ARTICLE IN PRESS

Tectonophysics xxx (xxxx) xxx-xxx

ELSEVIER

Contents lists available at ScienceDirect

Tectonophysics

journal homepage: www.elsevier.com/locate/tecto



Reply to the comment on "First records of syn-diagenetic non-tectonic folding in Quaternary thermogene travertines caused by hydrothermal incremental veining" by Billi et alii

Andrea Billi^a,*, Gabriele Berardi^b, Jean-Pierre Gratier^c, Federico Rossetti^b, Gianluca Vignaroli^a, Mehmet Oruç Baykara^{d,e}, Stefano M. Bernasconi^f, Sándor Kele^g, Michele Soligo^b, Luigi De Filippis^h, Chuan-Chou Shen^d

- a Consiglio Nazionale delle Ricerche, IGAG, Rome, Italy
- ь Dipartimento di Scienze, Università Roma Tre, Italy
- ^c ISTerre, Université Grenoble Alpes and CNRS, 38041 Grenoble, France
- d High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University, Taipei, Taiwan, ROC
- ^e Pamukkale University, Department of Geological Engineering, Denizli, Turkey
- f Geologisches Institut, ETH Zürich, Switzerland
- ⁸ Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary
- ^h Liceo Scientifico Statale 'L. Spallanzani', Tivoli, Italy

ARTICLE INFO

Keywords: Travertine diagenesis Diagenetic fluid Post-depositional change Rejuvenation Vein Secondary mineralization

ABSTRACT

In our previous paper (Billi et al., 2017), using field geological observations, U-Th dating, and stable isotope analyses, we studied two deposits of Pleistocene thermogene travertines from Tuscany in central Italy. We concluded our study (1) warning that the common stratigraphic concept of travertine being a sedimentary succession with age younging from bottom to top is not always correct, (2) demonstrating that CaCO3 mineralization and veins can develop within the travertines after their formation with this syn-diagenetic process being able to modify the continuous bottom-up age evolution, and (3) showing that this post-depositional mineralization-veining process can not only modify the temporal succession but also deform and change the initial depositional travertine structure and its petrophysical properties. These conclusions could potentially make the interpretation of a travertine series more difficult than commonly thought. Alcicek et alii questioned our conclusions claiming that the travertine structures that we observed in Tuscany and interpreted as post-depositional features should have been interpreted, in analogy to similar structures from travertines elsewhere, as primary structures. Although we recognize, as already thoroughly stated in Billi et al. (2017), that the travertine depositional/post-depositional processes generally require further studies, we reaffirm the validity of our original interpretation at least for the structures analyzed in our previous paper. We, therefore, counter all criticisms by Alcicek et alii and conclude by indicating the way forward to further explore the depositional and post-depositional processes of thermogene travertines.

1. Introduction

We thank Alcicek et alii for bringing their opinion to our attention and welcome their comments that allow us to further detail our arguments. We begin our reply by synthesizing and better explaining our main results together with some instructive additions. We then reply to the main comments raised by Alcicek et alii and finally conclude with some general inferences.

The travertine exposures addressed in this paper belong to the Pleistocene Pianetti and Pian di Palma deposits, which are located in Tuscany, central Italy, at 42° 38′ 00.52″N and 11° 30′ 40.43″E, and 42° 41′ 21.15″N and 11° 29′ 52.79″E, respectively. The geological setting of these deposits is described in Carmignani et al. (2013), Berardi et al. (2016), Vignaroli et al. (2016), and Billi et al. (2017), whereas the origin and genetic context of Quaternary travertines from central Italy are described in Chiodini et al. (1995), Minissale et al. (2002), and Minissale (2004).

* Corresponding author.

E-mail address: andrea.billi@cnr.it (A. Billi).

http://dx.doi.org/10.1016/j.tecto.2017.09.005

Received 21 July 2017; Received in revised form 2 September 2017; Accepted 6 September 2017 0040-1951/ © 2017 Elsevier B.V. All rights reserved.

A. Billi et al. Tectonophysics xxx (xxxxx) xxx-xxx

2. Rejuvenation, mineralization-veining, and post-depositional changes

2.1. Rationale

Since thermogene travertines are more and more often used as (temporal) indicators of climate change, active faulting, and other environmental processes (Rihs et al., 2000; Minissale et al., 2002; Pentecost, 2005; Crossey et al., 2006, 2009; Uysal et al., 2007, 2009; Dockrill and Shipton, 2010; De Filippis and Billi, 2012; De Filippis et al., 2013; Kampman et al., 2012; Burnside et al., 2013; Sinisi et al., 2016), in our previous paper (Billi et al., 2017):

- (1) We warned that the common stratigraphic concept of travertine registering sedimentary succession with age younging from bottom to top is not always correct.
- (2) We demonstrated that mineralizations and veins can develop within the travertines after their deposition, altering the continuous younging-upwards age succession.
- (3) We demonstrated that this post-depositional mineralization-veining process can not only modify the temporal succession, but also deform and change the initial depositional travertine structure and its petrophysical properties, making the interpretation of a travertine series more difficult than commonly thought. This is especially problematic when sampling is done by coring.

Below, we further explore these three main conclusions.

2.2. Rejuvenation

We firstly re-propose our set of U-Th ages along the travertine succession of the Pianetti Quarry (Fig. 1). In response to one of Alcicek et alii's comments, we point out that the U-Th dating method used, together with its limits, is thoroughly described in the supplementary material of Billi et al. (2017). The same method and limits are likewise described in Brogi et al. (2017), who produced travertine U-Th age data from the same laboratory where our U-Th age data were produced, in cooperation with the same scientists.

The main result from our geochronological analyses (Fig. 1) is that a

few mineralization-veins are not in agreement with the law of stratigraphic superposition. We refer, in particular, to the following four samples: ST3, ST1, CP14_2, and CP15_8. Each of them is younger than at least one geometrically superposed sample (either vein or host travertine), as shown in Fig. 1(c). The observed age inversion clearly demonstrates the rejuvenation processes in the Pianetti travertine succession, although their causes are obviously debatable (Billi et al., 2017).

To better understand that rejuvenation processes in thermogene travertines and related structures (e.g., mounds, fissure ridges) can be more common than previously thought, we here propose three additional documented cases: the Cukurbağ fissure ridge (Turkey: Fig. 2a-d: Uvsal et al., 2009; De Filippis and Billi, 2012), the Akköv fissure ridge (Turkey; Fig. 2e; De Filippis and Billi, 2012), and the Crystal Geyser mound (Utah, USA; Fig. 2f; Gratier et al., 2012; Frery et al., 2017). As shown by the rock ages reported in Fig. 2, in all these cases a host rock (either travertine or else) was affected by younger (documented by radiometric ages) travertine mineralization and veins that modified the original bottom-up younging direction of the rock succession. Further details can be found in Billi et al. (2017) and in the source papers (Uysal et al., 2009; De Filippis and Billi, 2012; Gratier et al., 2012; Frery et al., 2017). These cases, together with the Pianetti quarry case (Fig. 1; Billi et al., 2017), demonstrate the fact that rejuvenation processes can occur in travertine successions.

2.3. Veining and secondary mineralization

Here we re-propose a synthesis from some instructive examples of the Pianetti and Pian di Palma travertines (Fig. 3; Billi et al., 2017). The unconformity shown in Fig. 3(a) is consistent with the notion that bedded travertines can be characterized by cycles of deposition and non-deposition, where the non-deposition periods are typically marked by erosional horizons and unconformities. Over these erosional horizon-unconformities, new and younger sequences of travertine beds can onlap (e.g., Faccenna et al., 2008). In the shallow portion of the Pianetti quarry, we observed a stack of bed-parallel sub-horizontal veins cutting, from bottom to top, through the overlying unconformity (i.e., erosional horizon) and onlapping travertine beds (within the black rectangle in Fig. 3a). The crosscutting relation of Fig. 3(a) irrefutably

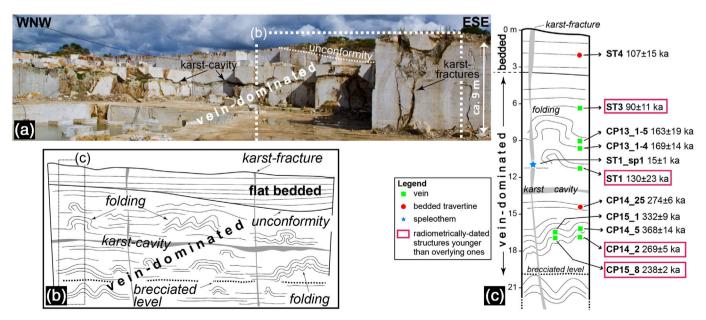


Fig. 1. Pianetti travertine deposit and related U-Th ages (modified after Billi et al., 2017). (a) Panorama of the Pianetti quarry travertines, Tuscany, central Apennines. (b) Conceptual architecture of the Pianetti travertine deposit. (c) Schematic stratigraphic log of the Pianetti travertine deposit. Sample location (depth) and age are shown. The age of four veins (ST3, ST1, CP14_2, and CP15_8) is inconsistent with the law of stratigraphic superposition. These veins are indeed younger than at least one overlying dated sample (either vein or host travertine).

A. Billi et al. Tectonophysics xxx (xxxx) xxx-xxx

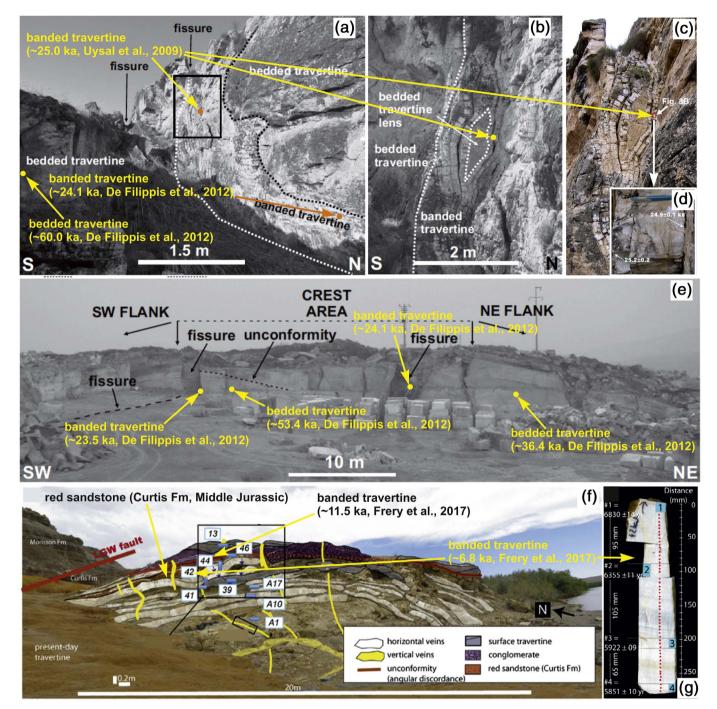


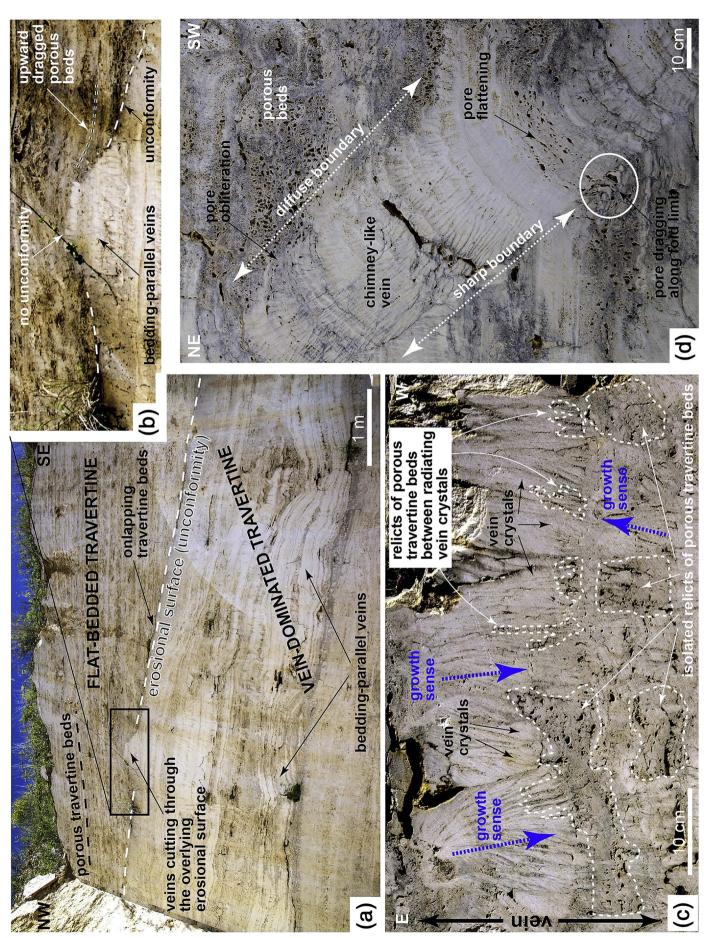
Fig. 2. Instances of veining and rejuvenation processes in thermogene travertines. (a), (b), (c), (d) Çukurbağ fissure ridge, Turkey (modified after Uysal et al., 2009 and De Filippis and Billi, 2012). (e) Akköy fissure ridge, Turkey (modified after De Filippis and Billi, 2012); (f), (g) Crystal Geyser mound, Utah, USA. (Modified after Gratier et al., 2012 and Frery et al., 2017).

indicates that the underlying stack of bed-parallel sub-horizontal veins is younger than both the overlying erosional horizon and the onlapping beds. This evidence is even more discernible in Fig. 3(b), where the vein stack breaks up the lateral continuity of the overlying erosional horizon that becomes missing on top of the stack itself. Moreover, the overlying travertine beds are gently folded upward forming synforms as induced by the bottom-up incremental veining.

Fig. 3(c–d) show further occurrences of secondary mineralizations and veins through the porous travertines of the Pianetti and Pian di Palma travertines. Among other significant occurrences, we point out Fig. 3(c), where a set of downward radiating crystals is perpendicular to bedding. The downward radiating pattern irrefutably shows a

downward growth of crystals (Hilgers et al., 2004; Gratier et al., 2012) and therefore their secondary origin with respect to the host porous travertine. Moreover, the occurrence of porous travertine relicts between the downward radiating crystals shows that they grew at the expense of pre-existing porous travertine beds. Fig. 3(d) shows a chimney-like crystalline structure interrupting the lateral continuity of porous travertine beds. In particular, the upper diffuse boundary between the chimney-like structure and the overlying porous beds shows that the crystalline structure grew upward progressively at the expense of the pre-existing porous beds that are partly consumed by the white crystals. In other words, the chimney-like structure is younger than the overlying porous beds.

A. Billi et al. Tectonophysics xxxx (xxxxx) xxxx-xxxx



A. Billi et al. Tectonophysics xxx (xxxxx) xxx-xxx

Fig. 3. Instances of post-depositional mineralizations and veins within the Pianetti and Pian di Palma travertines (modified after Billi et al., 2017). (a) Middle and upper section of the Pianetti deposit showing flat porous travertine beds (no or limited veins and folds) onlapping over an erosional surface (unconformity) and the underlying vein-dominated (bed-parallel veins) travertine beds. Note, in the black rectangle, that a stack of bed-parallel sub-horizontal veins cut through, from bottom to top, the overlying erosional horizon (unconformity) and the onlapping travertine beds. (b) Close-up photograph of the structure within the rectangle in (a). Note that the vein stack interrupts (i.e., cuts through) the lateral continuity of the southeastward-inclined unconformity that is absent, in contrast, on top of the vein stack itself. The overlying travertine beds are gently bent upward (synforms) consistently with the occurrence and upward growth of the vein stack relief. (c) Downward growth (blue arrows) of vein radiating crystals, which are perpendicular to bedding and form a bed-parallel gentle anticlinal vein (Pianetti). Note the occurrence of porous travertine relicts between the downward radiating crystals, which grew at the expense of pre-existing travertine beds. (d) Chimney-like stack of bed-parallel veins (Pianetti). In approaching the fold, note the flattening and dragging of primary pores. In this and other photographs, note the lateral expansion of crystal fans, implying a bed-parallel component of growth (growth competition) in addition to the main bed-perpendicular one. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We also call attention to the fact that the occurrence of secondary mineralizations and veins in the Pianetti and Pian di Palma deposits is supported by our stable isotope data (Fig. 8, S40, and S41 in Billi et al., 2017). These data suggest that the porous travertine (i.e., the host-bedded travertine) and the hosted veins precipitated from the same fluids, but possibly the veins at 2–3 °C cooler temperatures. We interpreted this as consequence of fluid cooling during longer residence times in intralithic environments (veins), in contrast with abrupt precipitation at higher temperatures in open-air environments (porous travertine).

To show that post-depositional veining and mineralization can be common in thermogene travertines, in addition to the occurrences reported in Figs. 2 and 3, in Fig. 4, we present two additional examples from Pamukkale (Turkey; Uysal et al., 2009) and Colle Fiorito (Italy; De Filippis et al., 2013). In both these cases, the secondary mineralization-veining process is demonstrated by sub-vertical banded veins cutting through the pre-existing travertine beds. From these sub-vertical veins, sub-horizontal veins laterally depart to form sill-like structures along the pre-existing travertine beds (Fig. 4). These cases are very similar to that from Utah presented by Gratier et al. (2012) and Frery et al. (2017).

Finally, we cover an unpublished case from the Canestrini quarry, Acquasanta Terme travertine (Fig. 5). This quarry is located in the Marche region in central Italy, at 42° 47′ 03.53″N and 13° 26′ 07.55″E.

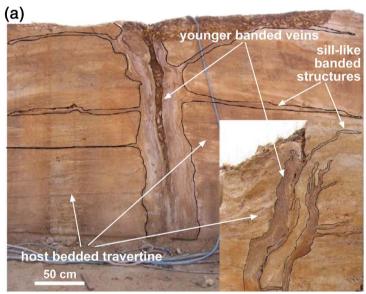




Fig. 4. Instances of across- and along-bed veining and mineralizations in thermogene travertines. (a) Pamukkale travertines, Turkey (modified after Uysal et al., 2009). (b) Colle Fiorito fissure ridge, Italy (modified after De Filippis et al., 2013). Both these instances show that bedded thermogene travertines can be affected by younger (banded) veins that develop either across beds, along beds, or both. This process can obviously modify the bottom-up younging succession of travertines – i.e., the sill-like mineralizations are obviously younger than the overlying bedded travertine.

A. Billi et al. Tectonophysics xxxx (xxxxx) xxxx-xxxx

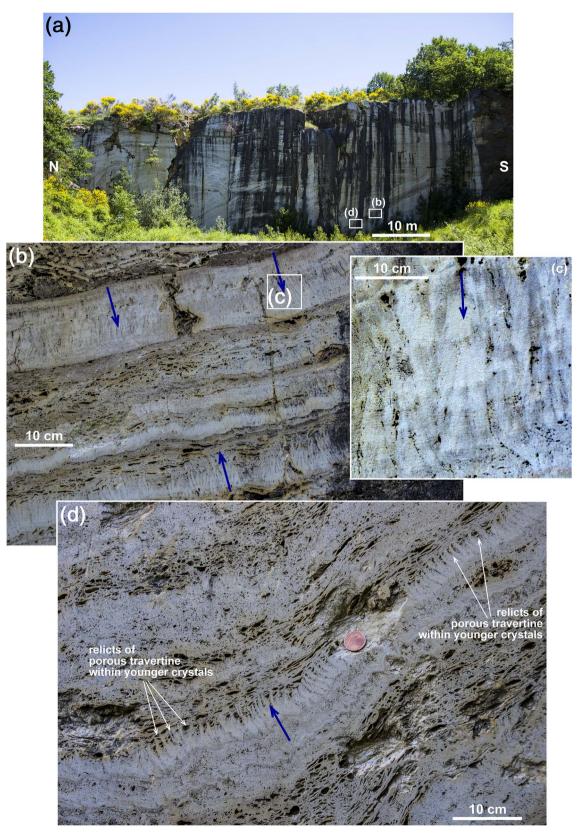


Fig. 5. Instances of along-bed veining and secondary mineralization in the Acquasanta Terme (central Italy) thermogene travertines. (a) Panoramic view of the Canestrini quarry. (b) Close-up view from (a) showing the occurrence of upward- and downward-directed fan-shaped crystals within a slope succession of travertines. The upward-directed crystals can theoretically be interpreted either as primary or as secondary features, whereas the downward-directed ones can be solely interpreted as secondary features as they grew from the upper bed toward the lower one (e.g., Gratier et al., 2012). (c) Close-up view from (b) showing downward-directed fan-shaped crystals. (d) Close-up view from (a) showing the presence of relicts of porous travertines in between crystals pertaining to upward-directed fan-shaped mineralization. The occurrence of these relicts indicates that the crystals overprinted the upper porous bed, thus showing their age younger than the upper porous bed itself.

A. Billi et al. Tectonophysics xxx (xxxxx) xxxx–xxx

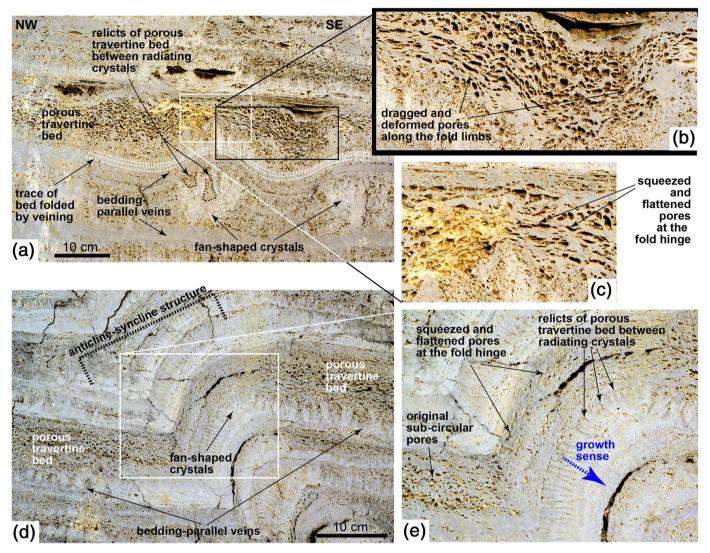


Fig. 6. Instances of post-depositional mineralizations, veins, and folds within the Pianetti travertines (modified after Billi et al., 2017). (a) Squeezing and flattening of original travertine pores in fold thickened hinges. Note that the anticline hinges overlie swarms of sub-vertical fan-shaped crystals that overprint the pre-existing porous beds. Such crystals seem to have pushed and bent the overlying levels. Note also the presence of post-depositional voids and of a detachment level between folded and flat travertines. (b) (c) Close-up photographs from (a) showing the squeezing and flattening of original travertine pores in approaching an anticline hinge. (e) Close-up photographs from (a).

Fig. 5 shows two close-up views (Fig. 5b-d) from the Pleistocene thermogene travertines of the Canestrini quarry (Fig. 5a). Fig. 5(b, c), in particular, show the occurrence of upward- and downward-directed fan-shaped crystals within a slope succession of travertines. The upward-directed crystals can theoretically be interpreted either as primary (Guo and Riding, 1998) or as secondary (Billi et al., 2017) features, whereas the downward-directed ones can only be interpreted as secondary features as they grew from the upper bed toward the lower one (e.g., Gratier et al., 2012; Billi et al., 2017). Moreover, Fig. 5(d) shows the presence of relicts of porous travertines in between crystals of the upward-directed fan-shaped mineralization. The occurrence of these relicts indicates that the crystals grew at the expense of the upper porous bed, progressively overprinting the porous bed itself. This evidence shows that these upward-directed fan-shaped crystals must be younger than the overlying porous bed. These examples (Figs. 3-5) collectively demonstrate that secondary mineralization and veins are present across and along pre-existing travertine beds of the Pianetti and Pian di Palma deposits (Billi et al., 2017) and elsewhere in thermogene travertines (e.g., Uysal et al., 2009; De Filippis and Billi, 2012; De Filippis et al., 2013; Gratier et al., 2012; Frery et al., 2017).

2.4. Post-depositional changes

Here we discuss again some illuminating examples from the Pianetti and Pian di Palma travertines (Fig. 6). Fig. 6 shows two successions of folded porous travertine beds from the Pianetti quarry. It is noteworthy that the pores along the fold limbs become compressed (and then strained) when approaching the fold hinge area. In the case of Fig. 6(a–c), it is also noteworthy that the anticline hinges overlie swarms of sub-vertical fan-shaped crystals overprinting the pre-existing porous beds. These examples unequivocally show that the pristine porous beds were affected by secondary mineralization that modified the original presumably-planar geometry of the deposit (contorting it). Primary sedimentary features such as the pores became squeezed and compressed in the anticline hinges (see also the online graphical abstract).

3. Replies

3.1. Organization

In this section, we summarize some of Alcicek et alii's main

A. Billi et al. Tectonophysics xxx (xxxx) xxx-xxx

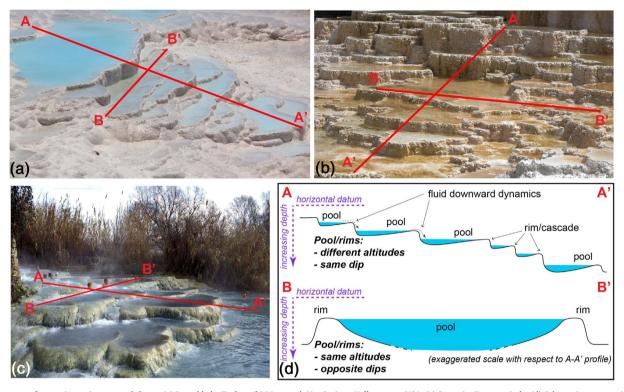


Fig. 7. Instances of travertine active terraced slopes. (a) Pamukkale, Turkey. (b) Mammoth Hot Springs, Yellowstone, USA. (c) Saturnia, Tuscany, Italy. (d) Schematic cross-sections along the A-A' and B-B' tracks in the previous three photographs. Note that both the A-A' and the B-B' cross-sections cannot be similar to natural cross-sections shown in Fig. 8, where the structures (chimney-like veins) are all at the same altitude and dip toward the same polarity. Primary crystalline crusts necessitate a topographic gradient (i.e., slope/cascade) and dynamic fluid to develop.

comments and briefly reply, with the aid of a few figures, to each of them under three main thematic sub-sections.

3.2. Structures and textures

3.2.1. Primary crystalline crusts vs. secondary mineralizations

Alcicek et alii stated that we did not recognize primary crystalline crusts, thus erroneously interpreting them as secondary mineralizations. We are aware of and did not challenge at all the fact that fanshaped calcite crystals in thermogene travertines can be primary features (crystalline crusts in Guo and Riding, 1998). We reaffirm, however, that, based on geochronological data (Fig. 1) and field observations (e.g., crosscutting relations; Figs. 2–6), some fan-shaped calcite crystals in the thermogene travertines of the Pianetti and Pian di Palma quarries have to be considered secondary features. Alcicek et alii mixed sites and structures. What is valid for some travertine sites (e.g., Guo and Riding, 1998) is not necessarily also valid for the Pianetti and Pian di Palma travertines (Billi et al., 2017).

Concerning the diffuse boundary between crystalline and porous travertines, we clearly explained in Billi et al. (2017) that the post-depositional processes affecting the studied travertines are at least in part connected with post-depositional (diagenetic) hydrothermal alterations that commonly generate cycles of mineralization and alteration characterized by diffuse boundaries of related structures (e.g., Vignaroli et al., 2015). One significant example is shown in Fig. 3(d).

3.2.2. Microstructural observations

Alcicek et alii proposed a general and theoretical comment on vein microscopic textures. This comment will be useful for future microscopic studies. In Billi et al. (2017), indeed, we did not perform this type of study. We only showed one micro-photograph from a travertine thin-section (Fig. 4e in Billi et al., 2017), without claiming to have realized a microscopic analysis of the studied travertines. For these reason, the comment by Alcicek et alii, although theoretically

appropriate, cannot be applied to our results.

3.2.3. On the sense of crystal growth

Alcicek et alii affirmed that "the growth-sense of the travertine beds cannot be considered indicative for reconstructing the growth-sense, since fan-like crystal arrangement may indicate different apparent growth-sense within the same bed." Elongate, fan-shaped crystals with competition textures provide an unambiguous indication of their sense of growth, where the narrow portion of the fan is the starting tip of the crystals and the broad portion of the fan is in the direction of growth. This is clearly demonstrated in both experiments (Hilgers et al., 2004) and natural examples (Gratier et al., 2012; Billi et al., 2017 and references therein). Photographs such as those shown in Figs. 3(c) and 5(c) unequivocally show the occurrence of travertine post-depositional mineralization processes. Accordingly, the presence of both downward and upward fan-shaped crystals in a single layer may be attributed to complex and/or multiple mineralization processes in 3D space and in time. In any case, while the upward fan-shaped crystals can be either primary or secondary features, the downward ones are certainly secondary, thus supporting the post-depositional mineralization processes proposed in Billi et al. (2017).

3.2.4. Pore shape changes

Alcicek et alii questioned our evidence of post-depositional changes in travertine pore shape. Although we agree with the fact that the initial shape of pores in travertines is largely unknown, we believe that exposures such as those shown in Fig. 6 (see also the online graphical abstract) are eloquent and telling enough to any geologist to demonstrate post-depositional changes of the primary sedimentary fabric in the Pianetti and Pian di Palma travertines. The change in pore shapes when moving from the fold limbs to the hinge (Fig. 6) are an unequivocal indication of a post-depositional shuttering of the primary porosity caused by folding of the travertine beds.

A. Billi et al. Tectonophysics xxx (xxxxx) xxxx–xxx

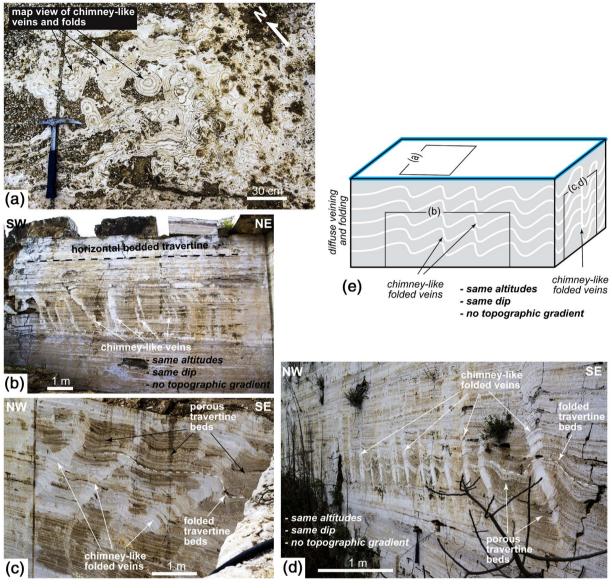


Fig. 8. Instances of chimney-like veins in the Pian di Palma travertines. (a) Bird's eye view of sub-vertical chimney-like veins. The 2D rounded shape of these structures suggests a 3D domal or botryoidal shape. (b), (c), (d) Chimney-like folded veins across originally-flat bedded porous travertine (Pian di Palma). (e) Block-diagram showing a hypothetical orientation of photographs in (a) to (d).

3.3. Primary vs. secondary geometries of travertine beds

3.3.1. Terraced pool rims vs. secondary chimney-like structures

As rightly stated by Alcicek et alii, in terraced slope environments, pools are arranged at progressively lower altitudes along the slope and generate fluid downward dynamics that can lead to flowstones characterized by elongate crystalline crusts. Examples from the active travertine terraced slopes of Pamukkale (Turkey), Yellowstone Mammoth Hot Springs (USA), and Saturnia (Italy) are shown in Fig. 7. By crosscutting these active cascade pool systems both downslope (A-A') and parallel-to-slope (B-B'), the result cannot be that shown in Fig. 8 from the Pianetti and Pian di Palma fossil travertines, where the hypothetical pools (post-depositional synclines according to our interpretation; Billi et al., 2017) are all at the same altitude with the hypothetical rims (post-depositional anticlines and chimney-like structures according to our interpretation; Billi et al., 2017) all dipping (inclined) toward the same direction. Such a horizontal system (Fig. 8b-d) cannot be defined as a down-sloping terraced pool system (Fig. 9) due to the lack of a topographic gradient. Moreover, the bird's eye view (Fig. 8a) of the structures (chimney-like veins) shown in Fig. 8(b-d) demonstrates that these structures are not laterally continuous, and hence they cannot be pool rims. In other words, Fig. 8 cannot find its natural analog in downsloping terraced pool systems such as those shown in Fig. 7 (see the comparison in Fig. 9).

3.4. Crystallization force, folding, and pressure solution

3.4.1. Force of crystallization and displacive capacity of calcite and aragonite

In their comments, Alcicek et alii ignore the force of crystallization and displacive capacity of calcite and aragonite (i.e., similar to that occurring in the swelling of anhydrite during hydration to gypsum) in various geological environments. Several sedimentary rocks show evidence of late (post-depositional) modifications to the pristine fabric due to syn-diagenetic CaCO₃ precipitation, as has been long documented in several papers including those mentioned by Billi et al. (2017): Taber (1916); Weyl (1959); Assereto and Kendall (1977); Watts (1978); Handford et al. (1984); Kendall and Warren (1987); Fletcher and Merino (2001); Wiltschko and Morse (2001); Hilgers and Urai (2005); Lokier and Steuber (2009); Noiriel et al. (2010); and Gratier et al.

A. Billi et al. Tectonophysics xxx (xxxxx) xxxx–xxx

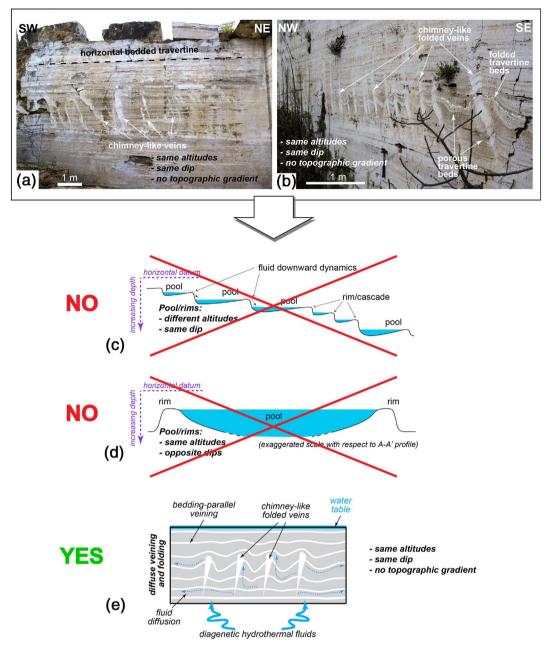


Fig. 9. Cross-sections through chimney-like structures in the Pian di Palma travertines. (a) Same as Fig. 8(b). (b) Same as Fig. 8(d). (c) Same as top cross-section of Fig. 7(d). (d) Same as bottom cross-section of Fig. 7(d). (e) Interpretative cross-sectional model for photographs in (a) and (b). Cross-sections in (c) and (d) cannot explain the photographs in (a) and (b) as the photographed chimney-like structures are all at the same altitude (i.e., no topographic gradient) and are all dipping in the same direction (same dip polarity). The longitudinal cross-section of a terraced slope should indeed show opposite polarities (dip) of the pool rims as drawn in (d).

(2012). We refer the reader to this literature, which shows how post-depositional deformation of travertines (or other carbonate sediments) by secondary calcite/aragonite growth is a viable process, particularly in shallow sedimentary-diagenetic environments such as those of thermogene travertines (Gratier et al., 2012).

3.4.2. Buckling

In response to one of Alcicek et alii's comments, we confirm that all parameters necessary and sufficient to apply the Biot-Ramberg equation to our studied folds are reported in table S3 of Billi et al. (2017). No further data are necessary. Moreover, as clearly stated in Billi et al. (2017), assuming layer-parallel shortening (buckling), the application of the Biot-Ramberg equation to the folds observed in the Pianetti and Pian di Palma travertines gives only an approximate estimate of the rheological contrast between single veins and host bedded travertine at

the time of folding. Assumptions and limits of this application are explained in Billi et al. (2017). Although approximate, this attempt constitutes, in our opinion, an interesting stimulus and motivation for future studies. While Alcicek et alii claim to know the brittle rheology of travertines early in their depositional stage well, this rheology is still substantially unknown and undocumented. Freshly-deposited thermogene travertines in active spots such as Pamukkale (Turkey), Saturnia (central Italy), or Acquasanta (central Italy) behave similarly to a very soft carbonate mud. The hydrothermal diagenesis and lithification of these muds are still to be substantially studied.

3.4.3. Pressure solution

Alcicek et alii questioned our evidence of pressure solution in the studied travertines. In highly-porous fine-grained rocks such as the studied travertines, pressure solution processes are very efficient. It A. Billi et al. Tectonophysics xxx (xxxx) xxx-xxx

takes only a few months to significantly deform gypsum-plaster aggregates by pressure solution (Gratier et al., 2015). Taking into account the difference in solubility between gypsum and carbonates, significant deformation of travertines may be reached in this context after just a few decades or centuries. Moreover, there is no minimum depth required to develop stylolites (Toussaint et al., 2017). Stylolite growth rate is indeed only controlled by the kinetics of the process, which, although rather slow, can potentially allow significant pressure solution to occur in freshly-deposited travertines within a few decades or centuries. Additionally, the observed stylolites are not necessarily generated by the overburden load during burial (e.g., Billi, 2003), but rather by post-deposition compression induced by secondary growth of calcite crystals (force of crystallization) in a confined environment. For instance, in a similar shallow environment, stylolites attesting for a slow growth process against the gravity developed at less than 10-20 m depth in some travertines of Utah (Gratier et al., 2012).

4. Conclusions

The comments by Alcicek et alii, although welcome, do not alter our previous conclusions (Billi et al., 2017), which we synthetically repropose here.

Since thermogene travertines are more and more often used as (temporal) indicators of climate change, active faulting, and further environmental processes, in Billi et al. (2017):

- (1) We warned that the common stratigraphic concept of travertine registering sedimentary succession with age younging from bottom to top is not always correct.
- (2) We then demonstrated that mineralizations and veins can develop within the travertines after their formation and this diagenetic process can modify the continuous age evolution.
- (3) Finally, we also demonstrated that this post-deposition process not only modifies the temporal succession but can also deform and modify the initial depositional travertine structure and petrophysical properties, making the interpretation of a travertine series difficult. This is especially problematic when sampling is done by coring.

These conclusions are valid for our two study sites (Pianetti and Pian di Palma travertines). As such, our results are opening new research perspectives and should be further tested with, for instance, micro-structural methods including optical and electron microscopy or cathodoluminescence. The applicability of our findings to other thermogene travertine deposits should be further explored. If similar conclusions can be drawn elsewhere, they may challenge the hitherto accepted genetic concepts of travertines. If not, our results would still be an interesting, albeit isolated, case.

Acknowledgments

Institutional funding from Roma Tre University, CNR-IGAG, Hungarian Academy of Sciences (János Bolyai scholarship to S.K.), Hungarian Scientific Research Fund (OTKA 101664), ETH Zürich, and ISTerre Grenoble are acknowledged. Dating at the HISPEC was supported by the Taiwan ROC MOST grants (105-2119-M-002-001 to CCS), and National Taiwan University (105R7625 to CCS). We acknowledge, in particular, no industrial funding for this study. We warmly thank P. Agard and an anonymous reviewer for constructive comments and professional editorial handling.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at $\frac{\text{http://dx.doi.org/10.1016/j.tecto.2017.09.005.}}{\text{These data includes the Google map of the most important areas described in this article.}}$

References

- Assereto, R., Kendall, C.G.St.C., 1977. Nature, origin and classification of peritidal tepee structures and related breccias. Sedimentology 24, 153–210.
- Berardi, G., Vignaroli, G., Billi, A., Rossetti, F., Soligo, M., Kele, S., Baykara, M.O., Bernasconi, S.M., Castorina, F., Tecce, F., Shen, C.-C., 2016. Growth of a Pleistocene giant carbonate vein and nearby thermogene travertine deposits at Semproniano, southern Tuscany, Italy: estimate of CO₂ leakage. Tectonophysics 690, 219–239.
- Billi, A., 2003. Solution slip and separations on strike-slip fault zones: theory and application to the Mattinata Fault, Italy. J. Struct. Geol. 25, 703-715.
- Billi, A., Berardi, G., Gratier, J.-P., Rossetti, F., Vignaroli, G., Baykara, M.O., Bernasconi, S.M., Kele, S., Soligo, M., De Filippis, L., Shen, C.-C., 2017. First records of syn-diagenetic folding in Quaternary thermogene travertines caused by hydrothermal incremental veining. Tectonophysics 700–701, 60–79.
- Brogi, A., Capezzuoli, E., Kele, S., Baykara, M.O., Shen, C.C., 2017. Key travertine tectofacies for neotectonics and palaeoseismicity reconstruction: effects of hydrothermal overpressured fluid injection. J. Geol. Soc. 174, 679–699.
- Burnside, N.M., Shipton, Z.K., Dockrill, B., Ellam, R.M., 2013. Man-made versus natural CO₂ leakage: a 400 k.y. history of an analogue for engineered geological storage of CO₂. Geology 41, 471–474.
- Carmignani, L., Conti, P., Cornamusini, G., Pirro, A., 2013. Geological map of Tuscany (Italy). J. Maps 9 (4), 487–497. http://dx.doi.org/10.1080/17445647.2013.820154.
- Chiodini, G., Frondini, F., Ponziani, F., 1995. Deep structures and carbon dioxide degassing in central Italy. Geothermics 24, 81–94.
- Crossey, L.J., Fischer, T.P., Patchett, P.J., Karlstrom, K.E., Hilton, D.R., Newell, D.L., Huntoon, P., Reynolds, A.C., de Leeuw, G.A.M., 2006. Dissected hydrologic system at the Grand Canyon: interaction between deeply derived fluids and plateau aquifer waters in modern springs and travertine. Geology 34, 25–28.
- Crossey, L.J., Karlstrom, K.E., Springer, A.E., Newell, D., Hilton, D.R., Fischer, T., 2009. Degassing of mantle-derived CO₂ and He from springs in the southern Colorado Plateau region - neotectonic connections and implications for groundwater systems. Geol. Soc. Am. Bull. 121, 1034–1053.
- Geol. Soc. Am. Bull. 121, 1034–1053.
 De Filippis, L., Billi, A., 2012. Morphotectonics of fissure ridge travertines from geothermal areas of Mammoth Hot Springs (Wyoming) and Bridgeport (California). Tectonophysics 548–549, 34–38.
- De Filippis, L., Anzalone, E., Billi, A., Faccenna, C., Poncia, P.P., Sella, P., 2013. The origin and growth of a recently-active fissure ridge travertine over a seismic fault, Tivoli, Italy. Geomorphology 195, 13–26.
- Dockrill, B., Shipton, Z.K., 2010. Structural controls on leakage from a natural CO₂ geologic storage site: Central Utah, U.S.A. J. Struct. Geol. 32, 1768–1782.
- Faccenna, C., Soligo, M., Billi, A., De Filippis, L., Funiciello, R., Rossetti, C., Tuccimei, P., 2008. Late Pleistocene depositional cycles of the Lapis Tiburtinus travertine (Tivoli, Central Italy): possible influence of climate and fault activity. Glob. Planet. Chang. 63, 299–308.
- Fletcher, R.C., Merino, E., 2001. Mineral growth in rocks: kinetic-rheological models of replacement, vein formation, and syntectonic crystallization. Geochim. Cosmochim. Acta 65, 3733–3748.
- Frery, E., Gratier, J.-P., Ellouz-Zimmerman, N., Deschamps, P., Blamart, D., Hamelin, B., Swennen, R., 2017. Geochemical transect through a travertine mount: a detailed record of CO₂-enriched fluid leakage from Late Pleistocene to present-day Little Grand Wash fault (Utah, USA). Quat. Int. 437, 98–106.
- Gratier, J.-P., Frery, E., Deschamps, P., Røyne, A., Renard, F., Dysthe, D., Ellouz-Zimmerman, N., Hamelin, B., 2012. How travertine veins grow from top to bottom and lift the rocks above them: the effect of crystallization force. Geology 40, 1015–1018
- Gratier, J.-P., Noiriel, C., Renard, F., 2015. Experimental evidence for rock layering development by pressure solution. Geology 43, 871–874.
- Guo, L., Riding, R., 1998. Hot-spring travertine facies and sequences, late Pleistocene, Rapolano Terme, Italy. Sedimentology 45, 163–180.
- Handford, C.R., Kendall, A.C., Prezbindowski, D.R., Dunham, J.B., Logan, B.W., 1984.
 Salina-margin tepees, pisoliths, and aragonite cements, Lake MacLeod, Western
 Australia: their significance in interpreting ancient analogs. Geology 12, 523–527.
- Hilgers, C., Urai, J.L., 2005. On the arrangement of solid inclusions in fibrous veins and the role of the crack-seal mechanism. J. Struct. Geol. 27, 481–494.
- Hilgers, C., Dilg-Gruschinski, K., Urai, J.L., 2004. Microstructural evolution of syn-taxial veins formed by advective flow. Geology 32, 261–264.
- Kampman, N., Burnside, N.M., Shipton, Z.K., Chapman, H.J., Nicholl, J.A., Ellam, R.A., Bickle, M.J., 2012. Pulses of carbon dioxide emissions from intracrustal faults following climatic warming. Nat. Geosci. 5, 352–358.
- Kendall, C.G.St.C., Warren, J., 1987. A review of the origin and setting of tepees and their associated fabrics. Sedimentology 34, 1007–1027.
- Lokier, S., Steuber, T., 2009. Large-scale intertidal polygonal features of the Abu Dhabi coastline. Sedimentology 56, 609–621.
- Minissale, A., 2004. Origin, transport and discharge of CO₂ in central Italy. Earth Sci. Rev. 66, 89–141.
- Minissale, A., Kerrick, D.M., Magro, G., Murrell, M.T., Paladini, M., Rihs, S., Sturchio, N.C., Tassi, F., Vaselli, O., 2002. Geochemistry of Quaternary travertines in the region north of Rome (Italy): structural, hydrologic, and paleoclimatic implications. Earth Planet. Sci. Lett. 203, 709–728.
- Noiriel, C., Renard, F., Doan, M.L., Gratier, J.P., 2010. Intense fracturing and fracture sealing induced by mineral growth in porous rocks. Chem. Geol. 269, 197–209.
- Pentecost, A., 2005. Travertine. Springer-Verlag, Berlin Heidelberg (445 pp.).
 Rihs, S., Condomines, M., Poidevin, J.L., 2000. Long-term behaviour of continental hydrothermal systems: U-series study of hydrothermal carbonates from the French Massif Central (Allier Valley). Geochim. Cosmochim. Acta 64, 3189–3199.
- Sinisi, R., Petrullo, A.V., Agosta, F., Paternoster, M., Belviso, C., Grassa, F., 2016. Contrasting fault fluids along high-angle faults: a case study from southern Apennines (Italy). Tectonophysics 690, 206–218. http://dx.doi.org/10.1016/j.tecto.2016.07. 023.
- Taber, S., 1916. The growth of crystals under external pressure. Am. J. Sci. 41, 532-556.

ARTICLE IN PRESS

A. Billi et al. Tectonophysics xxx (xxxx) xxx-xxx

- Toussaint, R., Aharonov, E., Koehn, D., Gratier, J.-P., Ebner, M., Baud, P., Rolland, A., Renard, F., 2017. Stylolites: a review. J. Struct. Geol (in revision).

 Uysal, I.T., Feng, Y., Zhao, J.X., Altunel, E., Weatherley, D., Karabacak, V., Cengiz, O., Golding, S.D., Lawrence, M.G., Collerson, K.D., 2007. U-series dating and geochemical tracing of late Quaternary travertine in co-seismic fissures. Earth Planet. Sci. Lett.
- Uysal, I.T., Feng, Y., Zhao, J.X., Isik, V., Nuriel, P., Golding, S.D., 2009. Hydrotermal CO₂ degassing in seismically active zones during the late Quaternary. Chem. Geol. 265, 442-454.
- Vignaroli, G., Aldega, L., Balsamo, F., Billi, A., De Benedetti, A.A., De Filippis, L., Giordano, G., Rossetti, F., 2015. A way to hydrothermal paroxysm, Colli Albani
- Volcano, Italy. Geol. Soc. Am. Bull. 127, 672–687.
 Vignaroli, G., Berardi, G., Billi, A., Kele, S., Rossetti, F., Soligo, M., Bernasconi, S.M., 2016. Tectonics, hydrothermalism, and paleoclimate recorded by Quaternary travertines and their spatio-temporal distribution in the Albegna basin, central Italy: insights on Tyrrhenian margin neotectonics. Lithosphere 8, 335–358.
- Watts, N.L., 1978. Displacive calcite: evidence from recent and ancient calcretes. Geology 6, 699–703.
- Weyl, P.K., 1959. Pressure solution and the force of crystallization: a phenomenological
- theory. J. Geophys. Res. 64, 2001–2025.

 Wiltschko, D.V., Morse, J.W., 2001. Crystallization pressure versus "crack seal" as the mechanism for banded veins. Geology 29, 79–82.