Veizer et al., 1999; McArthur et al., 2012) to determine if jonic solutions conducive to dolomite formation were derived from seawater or from continental runoff. To demonstrate contrasting origin of ionic solutions, Sr-isotope values were compared to values from dolomites from the Germanic Keuper, that are of clear continental origin, and to values in modern dolomites showing marine and/or continental influence. Based on new insights, we discuss possible scenarios of dolomite formation that could have prevailed along the western Tethys margin, and in similar evaporative

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2 Geological setting

The Dolomite mountains (Southern Tyrol and Venetian Alps; Fig. 1a) are well known for their characteristic peaks consisting of Triassic carbonate platform limestones and dolomites. These platforms developed all along the margins of the western Tethys ocean (Stampfli and Borel, 2002), and are separated by deep basins in the middle Triassic, and form an extended coastal plain during the Carnian and Norian. The Adriatic plate was rotated almost 90° counter clockwise as a result of the Alpine Orogeny (Ratschbacher et al., 1991; Handy et al., 2010). As a result, deep-water environments are found to the north today, although they were originally located to the east (Fig. 1a). Triassic paleogeography is largely preserved in the Dolomites in spite of Alpine deformation because the Dolomites form a ca. 60 km wide popup structure that is bound by the Periadriatic Line to the north and northwest and the Valsugana Fault to the southeast (Fig. 1a, inset). Therefore, the Dolomites were never buried to a greater depth, and did not experience metamorphic overprinting (Doglioni, 1987). The colour alteration index of conodonts in the Heiligkreuz Fm., which underlies the Travenanzes Fm. in this region is 1, suggesting maximum burial temperatures of less than 50°C_a which are confirmed by biomarker data (Dal Corso et al., 2012). The Travenanzes Fm. lies unconformably above the Heiligkreuz Fm., and is overlain by the Dolomia Principale (Hauptdolomit) along a transgressive boundary (Fig. 1b). Large amounts of siliciclastic material were deposited during the Carnian, presumably as a result of

The Travenanzes Fm. lies unconformably above the Heiligkreuz Fm., and is overlain by the Dolomia Principale (Hauptdolomit) along a transgressive boundary (Fig. 1b). Large amounts of siliciclastic material were deposited during the Carnian, presumably as a result of a change in climate and increasingly humid episodes, and led to filling of basins that were more than 100 m deep that existed between the carbonate platforms of the Cassian dolomite (Gattolin et al., 2013; 2015). These basin-filling deposits formed a coastal succession or mixed carbonate-siliciclastic ramp, that includes large clinoforms made up of sandstones and

conglomerates (Heiligkreuz Fm.; see Preto and Hinnov, 2003; Gattolin et al., 2013; 2015).

The topography was entirely evened out and overlain by the Travenanzes Fm. a ca. 100-m-

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276 thick and laterally extensive succession of red and green claystone with intercalated dolomites, evaporites and siliciclastic beds (Fig. 2; Kraus, 1969; Breda and Preto, 2011). The 277 Travenanzes Fm. shows interfingering along a south-north transect between conglomerates 278 Patrick 23-4-2019 17:18 Gelöscht: In a south-north transect, it and sandstones to the south and carbonate-dominated peritidal to sabkha facies to the north 279 Gelöscht: a typical 280 (Breda and Preto, 2011). The upper boundary to the Dolomia Principale is time-transgressive, Patrick 23-4-2019 17:20 Gelöscht: alluvial deposits with i.e., it becomes younger from north to south. The Travenanzes Fm. consists of three 281 Gelöscht: a transgressive-regressive cycles, with the highstand deposits showing identical peritidal 282 carbonate facies as the Dolomia Principale (Breda and Preto, 2011). The boundary with the 283 Patrick 23-4-2019 17 Gelöscht: to 284 Dolomia Principale is defined by the last occurrence of siliciclastic material (Gianolla et al., 285 1998). The depositional environment of the siliciclastic facies of the Travenanzes Fm. has been 286 Gelöscht: in interpreted as a dryland-river system by Breda and Preto (2011). Such a system occurs in arid 287 environments if rivers drain into a coastal alluvial plain, but do not reach the coast. 288 289 Evaporation along the way may lead to the formation of playa lakes on the seaward side of Patrick 23-4-2019 17:12 Gelöscht: , whereas the system extended evaporative areas, i.e. coastal sabkhas, develop. Both types of 290 Patrick 13-5-2019 01:3 Gelöscht: tidal environment are well known for giving rise to modern dolomite formation (see references 291 Patrick 13-5-2019 01:38 Gelöscht: ., 292 above). As the Southern Alps were located in tropical latitudes, a warm arid climate, perhaps influenced by a monsoon effect, developed (Muttoni et al., 2003). Rivers provided large 293 Patrick 23-4-2019 17:0 Gelöscht: had 294 amounts of clay, which were partially oxidized under subaerial conditions, leading to a typical Patrick 23-4-2019 17 Gelöscht: becoming 295 red and green clay succession containing palaeosols. This facies association is widespread Gelöscht: developed 296 throughout the Alpine and Tethyan realm during the Carnian, but similar deposits are strongly Patrick 28-4-2019 17:18 Gelöscht: 297 deformed by alpine tectonics in most Austroalpine units, forming a characteristic band of Patrick 23-4-2019 17:0 Gelöscht: the same 298 rauhwacke, the "Raibl beds" (e.g., Czurda and Nicklas, 1970). In the Travenanzes Fm. the 299 entire sequence <u>maintains</u> its depositional architecture, providing a pristine archive to study Patrick 23-4-2019 17:05 Gelöscht: still shows 300 the intercalated dolomites. Patrick 23-4-2019 17:05 Gelöscht: diverse

The Carnian and Norian deposits of the Keuper in the endorheic Germanic Basin contain a
similar facies association as the Travenanzes Fm., but clearly represent continental playa lake
deposits (Reinhardt and Ricken (2000; and references therein). Here we consider dolomites
from the Germanic Basin of confirmed continental origin for comparison of Sr-isotope
compositions of continental and coastal environments,

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3 Methods

3.1 Petrographic and mineralogical analysis

A total of 39 hand specimens were collected from the stratigraphic section at Rifugio Dibona, 5 km west of Cortina d'Ampezzo, Italy (46.532727N/12.067161E; Fig. 1; Breda and Preto, 2011). Additional samples of Triassic dolomites from the Germanic Basin (Weser Fm. and Arnstadt Fm. near Göttingen, Northern Germany) and modern dolomite from the Coorong Lagoon (South Australia) and Deep Springs Lake (California) were also analysed for comparison. Polished thin sections were carbon coated for analysis under the scanning electron microscope (SEM) using a FEI Inspect S-50 SEM (Thermo Fisher Scientific, Bremen, Germany). Element contents were determined semi-quantitatively using an EDX detector (EDAX Ametek, New Jersey, United States) under high vacuum, and 12.5 kV beam voltage at a working distance of 10 mm. Differences in mineralogy at the micron scale were mapped in backscatter mode with high contrast.

For bulk mineralogical analysis, three dolomite samples were ground to a fine powder with a disk mill. Clay mineralogy was determined on 40 g aliquots that were leached two times for 24 h in 250 ml of 25% acetic acid to dissolve all carbonate (Hill and Evans, 1965). The clay mineral separates were washed three times with H₂O and centrifuged. The grain size fraction <2 µm was collected by sedimentation in an Atterberg cylinder after 24 h 33 min. Oriented samples were prepared by pipetting the suspensions (10 mg clay/ml) on glass slides and analysed after air drying. To identify expandable clay minerals, the samples were additionally

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saturated with ethylene-glycol and heated to 550°C (Moore and Reynolds, 1997). X-ray diffraction analysis of bulk samples and clay mineral separates was performed with a PANalytical X'Pert Pro diffractometer using CuKα radiation with 40 kV and 40 mA. The samples were scanned from 1.76° to 70° 2θ with a step size of 0.0167° and 5 s per step. The X-ray diffraction patterns were interpreted using the Panalytical software "X'Pert High score plus" and Moore and Reynolds (1997) for the clay minerals.

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3.2 Carbon and oxygen isotope analysis

Carbon and oxygen isotopes were measured on 28 samples which where micro-drilled from thin section cuttings (see below). The samples were analysed with a Delta V Plus mass spectrometer coupled to a GasBench II (Thermo Fisher Scientific, Bremen, Germany) at ETH Zürich (Zürich, Switzerland), following the procedure described in Breitenbach and Bernasconi (2011). The precision was better than 0.1% for both isotopes. The oxygen isotope values were corrected for kinetic fractionation during dissolution of dolomite in anhydrous phosphoric acid at 70°C, using a fractionation factor of 1.009926 (Rosenbaum and Sheppard, 1986).

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3.3 Radiogenic Sr-isotope analysis

To ensure that Sr from the pure dolomite phase is extracted, specific areas free of clay minerals were defined by SEM and identified using an Olympus SZ61 microscope equipped with a MicroMill sampling system (Electro Scientific Industries). Eleven samples were drilled over an area of 5-10 mm², or along a line in laminated rocks, to a depth of 350 μm. To prevent the powder from being dispersed, the samples were drilled within a drop of MilliQ-H₂O, and the suspension was transferred to a centrifuge tube using a pipette.

A sequential extraction was used to determine the mildest reagent that efficiently extracts the pure dolomite phase without attacking other mineral phases. The extractions were

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[1] nach unten verschoben: Total organic carbon (TIC) and total inorganic carbon (TIC) contents were determined for seven samples of pure claystone, not containing any dolomite layers or nodules. This material was used as carbonate-free control for acid leaching experiments as explained below. Ca. 0.2 g of dry sample powder was measured in a LECO RC-612 multiphase carbon analyser, at the Department of Environmental Geosciences at the University of Vienna, with a temperature ramp of 70°C per min to a maximum temperature of 1000°C.

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402 routinely performed in capped 2 ml or 15 ml polypropylene tubes at room temperature on a 403 shaker for 10 min to 24 h. The following leaching reagents (always 2 ml) were used: 1 M NaCl, 3.3 M KCl, 0.1 N acetic acid, 1 N acetic acid and 6 N HCl. Each reaction step was 404 405 repeated once, and the residues were washed with 2 ml of MilliQ H₂O after each step to 406 remove remains of the previous solvent. Extraction efficiency was tested on bulk samples, clay samples, pure celestine and barite 407 purchased from W. Niemetz (Servitengasse 12, 1090 Vienna, Austria), pure dolomite powder 408 from Alfa Aesar (Thermo Fisher - Kandel - GmbH, Postfach 11 07 65, 76057 Karlsruhe, 409 Germany) and a fragment of a single dolomite crystal were analysed as controls. These 410 411 samples were crushed to a powder in an agate mortar and pestle. Dolomite, barite, and celestine were mixed in a similar ratio as they occur in the dolomites of the Travenanzes Fm. 412 and run through the entire procedure as a control of extraction efficiency; 14 mg of rock 413 powder was weighed out for isotope analysis. In order to rule out contamination by Sr from 414

clay samples do not contain carbonate, clay samples were analysed for total organic and inorganic carbon using a LECO RC-612 multiphase carbon analyser, at the Department of

Environmental Geosciences at the University of Vienna, with a temperature ramp of 70°C per

clay minerals, pure claystone of the Travenanzes Fm. was extracted separately. To ensure that

min to a maximum temperature of 1000°C

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Total element concentrations were measured in leachates of three dolomite specimens previously analysed by XRD, and the two claystones. Five ml of each fraction were used for element concentration analysis (the rest was further processed for Sr-isotope analysis; see below). The solutions were evaporated on a heating plate and the residues were re-dissolved in 5 ml 2.5 N HNO₃. This step was repeated with 5 ml 5% HNO₃. Concentrations were measured with a Perkin Elmer 5300 DV ICP-OES at the Department for Environmental Geosciences (University of Vienna). Detection limits for the different elements in rock (μmol/g) were: Al: 0.185, Ca: 0.025, Fe: 0.090, K: 0.026, Mg: 0.041, Mn: 0.002, Na: 0.004,

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Gelöscht: Total organic carbon (TOC) and total inorganic carbon (TIC) contents were determined for seven samples of pure claystone, not containing any dolomite layers or nodules. This material was used as carbonate-free control for acid leaching experiments as explained below. Ca. 0.2 g of dry sample powder was measured in a LECO RC-612 multiphase carbon analyser, at the Department of Environmental Geosciences at the University of Vienna, with a temperature ramp of 70°C per min to a maximum temperature of 1000°C.

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Gelöscht: As additional precaution to extract the most pure dolomite phase for Sr-isotope analysis, a sequential extraction was used. The extractions were routinely performed in 2 ml or 15 ml polypropylene tubes with cap at room temperature on a shaker for 10 min to 24 h. The following leaching reagents (always 2 ml) were used: 1 M NaCl, 3.3 M KCl, 0.1 N acetic acid, 1 N acetic acid and 6 N HCl. Each reaction step was repeated once, and the residues were washed with 2 ml of MilliQ H₂O after each step to remove remains of the previous solvent.

57	P: 0.032, Ti: 0.002, Ba: 0.001, Sr: 0.001 and Rb: 0.012. The precision of the measurements	
58	(relative standard deviation; RSD) for Al, Ca, K, Mg, Ti, Ba and Sr was ≤0.9% and for Fe,	
59	$Mn, Na, Rb, P \text{ was } \leq 6.8\%.$	
60	For Sr-isotope measurements, Sr was separated from interfering ions (e.g. Fe, K, Rb and	Patrick 28-4-2019 17:44
61	Ca) using an ion exchange column packed with BIO RAD AG 50W-X8 resin (200-400 mesh,	Gelöscht:
62	hydrogen form). Leachates were evaporated, dissolved in 6 N HCl and 2.5 N HCl and loaded	
63	onto the column in 2 ml 2.5 N HCl. Next. 51 ml of 2.5 N HCl were run through the column to	D-1-1-1-00 4 0040 40-50
64	wash out the interfering ions. Sr was eluted with a further 7 ml 2.5 N HCl and dried after	Patrick 23-4-2019 16:56 Gelöscht: Then
65	collection. Total procedural blanks for Sr were <1 ng and were taken as negligible (the	Patrick 23-4-2019 16:56 Gelöscht: The
66	amounts of strontium in the samples were always higher than 100 ng),	
67	The isotopic composition of Sr was measured with a Triton (Thermo Finnigan) thermal	Patrick 28-4-2019 17:36 Formatiert: Schriftfarbe: Schwarz
68	ionisation mass spectrometer. Sr fractions were loaded (dissolved in 1 µl H ₂ O) as chlorides	
69	and vaporized from a Re double filament. The double filament configuration was used to	
70	accelerate detachment of Sr from the filament. The cup configuration was calibrated such that	
71	masses 84, 85 (centre cup), 86, 87 and 88 are detected. The NBS987 Sr isotope standard	Patrick 23-4-2019 16:55 Gelöscht: the
72	(number of replicates = 40) shows a 87 Sr/ 86 Sr-ratio of 0.710272 ±0.000004 during the time of	
73	investigation, with the uncertainty of the Sr isotope ratios quoted as 2σ. Interference with ⁸⁷ Rb	
73	investigation, with the uncertainty of the Sr isotope ratios quoted as 2σ. Interference with ⁸⁷ Rb was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected	
.74 .75	was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected	
74	was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected	
74 75 76	was corrected using a 87 Rb/ 85 Rb ratio of 0.386. Within-run mass fractionation was corrected for 86 Sr/ 88 Sr = 0.1194.	
74 75 76 77	was corrected using a 87 Rb/ 85 Rb ratio of 0.386. Within-run mass fractionation was corrected for 86 Sr/ 88 Sr = 0.1194. 4 Results	
.74 .75 .76 .77	was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected for ⁸⁶ Sr/ ⁸⁸ Sr = 0.1194. 4 Results 4.1 Petrographic description of dolomites	
.74 .75 .76 .77 .78	was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected for ⁸⁶ Sr/ ⁸⁸ Sr = 0.1194. 4 Results 4.1 Petrographic description of dolomites Fig. 2 shows the distribution of the different types of dolomite through the 100-m-thick	
.774 .775 .776 .777 .778 .779	was corrected using a ⁸⁷ Rb/ ⁸⁵ Rb ratio of 0.386. Within-run mass fractionation was corrected for ⁸⁶ Sr/ ⁸⁸ Sr = 0.1194. 4 Results 4.1 Petrographic description of dolomites Fig. 2 shows the distribution of the different types of dolomite through the 100-m-thick lower, clay-rich interval of the Travenanzes Fm., above which the facies switches sharply to	

the clay-rich unit contains mainly homogeneous dolomite (Fig. 3a-c). The lower and middle part of the clay-rich unit contains mainly homogeneous dolomite beds in red clay. Between 40 and 70 m_a several horizons with gypsum nodules occur (Fig. 3d). A 30-cm-thick fluvial conglomerate with dolomite-cemented quartzarenites and pebbles of ripped up micritic carbonate occurs at 75 m (Fig. 3e), above which palaeosols with dm-scale vertical peds, possible root traces showing green reduction haloes, and nodular dolomite (calcic vertisols; cf. Cleveland et al., 2008), are more frequent (e.g., Fig. 3b). Ca. 20-cm-thick tempestite beds with Megalodon bivalves, foraminifers, and ostracods occur at 65 and 89 m. A pronounced transition occurs in the uppermost ca. 8 metres of the clay-rich interval (Fig. 2b), where the clay entirely changes from a red to a grey colour (Fig. 2c), and laminated dolomites become dominant, while evaporites and palaeosols are absent. The laminated dolomites (Fig. 3c) and cm- to dm-scale dolomite-clay interlayers show intense slumping and soft sediment deformation and pseudo-teepee structures (Figs. 3f, g). A short summary of petrographic analyses of thin sections of the different types of dolomite including the most important features appears below and is compiled in Table S1.

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Homogenous dolomites

Homogeneous dolomite beds are usually 10 cm to 50 cm thick, embedded within clays and exhibiting sharp, plane-parallel joints. The beds consist of dolomicrite, which was previously described as aphanotopic dolomite by Breda and Preto (2011), according to the extended nomenclature for dolomite fabrics by Randazzo and Zachos (1983). The sediment is matrix-supported and contains irregular, partially rounded mud clasts (intraclasts) that consist of aphanotopic dolomite, Some of the mud clasts contain smaller and somewhat darker mud clasts or peloids (Fig. 4a, arrow). Soft sediment deformation is often not clearly visible due to the homogeneous structure of the mud, but it can be observed where the mud clasts are deformed within the matrix (Fig. 4b). Some of the homogeneous beds in the lower part of the

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Gelöscht: megalodont

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Gelöscht: s

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Gelöscht: Here we provide a

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Gelöscht: analysis

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Gelöscht: with

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Gelöscht: table

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Gelöscht: with

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Gelöscht: an

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Gelöscht: as the matrix

Patrick 23-4-2019 18:15

Gelöscht: mudclast

porosity. In some laminae a clotted peloidal fabric is observed (e.g in Fig. 4f). Laminae are

typically graded, whereby the upper part is darker, indicating an increase in the clay content

(Fig. 4h, i). The top of the laminae is often truncated by an erosion surface, and rip-up clasts

of the fine mud are embedded in the overlying coarse layer. Some laminated dolomites

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section show sub-millimetre lamination that is only visible under the microscope, where it 529 consists of alternating layers of light (locally coarser) and dark aphanotopic dolomite. 530 Patrick 23-4-2019 16:49 Gelöscht: appears as an The clay content in the homogeneous beds is generally low. A few beds (e.g. at 33.5 m in 531 Patrick 23-4-2019 16:49 Gelöscht: o the section) consist of silty or sandy dolomite, as reflected in a high abundance of detrital 532 Patrick 23-4-2019 16:48 Gelöscht: in three quartz in thin section. Pseudomorphs after gypsum occur in a dolomite bed at 120 m (Fig. 4c, 533 Patrick 23-4-2019 16:48 Gelöscht: , within aphanotopic dolomite d). Moldic porosity occurs within aphanotopic dolomite layers at 43, 65 and 89 m, These 534 Patrick 23-4-2019 16:47 Gelöscht: are 535 <u>correspond to</u> the tempestite beds observed in outcrop (cf. Breda and Preto, 2011). Patrick 23-4-2019 16:48 Gelöscht: the One dolomite bed, located at 64 m in the section, appears homogeneous at outcrop scale, 536 Patrick 14-5-2019 12:27 Gelöscht: homogenous but consists of oolitic grainstone and lacks both an aphanotopic and a cement matrix (Fig. 4e). 537 Patrick 14-5-2019 12:2 Gelöscht: contains 538 Ooids show concentric, micritic layers and are either hollow (where the cores may have been Patrick 14-5-2019 12: Formatiert: Nicht Hervorhebung Patrick 23-4-2019 16:47 dissolved) or filled with sparite, and are surrounded with an isopachous cement rim, 539 Gelöscht: h Patrick 13-5-2019 01:58 540 Gelöscht:, Laminated dolomites Patrick 13-5-2019 01:58 541 Gelöscht: ing 542 Laminated dolomites occur in the upper part of the clay-rich interval, between 90 and 110 Patrick 13-5-2019 01:57 Gelöscht: m in the section (Fig. 4f-i). In the field, the laminated dolomites show an alternation between Patrick 14-5-2019 13:56 543 Gelöscht: ... [6] light grey dolomite laminae and dark grey to black clay laminae. Some dolomite laminae are Patrick 13-5-2019 02:08 544 Formatiert: Hervorhebung Patrick 23-4-2019 16:44 bent upward and are reminiscent of pseudo-teepee structures (Fig. 4f); the space within the 545 Gelöscht: clay teepee is sometimes infilled with sparry cement. In addition, the bending of the laminae Patrick 23-4-2019 16:44 546 Gelöscht: y towards the upward directed cuspids is reminiscent of load structures (dish structures), but Patrick 23-4-2019 16:44 547 Gelöscht: of Patrick 23-4-2019 16:45 548 they also may represent desiccation cracks. The laminae are frequently ripped apart and Gelöscht: in the mm-range Patrick 23-4-2019 16:45 549 fragments of laminae occur reworked as flat pebbles embedded in an aphanotopic dolomite Gelöscht: show matrix (Fig. 4g). Some laminae show a microsparitic appearance and laminar fenestral 550

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Gelöscht: (mud clasts)

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contain continuous layers with inclusions of celestine crystals in the 100-µm-range, some of them with barite in their centre (Fig. 5a-c). Pyrite also occurs.

Patrick 23-4-2019 16:42

atom with outle in their centre (1 ig. 54 c).

Gelöscht: Occasionally also p

difference in mineral structure and grain size is observed between mud clasts and the

Under the SEM, laminated dolomites show an anhedral structure in the 1-5 µm range. No

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Gelöscht: usually

surrounding, often lighter-coloured matrix. Dolomite crystals at the margins between

dolomite and clay interlayers often coalesce into 5-µm-scale, round aggregates consisting of

several subhedral crystals with different orientations (Fig. 6a, b; the crystals show orientation

contrast under BSE mode). Dolomite crystals are often porous, showing a somewhat disordered appearance, but they are surrounded by syntaxial rims. In most cases, the rims

entirely fill the intercrystalline space, forming almost hexagonal compromise boundaries (Fig.

6c, d). These rims occur both in homogeneous and laminated dolomites.

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Nodular dolomites

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Nodular dolomites (Fig. 3b) often occur in beds of vertical peds linked to palaeosols, as

indicated by horizons of vertical cracks showing green alteration fronts. Single nodules may

 $\underline{\text{also sporadically occur embedded within metre-thick beds of red and green clay}. \ Nodules \ are$

usually 5 to 10 cm in diameter, consist of aphanitic dolomite or occasionally somewhat

596 coarser microspar, and in cross section show both red and pale grey areas. Most nodules also

show a deformed or brecciated internal structure with the interstices between the clasts mostly

598 consisting of matrix and clay cutans.

600 Germanic Keuper dolomites

A sample from the Weser Fm. (middle Lehrberg bed; clay pit Friedland, 12 km south of

Göttingen, Northern Germany; Seegis, 1997; Arp et al., 2004) exhibits a brittle structure with

high porosity. The material consists mainly of packed ooids with few peloids in a sparitic

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Gelöscht: Carnian Lehrberg Beds

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Gelöscht: shows

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Gelöscht: or rarely

609 cement matrix. Under the SEM, subhedral to euhedral dolomite in the 5-µm-range are observed within the ooids (not shown). 610 A sample from the Norian Arnstadt Fm. (formerly termed "Steinmergelkeuper"; middle 611 grey series; locality of Krähenberg, 11 km SSW of Göttingen, Northern Germany; Arp et al. 612 2005) shows mm-scale lamination and cm- to dm-sized laminated clasts, which were 613 Gelöscht: a interpreted as a stromatolite breccia. The laminae contain abundant agglutinated siliciclastic 614 grains (mainly quartz, subordinate albite) and phosphoritic fish scales. The dolomicrite 615 exhibits a subhedral structure in the ≤5 µm range with a few larger, subhedral grains resulting 616 Gelöscht: shows in a porphyrotopic fabric. 617 Gelöscht: (not shown) 618 4.2 Mineralogy 619 Bulk dolomite shows a position of the 104 peak at a mean d-value of 2.88816 Å (Fig. 7a). 620 Gelöscht: ; Table 2 This indicates a Ca content of 50.7%, based on the equation of Lumsden (1979). The 621 622 structural order is indicated by the ratio of the superlattice-ordering peak at (015) to the (110) ordering peak. The height ratio is 0.44, which is near 0.519 (inset in Fig. 7a), indicated for an 623 Gelöscht: to ordered dolomite in the Highscore database. 624 Patrick 28-4-2019 18 Gelöscht: Table 2 Clay mineral analysis (Fig. 7b-d) reveals illite in samples TZ14-1 and TZ14-7 and an R3 625 Patrick 23-4-2019 16:38 Gelöscht: revealed ordered illite-smectite mixed-layer clay mineral in sample TZ14-9. In the ethylene-glycol-626 saturated state, the broad shoulder at 11.4 Å contains components of the illite 001 reflection 627 and of the fourth order of a 47 Å superstructure peak whose unit cell consists of three 10 Å 628 illite layers and one 17 Å smectite layer (Moore and Reynolds, 1997). This smectite 629 component <u>is</u> not observed in samples TZ14-1 and TZ14-7. 630 Gelöscht: was 631 Gelöscht: ... [7] 4.3 Carbon and oxygen isotopes 632 Patrick 28-4-2019 19:02 Gelöscht: 4 Carbon isotope values vary between -3.38 and +4% VPDB. Oxygen isotope values are 633 between -0.7 and +0.9% VPDB (three outliers show values as low as -1.5% VPDB; Fig. 8a; 634 Gelöscht: Table 4: 15

and between 0.57 and 0.79 µmol/g in the 1 N acetic acid fraction (except one extremely high

value of 34.91 µmol/g in sample TZ14-9). These contents are much higher than in pure clay

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PANGAEA Data Archiving & Publication PDI-20535). A clear distinction occurs between 647 nodular dolomites exhibiting negative δ^{13} C values and homogeneous dolomites showing 648 Patrick 23-4-2019 1 Gelöscht: showing positive values. Laminated dolomites demonstrate intermediate values and low variability. 649 Patrick 23-4-2019 15:3 Gelöscht: -The oxygen isotopes show an upward increasing trend (Fig. 8b). The calculated temperature 650 Patrick 23-4-2019 15:39 Gelöscht: show of formation assuming a Triassic seawater composition of -1% VSMOW using the 651 fractionation equation of Vasconcelos et al. (2005) results in temperatures between 29 and 652 Patrick 23-4-2019 15:40 Gelöscht: shows 39°C; more positive values would result in higher water temperatures. 653 Patrick 23-4-2019 15:4 Gelöscht: . A 654 Patrick 23-4-2019 15:4° Gelöscht: of the water 4.4 Elemental composition of the dolomites 655 Gelöscht: 5 Sequentially extracted samples TZ14-1, TZ14-7, and TZ14-9 (PANGAEA Data Archiving 656 Gelöscht: Concentrations of the elements & Publication PDI-20535) show Ca contents between 1.68 and 2.33 mmol/g in the 0.1 N 657 Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, Ba, Sr, and Rb (mmol/g sample) are shown in 658 acetic acid fraction and between 2.71 and 2.87 mmol/g in the 1 N acetic acid fraction. Mg Patrick 28-4-2019 19:21 Gelöscht: contents are between 1.61 and 2.34 mmol/g in the 0.1 N acetic acid fraction and between 2.48 659 Patrick 28-4-2019 19:0 Gelöscht: Table 5. and 2.64 mmol/g in the 1 N acetic acid fraction. Based on these concentrations, the amount of 660 Patrick 28-4-2019 19:21 Gelöscht: are dolomite dissolved is between 30 and 43 wt% of the bulk sample in the 0.1 N acetic acid 661 662 fraction and between 49 and 52 wt% in the 1 N acetic acid fraction of the sequential extraction. In total, between 84 and 90 wt% of the bulk sample were dissolved during these 663 two extraction steps. If molar concentrations of Ca are plotted vs. Mg, a linear trend with a 664 665 slope of 0.935 is observed (Fig. 9a), indicating 48.3 mol% MgCO₃ in the dolomite phase. Correlation of Sr contents to other elements did not show clear trends. In particular, Sr-666 Patrick 30-4-2019 18:50 [3] verschoben (Einfügung) content did not correlate with Mg or Ca. Sr correlates with K (Fig. 9b), but at the same time, 667 K is extremely low in all clay mineral leachates. The Sr-concentrations in bulk dolomite 668 samples (Fig. 10a-c) are in the range of 0.38 and 1.16 µmol/g in the 0.1 N acetic acid fraction 669 Patrick 28-4-2019 19:11

Gelöscht:

686	mineral samples (Fig. 10d) with 0.047-0.417 µmol/g in the 0.1 N acetic acid fraction and even		Patrick 30-4-2019 18:50
		/	[3] nach oben verschoben: Correlation
687	lower concentrations (<0.19 µmol/g) in the other fractions. In all samples measured by ICP-		of Sr contents to other elements did not show clear trends. In particular, Sr-content did not
	9/		correlate with Mg or Ca. Sr correlates v [8]
688	OES, rubidium (Rb) concentrations are below the detection limit of 0.012 μmol/g	/	Patrick 30-4-2019 18:52
000	OLO, radiation (Ro) concentrations are select the detection infinit of 0.012 pinions		Gelöscht:
689			Patrick 28-4-2019 19:07
003			Gelöscht: 6
690	4.5 Sr-isotopes		Patrick 30-4-2019 18:53
030	To Botopes		Gelöscht: 87Sr/86Sr-ratios of pure min [9]
691	⁸⁷ Sr/ ⁸⁶ Sr-evolution during <u>leaching experiments</u>		Patrick 30-4-2019 19:16
			Gelöscht: sequential
692	Results of Sr-isotope measurements are listed in PANGAEA Data Archiving & Publication		Patrick 30-4-2019 19:16
			Gelöscht: extraction of dolomites of [10]
693	PDI-20535. Results of sequential and non-sequential leaching tests of bulk samples TZ14-1,		Patrick 30-4-2019 18:55
			Gelöscht: Different modifications of the
694	TZ14-7, and TZ14-9, are shown in Fig. 10a-c, 87Sr/86Sr-ratios decrease in sample TZ14-1 from		Patrick 30-4-2019 18:55
			Gelöscht: extraction
695	0.708125 ± 0.000012 to 0.707666 ± 0.000004 with increasing strength of the leaching reagent,		Patrick 30-4-2019 18:55
			Gelöscht: were investigated using three
696	while the values remain almost constant in sample TZ14-9. The values of bulk dolomite are		Patrick 30-4-2019 18:55
			Gelöscht: samples
697	slightly lower in the 1 N acetic acid fraction than in the 0.1 N acetic acid fraction, only micro-		Patrick 30-4-2019 18:55
			Gelöscht: (Patrick 30-4-2019 18:55
698	<u>dilled samples show higher values.</u> However, repeating the 0.1 N acetic acid extraction (for		Gelöscht: ;
			Patrick 30-4-2019 18:54
699	36 h) after a rather intense first extraction (4h, 12h, 4h) results in extremely high values		Gelöscht: Table 6
			Patrick 30-4-2019 18:55
700	$(0.715417 \pm 0.000250 \text{ in TZ}14-1 \text{ and } 0.7192266 \pm 0.000455 \text{ in TZ}14-9; \text{ not shown in Fig. 10}).$		Gelöscht:)
	77		Patrick 23-4-2019 15:36
701	Standard deviations are also higher than in the other fractions, Highest 87Sr/86Sr-ratios of up to		Gelöscht: resulted
	0.500450 0.00005 1		Patrick 30-4-2019 18:56
702	0.730453 ±0.000005 in sample TZ14-7 are reached by extraction with 6 N HCl. These		Gelöscht:[11]
			Patrick 30-4-2019 19:07
703	fractions show at the same time the lowest Sr-concentrations (see above).		Gelöscht: fractions were extracted [12]
704	Securation extractions of the plan complex T716.1 and T716.10D with the largest TIC of		Patrick 30-4-2019 19:08
704	Sequential extractions of the clay samples <u>TZ16-1 und TZ16-19B with the lowest TIC of</u>		Gelöscht:
705	0.02 wt% (Fig. 10d; PANGAEA Data Archiving & Publication PDI-20535) show a similar		Patrick 30-4-2019 18:59
703	0.02 Wt/0 (Fig. 10d, 1 ANOAEA Data Alchiving & 1 doneadon 1 Di-20000) Show a shiftial		Formatiert: Schriftart:Kursiv
706	increase in the ⁸⁷ Sr/ ⁸⁶ Sr-ratio with the sequential extraction steps from 0.1 N acetic acid to 6 N		Patrick 28-4-2019 19:06
700	micrease in the Sit Si-ratio with the sequential extraction steps from 0.1 iv accide acid to 0.1v		Gelöscht: from the Travenanzes Fm.
707	HCl, reaching similar values as in the HCl-fraction of the dolomites (0.722998 ±0.000018 to		Patrick 30-4-2019 19:11
707	1101, teaching similar values as in the increased of the dolonines to the		Gelöscht: fraction
708	0.733910 ± 0.000024).		Patrick 30-4-2019 19:09
700	01755710 ±010000 ± 1)1		Gelöscht: where 87 Sr/86 Sr-ratios
709	Repeated extractions of chemically pure reference material (Fig. 10e,f) dissolved in 0.1 N		Patrick 30-4-2019 19:10 Gelöscht: extracts
	The state of the s		Patrick 30-4-2019 19:10
710	acetic acid show a range of ⁸⁷ Sr/ ⁸⁶ Sr-ratios in dolomite between 0.709942 ±0.000011 and		Gelöscht: from
			Patrick 30-4-2019 19:15
711	0.710831 ±0.000007. Pure single crystals of dolomite extracted sequentially show the highest		Gelöscht:
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756	value (0.708401 ±0.000040) in the 1 M NaCl fraction. Values in the 0.1 N acetic acid fraction
757	(0.707735 ±0.000006) and the 1 N acetic acid fraction (0.707666 ±0.000006) are lower by
758	almost 0.001 compared to the NaCl fraction.
759	In pure barite, ⁸⁷ Sr/ ⁸⁶ Sr-ratios decrease by about 0.0013 in the extraction sequence from 0.1
760	N acetic acid to 6 N HCl. Celestine is highly soluble and was only measured in the 1 M NaCl
761	fraction and once in 0.1 N acetic acid. Extracts of pure celestine show similar values as in the
762	1 M NaCl fraction of the barite-celestine-dolomite mixture (0.708038 ±0.000003), but the
763	mixture show higher values (0.709501 ±0.000040) in the 0.1 N acetic acid fraction.
764	
765	⁸⁷ Sr/ ⁸⁶ Sr-ratios in micro-drilled dolomite
766	Eleven dolomite samples were micro-drilled from areas where dolomite was most pure
767	based on examination by SEM and dissolved in 0.1 N acetic acid. The values of the
768	Travenanzes Fm. are in the range of 0.707672 ± 0.000003 to 0.707976 ± 0.000004 (Fig. 11).
769	The highest value occurs in a dolomite nodule, while no systematic difference between
770	homogenous and laminated dolomite was observed. Dolomite of the Germanic Keuper
771	samples shows much higher 87 Sr/ 86 Sr-ratios of 0.709303 ±0.000006 and 0.709805 ±0.000005,
772	respectively.
773	
774	⁸⁷ Sr/ ⁸⁶ Sr-ratios of modern dolomites (Deep Springs Lake, Coorong Lakes)
775	Dolomites of Deep Springs Lake show strongly radiogenic values of 0.713086 ±0.000004
776	and 0.713207 ±0.000004 (Fig. 12), which are much higher than modern seawater values, with
777	a ⁸⁷ Sr/ ⁸⁶ Sr-ratio of 0.709234 ±0.000009 (DePaolo and Ingram, 1985). In contrast, dolomite
778	from the Coorong Lakes (Milne Lake; Fig. 12) demonstrates ratios between 0.709251
779	±0.000004 and 0.709275 ±0.000003, which is very near to modern seawater. Different
780	incubation times (5 min und 10 h) in 0.1 N acetic acid had no influence on the isotope ratios.

5 Discussion

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5.1 Interpretation of microfacies within different types of dolomite

Homogeneous dolomite beds

The homogeneous dolomite beds, which are mainly intercalated in the lower, clay-rich part of the Travenanzes Fm., consist of fine-grained dolomicrite (aphanotopic dolomite), with occasional intraclasts of the same aphanotopic dolomite, Soft sediment deformation and dolomicrite infill between mud clasts indicate that this sediment consisted of unlithified, albeit cohesive, carbonate mud. Based on the abundance of fine mud, water energy was probably not very high (Demicco and Hardie, 1994), although reworking and partial rounding of the mud clasts requires at least occasionally higher water energies. According to the standard microfacies concept, homogeneous aphanotopic dolomite falls into SMF 23 ("nonlaminated homogeneous micrite and microsparite without fossils"), indicating deposition in "saline and evaporative environments, e.g. in tidal ponds" (Flügel, 2010). In addition, SMF 24 ("lithoclastic floatstones, rudstones and breccias") is observed in some of the beds where mud clasts are abundant. These facies types are consistent with supersaturation-driven precipitation of fine-grained authigenic carbonate in environments that were partially restricted from open seawater, and would match with a coastal sabkha environment and/or shallow ephemeral lake, Ephemeral lakes may have formed on extended coastal alluvial plains along the Tethyan margin during the Carnian, as suggested by Breda and Preto (2011). The fine mud may have been homogenized and redistributed due to minor wave action in the ponds (cf. Ginsburg, 1971), which is often observed in ephemeral lake settings, explaining the formation of homogeneous dolomite beds. Episodic flooding of the alluvial plain by the dryland river system may have supplied water to temporary evaporating ponds. Alternatively, the alluvial plain may have been sporadically

flooded by seawater, explaining the intercalations of authigenic dolomite layers with alluvial

clays (Breda and Preto, 2011). Homogeneous dolomites show a positive carbon isotope

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Gelöscht: which however mostly evaporated before reaching the coast, led to the formation of a dryland river system (Breda and Preto, 2011). The fluvial system

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signature between 0.7 and 4‰ VPDB (except one outlier), which is consistent with formation from unaltered marine carbon in evaporative brine, with no significant contribution of ¹²C derived from organic matter. Evaporative conditions are also indicated by several gypsum beds that occur between 45 and 70 m in the section, and pseudomorphs after gypsum, which are observed in a thin section of a dolomite at 120 m (Fig. 4c, d). However, evaporites may not always be preserved, as they are frequently dissolved due to seasonally wet conditions.

A bed of dolomitic ooid grainstone that is devoid of matrix occurs at 64 m (Fig. 4e), and

tempestites with moldic porosity indicative of dissolved allochems and dissolved fossils occurs at several levels in the section, always associated to homogeneous dolomites. These beds must represent events of higher water energy, contributing sediment from more open marine areas. The presence of marine fossils, such as *Megalodon_bivalves*, indicate that the environment was influenced by marine conditions, at least episodically. The microfacies of the oolite falls into SMF 15, which indicates proximity to the seaward edge of the platform. Several beds containing abundant siliciclastic material (mainly angular quartz clasts) are likely due to a riverine flooding event, which provided detrital material from the continent. In general, the microfacies in the homogenous dolomite beds reflects both marine and continental influences on the depositional environment.

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Laminated dolomite

Laminated dolomites reminiscent of loferites (Fischer, 1964) occur in the upper part of the clay-rich interval. The change from more homogeneous to laminated dolomite intercalations correlates with the change from red to dark grey clay. The laminations consist of millimetrescale dolomite/clay interlayers suggesting alternating deposition of clay and fine dolomite. This microfacies falls into SMF 25 ("laminated evaporite-carbonate mudstone facies"), indicating an "upper intertidal to supratidal sabkha facies in arid and semiarid coastal plains and evaporitic lacustrine basins" (Flügel, 2010). Laminae showing soft sediment deformation

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Gelöscht: While most homogeneous dolomite beds consist of aphanitic dolomite, a

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Gelöscht: showing

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Gelöscht: at least episodically

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Gelöscht: influenced

Patrick 29-4-2019 16:10 **Gelöscht:** A similar facies, however, is

encountered in the Carnian Lehrberg Beds (Seegis, 1997) in a lacustrine setting.

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interval

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cannot be attributed to stromatolitic bindstone facies (SMF 19 to 21). Only some layers that show, a coarser fabric with interstitial dolosparite or dolomicrosparite containing putative peloids have been interpreted as microbial laminites (Preto et al., 2015). Graded bedding mostly indicates a direct sedimentation process rather than *in situ* precipitation of the primary carbonate within a microbial mat (Vasconcelos et al., 2006; Bouton et al., 2016; Court et al., 2017; Perri et al., 2018). A detrital origin of the clay in the dolomites is confirmed by a well-ordered illite-smectite mixed-layer composition, which is atypical for authigenic clay minerals. Frequent subaerial exposure and desiccation may explain why the sediment was not homogenized and the lamination is preserved. This is supported by the occurrence of pseudoteepee structures as remnants of desiccation cracks. Rip-up clasts were formed during subsequent flooding, when angular flat pebbles formed when the sediment was desiccated or partially lithified. However, laminae also frequently exhibit plastic deformation (e.g. in Fig. 3g) where the mud was still unlithified.

Some uncertainty exists as to whether this facies was peritidal, or represents an ephemeral lake, as suggested for the homogeneous dolomites above. Episodic high water-energy, as indicated by the rip-up clasts, combined with frequent desiccation, could point to evaporative tidal conditions, that occur in a sabkha. What is atypical for a modern sabkha is the large amount of clay input. This is attributed to seasonally wet conditions during the Carnian, and the sediments can be considered to be a mixed facies of alluvial plain and coastal sabkha: a "dirty" sabkha (see discussion below). Under such conditions, large amounts of evaporites, in particular gypsum, could have been dissolved. Why the occurrence of laminated dolomites coincides with the transition from red to grey clays is not clear, but may be related to more permanently water-saturated conditions in the subsurface, while the surface was exposed to periodic desiccation. These conditions would also be consistent with a sabkha environment.

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During intervals of arid conditions, the clay beds were subject to strong evaporation and vadose diagenesis, causing oxidation and the red colour. Although red beds may also form in humid environments if drainage is rapid (Sheldon, 2005), drainage was certainly slow due to the large amounts of poorly permeable clay in the Travenanzes Fm., and the climate was clearly seasonally, arid (Breda and Preto, 2011). Dolomite nodules that occur sporadically within certain intervals show internal brecciation, which must have occurred after sedimentation. Internal brecciation is a typical feature of present day calcretes in arid environments (e.g. Mather et al., 2018). Slightly negative δ¹³C-values indicate a contribution of carbon derived from organic matter degradation, further suggesting that they formed within the sediment. The formation of dolomite nodules could presumably be related to diagenesis in palaeosols. In the upper part of the section (between 80 and 105 m) dolomite nodules are associated with green reaction haloes along vertical peds in palaeosols of vertisol-calcisol type (Preto et al., 2015). Carbonate formation may have been related to reducing fluids in water-logged soils during humid intervals, while the cracks formed during desiccation in dry periods, perhaps facilitated by the presence of expandable clay minerals (smectite).

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5.2 The origin of ionic solutions conducive to dolomite formation

Overall, the dolomites in the Travenanzes Fm. show a facies association that matches a variety of potential depositional environments. They have similarities to the Germanic Keuper succession, and it is not entirely clear if a marine influence occurred, except where indicated by marine fossils, as in the tempestite beds. Sr-isotopes were analysed in order to better trace the origins of ionic solutions to the environments that were conducive to dolomite formation.

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Strontium derived from seawater

Radiogenic ⁸⁷Sr/⁸⁶Sr ratios can be indicative of the source of ionic solutions that the dolomite precipitated from (Müller et al., 1990a; Müller et al., 1990b). Sr-isotopes in selected

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model for dolomite formation, where alkalinity is largely derived from continental

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970 dolomites from the Travenanzes Fm. at the Dibona section show values between 0.707672 Patrick 23-4-2019 14:55 Gelöscht: through ±0.000003 and 0.707976 ±0.000004. Ammonoids found at the base of the succession suggest 971 Patrick 23-4-2019 14:5 Gelöscht: ed a Tuvalian II age (subbullatus zone, 232.5-231.0 Ma; Ogg, 2012). The upper boundary of the 972 Patrick 13-5-2019 02 Gelöscht: We correlate the Dibona section 973 Travenanzes Fm. is time-transgressive, and hence the exact age is not known. We assume that (Fig. 10) with the Carnian seawater curve (Korte et al., 2003). Although the age interval 974 the sedimentation rate was at least as high, or higher, than in the peritidal carbonates of the of the Travenanzes Fm. is not precisely constrained, findings of ammonites Dolomia Principale. In this region, the Dolomia Principale includes a part of the Rhaetian 975 Gelöscht: precisely constrained 976 (Neri et al., 2007) and, thus, its upper boundary is near the Triassic-Jurassic boundary at 201.3 977 Ma. Although the age interval of the Travenanzes Fm. is not precisely constrained, we correlate the Dibona section (Fig. 11) with the Carnian seawater curve (Korte et al., 2003). 978 979 The seawater curve was fixed at the lower boundary of the Travenanzes Fm. and the time axis was varied to fit the seawater curve parallel to the envelope of minimal 87Sr/86Sr-ratios 980 measured in the dolomites (Fig. 11). The base of the first massive dolomite at 110 m in the 981 Patrick 30-4-2019 13:10 Gelöscht: 10 profile would therefore have an age of approximately 229 Ma. 982 Patrick 23-4-2019 14:57 Gelöscht: then 983 Comparison with the seawater curve shows that the dolomites of the Travenanzes Fm. have Formatiert: Schriftart: (Standard) Times, largely marine 87Sr/86Sr-ratios (Fig. 11). Only values from micro-drilled samples extracted 984 12 pt, Schriftfarbe: Schwarz, Englisch (Vereinigtes Königreich) 985 with 0.1 N acetic acid were used for this reconstruction, and the resulting values all lie within Gelöscht: 10 0.00022 of seawater values (grey shaded area). This scatter towards more positive values, 986 Patrick 23-4-2019 14:53 Gelöscht: most gently compared to seawater, may be due to a small influence by continental water. Indeed, during 987 Patrick 23-4-2019 14:53 Gelöscht: a range of 988 deposition of the Travenanzes Fm. sufficient continental water would have been available Patrick 23-4-2019 14:53 Gelöscht: with the 989 from rivers, and ions may have become concentrated while the water was evaporating in the Patrick 23-4-2019 14:54 Gelöscht: of 990 distal alluvial plain. Alternatively, Sr desorbed from clay minerals could have added more radiogenic values to the brine. But even if a small influence of Sr of continental origin is 991 992 present, the marine signal is dominant because of the much higher Sr concentrations in Patrick 23-4-2019 14:52 Gelöscht: because of the much higher Sr 993 seawater. concentrations in seawater 994 The marine signature shown by the Sr-isotopes does not support the classical Coorong Gelöscht: This

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groundwater. The Coorong Lakes in South Australia are ephemeral lakes largely supplied by 1015 groundwater (Von der Borch et al., 1975). Strangely, though, the ⁸⁷Sr/⁸⁶Sr ratios we measured 1016 1017 from Milne Lake (one of the Coorong Lakes) exhibit a modern seawater composition (Fig. 11), but this can be explained, as the local groundwater largely originates from a Pleistocene 1018 1019 carbonate aquifer, and accordingly, carry a Pleistocene Sr-isotope signature. A similar 1020 scenario for the Travenanzes Fm. is unlikely as the only large-scale preceding carbonate platforms at that time were the upper Ladinian-Carnian Cassian dolomite platforms (Russo et 1021 1022 al., 1997). Based on the stratigraphic context, all basins between these platforms were infilled 1023 by the Heiligkreuz Fm. and an extremely flat topography was later established that is 1024 stratigraphically overlain and sealed by the alluvial deposits of the laterally persistent 1025 Travenanzes Formation. Furthermore, the Travenanzes Fm. consists of 100 m of impermeable clay (including expandable clays), such that the long-distance transport of groundwater can be 1026 1027 excluded.

We conclude that the ⁸⁷Sr/⁸⁶Sr ratios of the dolomites represent a <u>predominantly</u> marine influence. Presumably, seawater was transported to the interior of <u>a coastal plain</u> by episodic flooding (spring tide or storm) events. Even in a seasonally wet climate, the input of river water on Sr-isotopes was insignificant compared to the influence of ions (including Sr) from seawater that <u>were</u> concentrated by evaporation. Laminated dolomites in the uppermost part of the section show values most similar to seawater composition, which is consistent with a greater influence of peritidal conditions.

1036 The influence of Sr adsorbed to clay minerals

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Despite precautions to prevent contamination by other mineral phases by micro-drilling and using mild reagents, some scatter occurs in the Sr-isotope data. Higher ⁸⁷Sr/⁸⁶Sr ratios in a dolomite nodule may be due to a continental influence or perhaps more seasonally wet and evaporative conditions with less of a marine influence. But higher values also may be due to

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contamination and partial leaching of clay minerals within the dolomite samples. Within the extraction sequence (1 M NaCl → 0.1 N acetic acid → 1 N acetic acid), the ⁸⁷Sr/⁸⁶Sr ratio generally remains constant or becomes slightly less radiogenic, i.e., more similar to seawater. However, the values strongly increase with leaching in 6 N HCl (Table 6). A modification of ⁸⁷Sr/⁸⁶Sr ratios due to contamination by ⁸⁷Sr from the radioactive decay of ⁸⁷Rb to ⁸⁷Sr can be considered as negligible since the concentrations of Rb was below the detection limit of 0.05 ppm (Table 5)₂ and the half <u>life</u> is 48.8 billion years. <u>In addition, the</u> influence of celestine and Sr-rich barite, <u>which were</u> observed under <u>SEM</u>, on <u>Sr-isotope values can also be largely excluded. These mineral phases are bound to distinct layers of the laminated dolomites, <u>and</u> they could be avoided by micro-drilling areas where the dolomite <u>is</u> pure. Only one value from sample TZ14-9 shows extremely high Sr-concentrations. This sample was micro-drilled near a celestine layer, and it is therefore not surprising that a celestine crystal may have been <u>inadvertently sampled</u>. The isotopic composition of the celestine is also similar to Carnian seawater.</u>

In the NaCl-fraction, only minimal amounts of dolomite are dissolved. The slightly more radiogenic ⁸⁷Sr/⁸⁶Sr ratio may be derived from Sr that is lightly adsorbed to clay minerals and finely dispersed in the clay matrix, although Sr²⁺ as a two-valent cation is more strongly adsorbed to clay minerals than Na⁺, and thus is not easily desorbed by NaCl. The values approach seawater values in the 1 N acetic acid fraction with increasing extraction efficiency and purity of the carbonate phase. Values from micro-drilled samples are also generally more similar to seawater values, probably because more pure dolomite was sampled (PANGAEA Data Archiving & Publication PDI-20535). 1 N acetic acid is usually observed to not strongly attack interlayer ions in clay minerals.

Clay minerals leached in 6 N HCl show significantly more radiogenic values compared to dolomite samples. This finding is consistent with strongly radiogenic values in the 6 N HCl-fraction of dolomite samples (up to 0.730453 ±0.000005) and supports that the clay minerals

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are the carriers of a Sr-pool significantly more radiogenic than the carbonate phase showing marine values. Sr is known to adsorb to illite-smectite mixed layer clay minerals (Missana et al., 2008). The HCl-fraction most likely includes adsorbed Sr, and Sr occupying the interlayer positions of the clay minerals, and presumably also structurally bound Sr in the clay mineral phase. In particular, illite-smectite mixed-layer clay minerals, as detected by XRD of the clay mineral separate in sample TZ14-9 (Fig. 7d), could have two different origins; burial diagenesis and continental weathering. Based on the tectonic setting and shallow burial depth of the Dolomites, the burial depth for smectite-illite transition has not been reached. Therefore, these minerals are most likely derived from silicate weathering, with the Sr-signature representing the crustal origin of the parent rock. Our finding of radiogenic Sr-isotope ratios supports that clay minerals did not incorporate Sr from seawater during a sealevel stand. It is therefore clear that Sr extracted from the dolomites is not derived from clay minerals.

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Dolomite as primary archive of Sr-isotope signatures

The question is, whether Sr truly represents the conditions of dolomite formation or whether it inherited the Sr content of some precursor phase. Baker and Burns (1985) and Vahrenkamp and Swart (1990) document very small distribution coefficients between aqueous and solid solutions, and high Sr-contents measured in Abu Dahbi sabkha dolomites (Müller et al., 1990b) may be derived from precursor aragonite. However, if dolomite in the Travenanzes Fm. is largely primary (Preto et al., 2015) and thus not formed from an aragonite precursor, the Sr-content should truly derive from the dolomite phase. Although some Sr may have been released due to replacement of the dolomite, and excess Sr can explain the occurrence of celestine and barite inclusions, nanocrystal structures imply that primary dolomite is partially preserved. Indeed, Sánchez-Román et al. (2011) demonstrate a protodolomite forming in culture experiments that contains Sr in the range of several

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thousand ppm. The incorporation mechanism of Sr is still not entirely clear, since Sr is a large ion that should occupy the sites of Ca in the crystal lattice. However, in Sánchez-Román et al. (2011), Sr appears to correlate with the Mg content, and another incorporation mechanism may occur, such as surface entrapment. Also the correlation of Sr-contents with K-contents could be explained by such a mechanism of Sr-incorporation. Even if only protodolomite formed in microbial culture experiments (Gregg et al., 2015), natural modern dolomites are often rich in Sr (e.g. Meister et al., 2007). The Sr could occur in disordered nano-structural domains that are not picked up in the bulk XRD-signal. Non-classical nucleation and growth pathways, e.g. by nanoparticle attachment, could play a role in the abnormal partitioning of Sr in the dolomite lattice. Thus, a high Sr-content in the Travenanzes Fm. or in Abu Dhabi Sabkha dolomites is likely a true signature of primary dolomites.

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5.3 Mode of dolomite formation and comparison with known models

Primary dolomite formation

Several <u>results</u> support a <u>largely primary</u> origin of dolomite in the Travenanzes <u>Formation</u>. Formation temperatures reconstructed from oxygen isotopes (assuming Triassic seawater composition of -1% VSMOW) are between 28 and 33°C. If a typical ¹⁸O enrichment of 3% due to evaporation in a sabkha is assumed (McKenzie et al., 1980; McKenzie, 1981), the calculated temperatures are between 40 and 50°C, which is still within the possible range in a sakbha (cf. Hsü and Schneider, 1973). Both temperature and evaporation may have changed over time, which may explain the observed linear trend in oxygen isotopes across the section (Fig. 8B) although there is no co-variation between $\delta^{13}C$ and $\delta^{18}O$ as it would be expected due to evaporation in hydrologically closed settings, such as the Germanic Keuper basin (Reinhardt and Ricken, 2000; Arp et al., 2005). But also, the observed trend in δ^{18} O would be too steep to be explained by overprinting within a normal geothermal gradient, and no signs of any hydrothermal activity occur in this region. In any case, the oxygen isotope data do not

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imply any post-depositional overprint, while nano-crystalline structures observed by Preto et al. (2015) preclude a later pervasive recrystallization during burial diagenesis. Sedimentary structures indicate that most of the homogenous dolomite and laminae containing aphanotopic dolomite was unlithified, and dolomite was therefore deposited as fine-grained mud. This is further supported by mm-scale interlayering of clay and dolomite in the laminated dolomites near the top of the sequence, and some dolomite/clay couplets exhibiting fining-upward bedding. Based on the observation of nano-crystal structures, replacement did not take place, and it appears logical to assume that the primary phase was already dolomite.

While most of the dolomite may have been primary, micron-scale interstices between the dolomicrite grains must have been cemented after deposition. This cementation resulted in rims visible under SEM and result in near hexagonal compromise boundaries. The cement may have contributed 13 C-depleted carbon during early diagenesis. The lowest δ^{13} C values of 3 4% VPDB occur in the nodules. These nodules formed within the sediment, probably due to reducing conditions and influenced by dissolved inorganic carbon from degrading organic matter in the palaeosols. Homogeneous and laminated dolomites are clearly distinct from nodules in their carbon isotope compositions (Fig. 8a), indicating only a minor contribution from pore-water derived dissolved inorganic carbon. Carbon isotope values are thus largely consistent with a primary precipitation. The mode of dolomite formation as fine mud and subsequent cementation is comparable to several modern sites of dolomite formation.

While dolomite formation under Earth surface temperatures has been suggested to be catalysed by microbes, perhaps by secreted organic polymers (EPS; cf. Bontognali et al., 2013), this mechanism is currently under debate (cf. Gregg et al., 2015). The present study does neither support nor rule out such a mechanism. We can raise the question whether microbial EPS is enriched in the surface waters, where it may affect precipitation of fine dolomite mud.

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1228 The sabkha model 1229 The classical sabkha model involves dolomite formation under intra-supratidal conditions, 1230 1231 1232 1233 1234 1235 1236 1237 1238 1239 1240 1241 1242

the concentration of brines through either seepage reflux (Adams and Rhodes, 1960) or evaporative pumping (Hsü and Siegenthaler, 1969; Hsü and Schneider, 1973; McKenzie et al., 1980; McKenzie, 1981), and precipitation of dolomite as Mg/Ca ratios increase due to gypsum precipitation (see Machel, 2004, for a more detailed discussion of varieties of sabkha models). This sabkha model allows for a mixture of seawater and continental groundwater, with seawater mainly providing the ions for dolomite precipitation. Coastal sabkhas are typically characterized by laminated (Lofer-type) dolomites, where the laminae are largely unlithified after deposition (Illing, 1965; Bontognali et al., 2010; Court et al., 2017). In the sabkha of Abu Dhabi, both pathways, via replacement of precursor aragonite and by direct precipitation of dislocation-ridden primary dolomite, are observed (Wenk et al., 1993). The sabkha model is thus a reasonable model for the uppermost parts of the Travenanzes section, which contain laminated dolomites, marine Sr-isotope values and indications of frequent desiccation and flooding in a peritidal setting. Yet, the conditions differed from the

modern sabkhas along the Persion Gulf due to the large amount of alluvial clay (dirty sabkha),

as opposed to aeolian sand. Most of the fine laminations may therefore result from

periodically varying conditions, perhaps with clay deposition during episodes of fluvial

discharge and carbonate deposition during evaporative conditions.

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The continental playa lake model

The playa lake model was originally suggested by Eugster and Surdam (1973) for dolomite 1249 1250 of the Green River Formation (Wyoming), but the primary formation of fine dolomite mud is 1251 observed in many alkaline playa lakes, such as Deep Springs Lake (Peterson et al., 1963; Clayton et al., 1968; Meister et al., 2011), Lake Acigöl (Turkey; Balci et al., 2017), Lake 1252 1253 Neusiedl (Austria; cf. Neuhuber et al., 2016), and Lake Van (Turkey; McCormack et al., Patrick 23-4-2019 14:2

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from an inland karst system. But other coastal ephemeral lakes exist, jncluding along the

Brasilian coast, north of Rio de Janeiro. Partially unlithified dolomite occurs in Brejo do

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2018). For an overview see Eugster and Hardie (1978) and Last (1990). This type of setting 1265 Patrick 23-4-2019 14:09 Gelöscht:: 1266 has also been suggested for the Germanic Keuper deposits during the late Carnian and Norian, Patrick 23-4-2019 14:09 Gelöscht: f when the Germanic Basin was entirely disconnected from Panthalassa and was continental 1267 Patrick 23-4-2019 14:09 Gelöscht:, (Reinhardt and Ricken, 2000). The Travenanzes Fm., with its homogeneous dolomite 1268 Patrick 23-4-2019 14:09 Gelöscht:, 1269 intercalations in red and green clays, is strikingly similar to playa-lake Keuper facies in the Gelöscht:, Germanic Basin. There, dolomite formed following evaporation and concentration of the 1270 Patrick 23-4-2019 14:09 Gelöscht: the 1271 continental brines under a semi-arid climate. Gelöscht: ocean Sr-isotope data, however, support a dominantly marine origin of ionic solutions to the 1272 Patrick 23-4-2019 14:08 Gelöscht: upon Travenanzes Fm., whereas Sr-isotopes are strongly radiogenic in the Germanic Keuper 1273 Patrick 23-4-2019 14:06 Gelöscht: However, 1274 dolomites (or in Deep Springs Lake; Fig. 12). The two settings are thus fundamentally Patrick 30-4-2019 13:08 Gelöscht: 1 different. Even dolomite nodules, showing somewhat more radiogenic values than seawater in 1275 the Travenanzes Fm., still indicate a predominantly marine influence. The slightly more 1276 Gelöscht: are radiogenic influence could be due to clay minerals present in the nodules that were difficult to 1277 Patrick 23-4-2019 14:07 Gelöscht: ing 1278 entirely separate from the carbonate. Also, dolomite nodules may have formed in relation to Patrick 23-4-2019 14:07 Gelöscht: ing palaeosols, during somewhat more humid times and, thus, may have been slightly influenced 1279 Patrick 23-4-2019 14:08 Gelöscht: the 1280 by continental water input from rivers. Patrick 23-4-2019 14:08 Gelöscht: the 1281 The coastal ephemeral lake model (Coorong model) 1282 The Coorong model was proposed by Von der Borch et al. (1975). Von der Borch (1976). Patrick 23-4-2019 14:03 1283 Gelöscht:, Patrick 23-4-1284 Rosen et al. (1989) (see Warren, 2000, for detailed information) to explain the formation of Gelöscht:; Patrick 23-4-2019 14:03 1285 primary and uncemented dolomite in the Coorong lakes of South Australia. The Sr-isotope Gelöscht:; values (Fig.12) show that the contribution of ionic solutions, and hence alkalinity, of 1286 Gelöscht: . Patrick 23-4-2019 14:04 1287 continental origin to the dolomitizing fluids was minimal, and that the dolomites are seawater Gelöscht:; Patrick 23-4-2019 14:04 derived. This may be distinct from the typical Coorong model, where alkalinity is provided 1288 Gelöscht:,

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Espinho (Sánchez-Román et al., 2009), which is largely similar to the Coorong lakes, but ionic solutions are mostly derived from seawater.

A coastal ephemeral lake model would probably be most suitable to explain homogeneous dolomite beds of the Travenanzes Fm., where hypersaline ponds may have formed in a dryland river system. However, unlike recent ephemeral lakes (such as Lagoa Vermelha, Brejo do Espinho and the Coorong Lakes) the clay-rich sediment must have inhibited groundwater flow. Hence, while modern coastal ephemeral lakes receive their water largely through seawater percolating through porous dune sand, episodic flooding with seawater must have provided ionic solutions for dolomite formation on a coastal plain.

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A non-actualistic system

Overall, the depositional environment reconstructed for the Travenanzes Fm. shows similarities to modern systems were dolomite forms. Among all the modern scenarios, a coastal ephemeral lake model would be most similar to the conditions conducive to homogeneous dolomites, lacking signs of frequent desiccation, while a coastal sabkha model may explain the laminated intervals near the top of the studied succession. In contrast to modern systems, the clay rich sediments of the Travenanzes Fm. preclude any input of groundwater, which plays a role for ionic transport in both the modern day ephemeral lake model and the different versions of sabkha models. Although modern systems provide valid analogues for the mechanism of dolomite formation in the past, and probably throughout Earth history, none of them is an exact environmental analogue. The Carnian coastal plains that covered an enormous area along the Tethys margin (e.g. Garzanti et al., 1995) represent a non-actualistic system in terms of their sedimentary, hydrological and climatic boundary conditions. In addition, the geochemistry of Tethys seawater may also have been different from today, an issue that requires further investigation (cf. Burns et al., 2000; Li et al., 2018). These aspects need to be taken into account if we intend to understand the conditions that led

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1351 to dolomite formation through Earth history. Patrick 23-4-2019 14:02 Gelöscht: of In the light of the possibility of spontaneous precipitation of fine dolomite mud in the 1352 Patrick 23-4-2019 13:5 Gelöscht: a water column, perhaps via formation and aggregation of nano-particles, further discussion of 1353 Patrick 23-4-201 Gelöscht: e a nucleation and growth pathway of dolomite is necessary. While several modifiers may also 1354 Patrick 23-4-2019 Gelöscht: as play a role in the water column, such as dissolved organic matter (Frisia et al., 2018), 1355 Gelöscht: will be microbial EPS (Bontognali et al., 2013), or suspended clay particles (Liu et al., 2018), 1356 1357 fluctuating conditions inducing spontaneous nucleation and growth of dolomite, in agreement with Ostwald's step rule (Deelman, 1999), require further consideration as a factor favourable 1358 for dolomite formation on a seasonally variable platform (Meister and Frisia, 2019). 1359 Gelöscht: accepted 1360 The main finding of this study is that most of the dolomite in the >100 m thick Travenanzes Fm. probably formed through direct precipitation from a seawater-derived 1361 Gelöscht: in solution. This mode of primary dolomite formation has rarely been considered in the study of 1362 dolostone formations, but may explain the genesis of many other large-scale, fine-grained 1363 Patrick 23-4-2019 13:58 Gelöscht: geological dolomite bodies 1364 dolomite units that preserve fossils and sedimentary structures. 1365 1366 **6 Conclusions** 1367 Dolomite beds intercalated in a 100-m-thick Carnian alluvial clay sequence in the Patrick 13-5-2019 02:30 Travenanzes Fm. largely formed as fine-grained primary mud. The depositional environment 1368 Gelöscht: was minimally affected by currents and during times of dolomite formation most likely prevailed as ephemeral lakes in an extended Patrick 13-5-2019 02:37 1369 Gelöscht: alluvial Patrick 23-4-2019 1370 coastal plain or dryland river system. The large amounts of clay are related to at least Gelöscht: . Also Patrick 23-4-2019 13 1371 seasonally wet conditions; in addition, palaeosols and diagenetic dolomite nodules could have Gelöscht: strongly 1372 also formed under such conditions. The facies strongly resembles those of Triassic playa lakes Gelöscht: the 1373 found in the Germanic Basin, or in the modern Deep Springs Lake. Gelöscht: prevailing Patrick 23-4-2019 13:55 1374 Sr-isotopes clearly show a marine signal, indicating seawater as the main source of ions. Gelöscht: shows Patrick 23-4-2019 13:55 The depositional environment is most similar to coastal ephemeral lakes resulting in the 1375 Gelöscht: ities Patrick 23-4-2019 13:55 1376 deposition of homogeneous dolomite beds through most of the sequence, changing into a Gelöscht: with

1395	"dirty" sabkha near the top of the sequence, where fine dolomite/clay interlayers suggest		
1396	alternating deposition of extremely fine authigenic dolomite from evaporating water, and		
1397	clay.		
1398	Overall, Sr-isotopes and petrographic observations provide insight into a non-		
1399	uniformitarian system including elements of both coastal ephemeral lake systems and sabkhas		
1400	as the environment of primary dolomite formation. Considering the precipitation of primary		
1401	dolomite from coastal lakes or ponds may help explain other dolomite deposits with preserved		
1402	<u>primary</u> sedimentary features <u>from</u> throughout geologic history.		
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1405	quality petrographic thin sections. Thanks also to W. Obermaier for analysing element		
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1409	support in the laboratory. Thanks also to M. Lorencak for the help during sampling of		
1410	dolomite from the Coorong Lagoon. We thank S. Frisia for input and constructive criticism.		
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1413	626025).		
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Inset: Tectonic map of the Southern Alps (Brack et al., 1996, modified) showing the sampling

location at Rifugio Dibona. GL: Giudicarie Line; PL: Pustertal Line; VL: Val Sugana Line.

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1730	Figure Captions	
1731	Figure 1. (a) Palaeogeographic map of Southern Alpine to Germanic domains during the	Patrick 24-4-2019 13:03
1732	middle Triassic; reproduced from Brack et al. (1999; modified). Bal: Balaton; BG: Burgundy	Gelöscht: Patrick 23-4-2019 13:49
1733	Gate; Car: Carnian Alps; ECG: eastern Carpathian Gate; Lomb: Lombardy; NCA: Northern	Gelöscht: the Patrick 23-4-2019 13:49
1734	Calcareous Alps; SMG: Silesian Moravian Gate. The following cities are indicated for	Gelöscht: ,
1735	orientation: Mr: Marseille; Wa: Warsaw; Kr: Krakow; Be: Berlin; Fr: Frankfurt; Ly: Lyon.	

1741	(b) Middle to Upper Triassic stratigraphy and distribution of facies within the Venetian Alps,	
		Patrick 23-4-2019 13:50
1742	showing a transition in geometries from a basin and platform topography during the lower	Gelöscht: Stratigraphy of the m Patrick 23-4-2019 13:50
1743	Carnian to an extended alluvial to tidal plain in the upper Carnian. The shaded area indicates	Gelöscht: late
	1	Patrick 23-4-2019 13:51
1744	the Travenanzes Fm., showing a lateral transition in facies and a transgressive boundary with	Gelöscht: t
		Patrick 23-4-2019 13:51
1745	the Dolomia Principale. Compiled from Breda and Preto (2011), after De Zanche et al.	Gelöscht: L Patrick 23-4-2019 13:51
1746	(1993), modified.	Gelöscht: is Patrick 23-4-2019 13:51
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1748	Figure 2. Stratigraphic section at Rifugio Dibona: (a) Complete section modified after Breda	Gelöscht: to
1749	and Preto (2011), showing sampling locations; (b) detailed section of the uppermost part of	Patrick 23-4-2019 13:48
1750	the clay-rich interval, showing sampling locations. (c) Outcrop photograph showing the	Gelöscht: a
1751	uppermost grey part of the clay-rich interval <u>including</u> the location of the profile shown in (b).	Data 1 00 4 0040 4040
1752		Patrick 23-4-2019 13:49 Gelöscht: with
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1753	Figure 3. Outcrop images of different types of dolomite intercalated with red and grey clay of	
		Patrick 23-4-2019 13:46
1754	the Travenanzes Fm. at Rifugio Dibona: (a) Homogeneous dolomite bed (15 cm thick; 33 m).	Gelöscht: in
1755	(b) Upper part: dolomite nodules embedded in red clay, crosscut by green coloured cracks	
1756	that are part of a calcic vertisol (95 m). (c) Laminated dolomite (110-112 m) interbedded with	Patrick 23-4-2019 13:47
1757	grey clay. (d) Bed containing gypsum nodules (Gy), along with gypsum-filled cracks at 50 m;	Gelöscht: as
		Patrick 23-4-2019 13:47
1758	(e) Dolomite-cemented conglomerate bed at 75 m. (f) Laminated bed showing soft sediment	Gelöscht: in
		Patrick 23-4-2019 13:47 Gelöscht: with
1759	deformation (106 m); an isoclinal synsedimentary fold is indicated by the arrow. (g)	Patrick 23-4-2019 13:47
1760	Laminated dolomite showing folding of the laminae due to soft sediment deformation (same	Gelöscht: and
1761	had as in A	Patrick 23-4-2019 13:48 Gelöscht: filled with gypsum,
1761	bed as in f).	331
1762		
1763	Figure 4. Photomicrographs of thin sections of dolomites of the Travenanzes Fm.: (a)	
1764	Rounded mud clasts embedded in dolomicrite matrix. The larger_ mm-size intraclast in the	
1765	upper left side of the image (arrow) consists itself of matrix with darker_embedded <u>mud clasts</u>	Patrick 23-4-2019 18:16 Gelöscht: mudclast
1766	(sample TZ16-St1; 104 m). (b) Mud clasts in dolomicrite matrix. Mud clasts are deformed	Patrick 23-4-2019 18:16
1,00	(sample 1210-501, 107 m). (b) mad clasts in dolometre matrix. Frad clasts are deformed	Gelöscht: Mudclast
	46	

the 104 peak using the equation of Lumsden (1979) and the structural ordering calculated

1809

1784 (e.g., arrow); layers of coarser (C) and finer matrix (F) are equally affected by plastic Patrick 23-4-2019 13:44 Gelöscht: and 1785 deformation (sample TZ16-22; 120 m). (c, d) Pseudomorphs after gypsum in fine-grained dolomudstone (e.g., arrows). (e) Oolitic grainstone (sample TZ14-4; 64 m). The cortices 1786 consist of microcrystalline dolomite and lack a radial structure, some showing a concentric 1787 Gelöscht: ing 1788 structure (arrow). (f) Laminated dolomite showing pseudo-teepee structures (arrow). Vertical Patrick 23-4-2019 Gelöscht: . cracks are often, but not always, associated with pseudo-teepees (sample TZ14-10; 107 m). 1789 Gelöscht: S Some coarser grained laminae may contain microsparite and peloids (P with small arrows). 1790 (g) Laminated dolomite showing both plastic and brittle deformation of laminae. A cm-scale 1791 1792 pseudo-teepee occurs in the centre of the image (sample TZ 16-21; 107 m). (h, i) Closeup of 1793 graded lamina in (g) showing plastic deformation. The top of the lamina shows an erosion 1794 surface with small rip-up clasts (arrow), overlain by a coarser layer. Patrick 23-4-2019 13:42 1795 Gelöscht: enriched in Patrick 23-4-2019 13:43 Figure 5. SEM images of dolomites in backscatter mode: (a) Overview showing a dolomite Gelöscht:) 1796 Patrick 23-4-2019 13:42 1797 layer containing celestine inclusions (bright areas; Sample TZ14-9d; 95 m); (b) Celestine Gelöscht: in dolomite (Patrick 23-4-2019 13:40 Gelöscht: domain but 1798 inclusion with barite in the centre (same sample as in a); (c) Barite crystals in dolomicrite Patrick 23-4-2019 13:41 Gelöscht:). (1799 (sample TZ14-4; 65 m). Patrick 23-4-2019 13:41 Formatiert: Schriftart: Nicht Fett 1800 Patrick 23-4-2019 13:41 Gelöscht:) Similar as in (c; 1801 Figure 6. SEM images of dolomites in backscatter mode showing different types of crystal Patrick 28-4-2019 17:53 Formatiert: Schriftart: Nicht Fett 1802 shape: (a) Spheroidal growth of dolomite (darker areas) in clay layers (brighter areas; sample Patrick 28-4-2019 17:53 [2] verschoben (Einfügung) 1803 TZ14-9d; 95 m). (b) Closeup of a. (c, d) Dolomite crystals showing a porous interior and Gelöscht: Table 2 1804 homogeneous syntaxial cement rims (c: sample TZ14-12; 90 m; d; sample TZ14-9d; 95 m). Gelöscht: Relative abundances and ordering 1805 parameters of dolomites from the Travenanzes Formation. Relative abundances were 1806 Figure 7. X-ray diffraction patterns: (a) Bulk analyses of homogeneous dolomite (Samples estimated based on the 104 peak height. The stoichiometry Patrick 28-4-2019 17:56 TZ14-1, TZ14-7, and TZ14-9); main peaks and ordering peaks are labelled with (hkl) indices, 1807 Gelöscht: was Patrick 28-4-2019 17:56 The inset in (a) shows the Mg/(Ca+Mg) ratios in the dolomites determined from the shift of 1808 Gelöscht: . T

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Gelöscht: was

from the ratio of the 015 ordering peak to the 110 peak according to Füchtbauer and 1829 Goldschmidt (1966), (b-d) Clay mineral separates of samples TZ14-1, TZ14-7 and TZ14-9, 1830 Patrick 28-4-2019 17:5 Gelöscht: ... [14] 1831 air dried (N), saturated with ethylene glycol (EG), and heated to 550°C (T); d-values in Å. The illite-smectite mixed-layer is best seen in the ethylene-glycol saturated sample TZ14-9, 1832 Patrick 23-4-2019 13:39 Gelöscht: I 1833 The arrow points to the expandable (smectite) part of the mixed-layer. Patrick 23-4-2019 13:39 Gelöscht: the illite-smectite mixed-layer is 1834 best seen Patrick 23-4-2019 13:40 Figure 8. (a) Carbon/oxygen isotope cross-plot shows a clear distinction between 1835 Gelöscht: at homogeneous, laminated, peloidal and nodular dolomites. Nodular dolomites are probably 1836 Patrick 14-5-2019 11:30 Gelöscht: . influenced by carbon derived from organic matter. (b) Oxygen isotope values (δ^{18} O) show a 1837 positive trend with a gradient of 2% over the 100-m-thick stratigraphic section. This could be 1838 Patrick 30-4-2019 14:26 Gelöscht: through the due to a decrease in precipitation temperature or to a change in the δ^{18} O of the water over 1839 1840 time. 1841 1842 Figure 9. Element concentrations in sequentially extracted fractions of bulk dolomite and clay samples of the Travenanzes Fm.: (a) Ca plotted vs. Mg shows a linear trend, reflecting 1843 Patrick 25-4-2019 00:35 Gelöscht: vs. nearly the 1:1 stoichiometry of dolomite; (b) Sr shows some correlation with K, which could 1844 Patrick 25-4-2019 00:36 Gelöscht: vs. 1845 be due to incorporation in rapidly precipitating dolomite (see text for discussion). 1846 Figure 10. Sr-isotope ratios and Sr-concentrations measured in sequential and non-sequential 1847 Formatiert: Schriftart: Fett extractions of dolomite and different control minerals. (a-c) Dolomite samples of the 1848 Patrick 30-4-2019 12:04 Formatiert: Schriftart:Fett 1849 Travenanzes Fm. show consistently low Sr-isotope values (below 0.708000) in the 0.1 N 1850 acetic acid fraction and very high values in the HCl fraction. The values in the 1 N acetic acid 1851 fraction are higher in the micro-drilled samples, perhaps due to partial leaching of residual 1852 clay minerals. In bulk samples values are low, while concentrations indicate still abundant Sr, presumably from the dolomite phase. (d) Claystone samples show generally elevated Sr-1853 Patrick 30-4-2019 12:04 Formatiert: Schriftart:Fett 1854 isotope values (compared to the dolomite samples) and lower concentrations. Low Sr-isotope 48

1865	values and higher concentrations in the acetic acid fractions of Sample TZ16-19B could be	
1866	due to traces of carbonate in the sample. (e, f) Pure control materials, including barite,	
1867	celestine, dolomite, and a mixture of these minerals show clear separation of the three	Patrick 30-4-2019 12:04 Formatiert: Schriftart:Fett
1868	fractions. Sr- isotope values in dolomites show some scattering, probably due to	
1869	inhomogenities in the powder and the single crystals. The 2-sigma uncertainties are smaller	
1870	than the symbol size.	
1871		
1872	Figure 11. Comparison of Sr-isotopes in dolomites of the Travenanzes Fm. with the Carnian	
1873	seawater curve (Korte et al., 2003) in grey. The 2-sigma uncertainties are smaller than the	Patrick 30-4-2019 00:25 Gelöscht: 10
1874	symbol size. Circled datapoints are clay samples or samples of nodules containing clay.	
1875		
1876	Figure 12. Sr-isotope values (87Sr/86Sr ratios) in dolomites from different modern	Patrick 30-4-2019 00:26
1877	environments: Abu Dhabi Sabkha, Deep Springs Lake, Coorong Lakes; and from ancient	Gelöscht: 11 Patrick 23-4-2019 13:38
1878	environments; Germanic Keuper (Weser Fm. and Arnstadt Fm.); Travenanzes Fm. of the	Gelöscht: from Patrick 23-4-2019 13:38
1879	Dolomites, Southern Alps; in comparison with modern seawater (DePaolo and Ingram, 1985)	Gelöscht: of Patrick 13-5-2019 02:36
1880	and Triassic seawater (Korte et al., 2003)	Gelöscht: Travenanzes Fm. in the Dolomites, Southern Alps;
1881		Patrick 28-4-2019 17:59 Gelöscht: Formation
1882	ELECTRONIC SUPPLEMENT	Patrick 28-4-2019 17:59 Gelöscht: Formation
1883	Table S1. Petrographic summary including sedimentary structures from thin section analysis	Patrick 24-4-2019 17:15
		Gelöscht:); Coorong Lagoon; Deep Spring Lake. 87Sr/86Sr ratios
1884	of dolomites from the Travenanzes Fm. at the Dibona section.	Patrick 24-4-2019 17:17 Gelöscht: of modern seawater are from
1885		DePaolo and Ingram (1985). Patrick 28-4-2019 17:52
1886	DATA IN REPOSITORY	Gelöscht: TABLES
		Patrick 23-4-2019 13:37
1887	PANGAEA Data Archiving & Publication PDI-20535	Gelöscht: Compilation Patrick 23-4-2019 13:38
1888		Gelöscht: of
1889	PDI-20535 Table 1. Compiled ⁸⁷ Sr/ ⁸⁶ Sr ratios of sequentially leached dolomites from	Patrick 30-4-2019 13:37 Formatiert: Schriftart: Times, 12 pt
1890	different locations, clays and test minerals, using different extraction solutions.	Patrick 30-4-2019 13:37 Formatiert: Schriftart:Fett
1000	and the state of t	

1906

1907	PDI-20535 Table 2. Elemental concentrations of leacheates from dolomites and clays used	
1908	for Sr-isotope analysis.	Patrick 30-4-2019 13:38 Formatiert: Schriftart:Fett
1909		Patrick 28-4-2019 17:53 [2] nach oben verschoben: Table 2.
1910	PDI-20535 Table 3. Total inorganic and organic carbon (TIC, TOC) contents of clay samples	Relative abundances and ordering parameters of dolomites from the Travenanzes Formation. Relative abundances were estimated based on
		Relative abundances were estimated based on the 104 peak height. The stoichiometry Mg/(Ca+Mg) was determined from the shift of
1911	from the Travenanzes Formation	the 104 peak using the equation of Lumsden (1979). The structural ordering was calculated
1912		from the ratio of the 015 ordering peak to the 110 peak according to Füchtbauer and Goldschmidt (1966).
1913	PDI-20535 Table 4. Carbon and oxygen isotope values of different types of dolomite from	Patrick 30-4-2019 00:26
1914	the Travenanzes Formation.	Formatiert: Schriftart:(Standard) Times, 12 pt, Englisch (Vereinigtes Königreich)
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