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Growth of a Pleistocene giant carbonate vein and nearby thermogene travertine deposits at Semproniano, southern Tuscany, Italy: Estimate of CO₂ leakage

Gabriele Berardi a,*, Gianluca Vignaroli b, Andrea Billi b, Federico Rossetti a, Michele Soligo a, Sándor Kele c, Mehmet Oruç Baykara d,g, Stefano M. Bernasconi e, Francesca Castorina b,f, Francesca Tecce b, Chuan-Chou Shen d

a Dipartimento di Scienze, Sezione di Geologia, Università degli Studi di Roma Tre, Rome, Italy
b Istituto di Geologia Ambientale e Geoginegetica, CNR, Rome, Italy
c Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary
d High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University, Taipei, Taiwan, ROC
e ETH Zürich, Geological Institute, Zürich, Switzerland
f Dipartimento di Scienze della Terra, Sapienza Università di Roma, Rome, Italy
f Department of Geological Engineering, Pamukkale University, Denizli, Turkey

A B S T R A C T

A giant carbonate vein (≥50 m thick; fissure ridge travertines) and nearby travertine plateaus in the Semproniano area (Mt. Amiata geothermal field, southern Tuscany, Italy) are investigated through a multidisciplinary approach, including field and laboratory geochemical analyses (U/Th geochronology, C, Nd, O and Sr isotope systematics, REE abundances, and fluid inclusion microthermometry). The main aim of this work is to understand: (1) modes and rates for the growth of the giant vein and nearby travertine deposits within a Quaternary volcanic tectonic domain; (2) implications in terms of the CO₂ leakage; and (3) possible relationships with Quaternary paleoclimatic and hydrological oscillations. Results show that the giant vein was the inner portion of a large fissure ridge travertine and grew asymmetrically and ataxially through repeated shallow fluid injections between ~650 and 85 ka, with growth rates in the 10⁻² - 10⁻³ mm/a order. The giant vein developed mainly during warm humid (interglacial) periods, partially overlapping with the growth of near by travertine plateaus. Estimated values of CO₂ leakage connected with the vein precipitation are between about 5 × 10⁶ and 3 × 10⁷ mol a⁻¹ km⁻², approximately representing one millionth of the present global CO₂ leakage from volcanic areas. Temperature estimates obtained from O isotopes and fluid inclusion microthermometry indicate epithermal conditions (90 - 50 °C) for the circulating fluid during the giant vein growth, with only slight evidence of cooling with time. Geochemical and isotope data document that the travertine deposits formed mainly during Pleistocene warm humid periods, within a tectonically controlled convective fluid circuit fed by meteoric infiltration and maintained by the regional geothermal anomaly hosted by the carbonate reservoir of the Mt. Amiata field.

1. Introduction

Thermogene travertines form through precipitation of CaCO₃ from supersaturated fluids usually generated and discharged in volcano tectonic settings, often deposited in proximity of active geothermal springs or along open fissures (Pentecost, 1995; Ford and Pedley, 1996; Pentecost, 2005; Crosseby et al., 2006). In addition of being important decorative and construction stones since at least the Roman time (Calvo and Regueiro, 2010), a renewed world wide interest for thermogene travertine deposits resides in their importance to be potential analogs of long term outflow from artificial CO₂ storages (Shipton et al., 2004; Bickle and Kampman, 2013; Burnside et al., 2013; Frey et al., 2015). Moreover, recent discoveries of large hydrocarbon reserves in subsalt porous microbial and travertine like rocks along the Brazilian and Angolan margins of the Atlantic Ocean place thermogene travertines among the best exposed analogs of these hydrocarbon reservoir rocks, which are hitherto known only from seismic data and well cores (e.g., Beasley et al., 2010; Rezende and Pope, 2015; Ronchi and Cruciani, 2015; Soete et al., 2015).

Following the terminology proposed by Capezzuoli et al. (2014), we henceforth use the term travertine to refer to deposits derived from hydrothermal waters, related to abiogenic processes, constituted by calcite and/or aragonite, and with a high δ¹³C signature (−1%o). In contrast, the term tufa, which is not used in this paper, refers to deposits derived...
from ambient temperature waters, linked to biotic processes, constitut ed by calcite, and with a lower δ¹³C signature (~0‰).

Travertines can show various deposit morphologies such as cas cades, terrace mounds, fissure ridges, plateaus, and towers (Bargar, 1978; Chafetz and Folk, 1984; Altunel and Hancock, 1993a, 1993b; Pentecost, 1995; Pentecost, 2005). These morphologies are only partially dependent on the topography over which the travertines precipitate. Other factors such as (neo)tecutonics (Altunel and Hancock, 1996; Hancock et al., 1999; Brogi, 2004a; Brogi and Capezzuoli, 2009; Brogi et al., 2010, 2012; De Filippis et al., 2013a; Ricketts et al., 2014; Maggi et al., 2015), climate oscillations (Sturchio et al., 1994, Rihs et al., 2000; Faccenna et al., 2008, De Filippis et al., 2012), earthquakes (Uysal et al., 2007, 2009; Brogi et al., 2014; Gradziński et al., 2014), and hydrological regimes (Prieisch et al., 2014; Crosse y et al., 2015) have been proposed to influence travertine growth and morphology; however, the way these and other factors control the travertine development and shape is still uncertain. It is, in particular, unclear what are the factors controlling travertine deposits that are completely different in morphology and volume such as travertine fissure ridges and pla teaus, which can, nonetheless, form close proximity during the same time span (e.g., De Filippis et al., 2013b).

In this paper, we address the growth of travertine fissure ridges and plateaus. Fissure ridges are deposits of travertines with an elongate mound shape characterized by a length between a few meters and over 2000 m, and a main crestal fissure from which the travertine feeding fluids gush out (Bargar, 1978; Chafetz and Folk, 1984; Altunel and Hancock, 1993a,b, 1996; Calú, 1999; Hancock et al., 1999; Uysal et al., 2007, 2009; De Filippis et al., 2012, 2013a). Fissure ridges are usually formed by two main travertine types: (1) the bedded travertine, which consists of a porous and stratified deposit constituting the flanks (often clinostratified) and the bulk of the fissure ridge and (2) the bed ed travertine, which consists of subvertical bands of sparry nonporous carbonate (usually calcite, aragonite, or both) filling large veins that in trude the axial region of the fissure ridge. In places, these veins can also develop as sill like structures along the beds of the bedded travertine or host rocks (Uysal et al., 2007; Gratier et al., 2012). Travertine plateaus, in contrast, are characterized by massive and tabular deposits consisting of subhorizontal to gently clinostratified travertine beds usually filling a tectonic or morphological depression and producing no prominent topography (Faccenna et al., 2008; De Filippis et al., 2013a; Billi et al., 2016).

Tuscany (Fig. 1), central Italy, is a region characterized by Neogene Quaternary formation of extensional basins, widespread magmatism, associated contact metamorphism, hydrothermalism, ore mineralization, and also numerous thermogene travertine deposits (Marinelli et al., 1993; Serri et al., 1993; Barberi et al., 1994; Carmignani et al., 1994; Dini et al., 2005; Gandin and Capezzuoli, 2008; Brogi and Capezzuoli, 2009; Rossetti et al., 2008, 2011; Vignaroli et al., 2016). Travertine deposition in Tuscany has occurred near highly productive geothermal areas (Larderello Travale and Mt. Amiata; Batini et al., 2003), where endogenous fluids permeate Meso Cenozoic carbonate reservoirs and mix before feeding thermal springs and CO₂ emission centers (e.g., Minissale, 2004). Both travertine fissure ridges and plateaus are documented in Tuscany. In particular, studied fissure ridges are exposed in the Rapolano Terme (e.g., Brogi and Capezzuoli, 2009; Guo and Riding, 1999) and Castelnuovo dell‘Abate (Rimondi et al., 2015) localities (Fig. 1b), where banded travertine forms centimeters to meters thick veins within meters sized elongate mounds accreted over a restricted time interval between Pleistocene and Holocene times.

We focus our study on travertines exposed in the village of Semproniano (northern Albe gna basin, southern Tuscany), which is built on top of a hill at an altitude of about 600 m. Semproniano is located ed only about 15 km south of the Mt. Amiata Pleistocene volcanic district and about 10 km north of the Saturnia thermal spring (Figs. 1 and 2), where active travertine deposition still occurs. The Semproniano village lies on a travertine fissure ridge (Capezzuoli et al., 2013), a composite carbonate vein (≥50 m thick) consisting of subvertical banded travertine, which crops up from the surrounding host carbonate rocks (Paleogene). Other travertine deposits or carbonate mineralizations, including travertine plateaus, small veins, and bedded travertines, are exposed within a few kilometers from the Semproniano village (Fig. 3a). The origin and growth modes of these deposits and mineralizations in the Semproniano area are unknown and the main driving factors (e.g., tectonics, paleohydrology, paleoclimate, etc.) are still uncertain. Moreover, absolute dating of these travertines is missing, thus making very difficult the regional correlation among these deposits as well as between the deposits themselves and the dated tectonic, volcanic, and paleoclimate events in the region.

The coexistence of different nearby CaCO₃ mineralizations and travertine deposits in a region of recent tectonic and volcanic activity makes the Semproniano area an excellent case study to understand the nature of these carbonate deposits. Using a multidisciplinary approach consisting of geological, structural, geomorphologic, and geochemical methods (including fieldwork, remote observations, U-Th dating, C Nδ O and Sr isotope systematics, rare Earth element abundances, and fluid inclusion microthermomometry), this study is aimed at understanding the development of the different travertine bodies (vein and plateau type), their mutual relationships, and the feedback relationships between travertine deposition and driving factors such as volcanism, paleoclimate, and tectonics. The novelty of this work concerns growth modes and rates of the Semproniano fissure ridge and implications for the associated CO₂ leakage (e.g., Frery, 2012; Crosse y et al., 2016; Lee et al., 2016).

2. Geological setting

Southern Tuscany is located in the inner (western) sector of the northern Apennines chain (Fig. 1), which is a NW SE trending Cenozoic orogenic belt developed through a general eastward migration of thrust sheets in a classical piggy back sequence toward the Adriatic foreland (e.g., Patacca et al., 1990; Cipollari and Cosentino, 1995; Massoli et al., 2006). In Tuscany, post orogenic extension started in middle late Mio cene time, concurrently with active shortening in the external orogenic domains (e.g., Malinverno and Ryan, 1986; Dewey, 1988; Jolivet et al., 1998; Cavinato and De Cellis, 1999; Pauselli et al., 2006; Brogi and Liotta, 2008; Brogi, 2011). The extensional process generated normal faults that dismantled the previously formed fold thrust belt (e.g. Carmignani et al., 1994; Keller et al., 1994; Barchi et al., 1998; Jolivet et al., 1998; Collettini et al., 2006; Marroni et al., 2015) and produced significant crustal thinning (present day crust thickness is about 22 24 km; Locardi and Nicollich, 1988; Billi et al., 2006). The emplacement of the dominantly anatetic magmatic products of the late Miocene Quaternary Tuscan Magmatic Province (Serri et al., 1993; Peccerillo, 2003) accompanied crustal thinning in the region (Rossetti et al., 2008). The geothermal fields of Larderello and Monte Amiata attests for high heat flow conditions maintained by polyphase magma emplacement at shallow crustal levels during the last 3 Ma (Franceschini, 1998; Mongelli et al., 1998; Dini et al., 2005; Rossetti et al., 2008). Fossil and active, structurally controlled hydrothermal mineralizations are widespread evidence of the interaction between hydrothermal systems and extensional faults in the region (e.g., Barberi et al., 1994; Buonasorte et al., 1988; Chiarabba et al., 1995; Gianelli et al., 1997; Batini et al., 2003; Bellani et al., 2004; Annuziatellis et al., 2008; Brogi, 2008; Liotta et al., 2010; Rossetti et al., 2011; Vignaroli et al., 2013).

Southern Tuscany (Fig. 1) is characterized by main NW SE trending and minor NE SW trending Miocene to Quaternary sedimentary b ains formed during post orogenic extensional processes and bounded by extensional to transtensional structures (Martini and Sagri, 1993; Liotta, 1994; Pascucci et al., 2006; Brogi and Liotta, 2008, Brogi, 2011; Brogi et al., 2013, 2014, 2015). These structures include the Tevere-Paglia, Siena Radicofoli, and Albe gna basins. The Semproniano thick vein and surrounding travertine deposits are located in the Albe gna
The study area (Semproniano, upper Albegna basin) is located. (b) Geological map of the southern Tuscany and northern Latium regions showing the main geothermal fields and travertine deposits (including fissure ridges).

Fig. 1. (a) Schematic map of Italy showing the Apennines fold-thrust belt and the area affected by crustal extension at the rear (west) of the belt. This latter area includes Tuscany, where the study area (Semproniano, upper Albegna basin) is located. (b) Geological map of the southern Tuscany and northern Latium regions showing the main geothermal fields and travertine deposits (including fissure ridges).

The geological setting of the Albegna basin is characterized by subsurface and surface metamorphic and non metamorphic tectonic units stacked during the formation of the Apennines fold thrust belt. From bottom to top, these units are as follows (e.g., Carmignani et al., 2013): (1) low grade metamorphic rocks of the Tuscan Metamorphic Complex; (2) Upper Triassic to Oligocene kilometers thick sedimentary succession composed of basal evaporites followed by shelf carbonates and marls (Tuscan Nappe); (3) Jurassic to Eocene ophiolite derived clays and marls succession (Ligurian Domain); and (4) late Miocene to Pleistocene terrigenous post orogenic deposits. These latter consist of fluvo lacustrine granular deposits and marine clays that sedimented in subsiding areas concomitantly with the regional tectonic extension (Zanchi and Tozzi, 1987; Bonazzi et al., 1992; Bosio et al., 2004).

In the Albegna basin, travertine deposits unconformably lie on top of the Neogene Pleistocene deposits (Zanchi and Tozzi, 1987; Martelli et al., 1989; Bosi et al., 1996; Croci et al., 2016). The travertine deposition occurred in distinct phases and over a long time interval (Bosi et al., 1996). In particular, based on the travertine morphological and stratigraphic characters, Bosi et al. (1996) proposed a travertine deposition spanning from Messinian to Holocene times, suggesting that the traver tines of the Semproniano area deposited during Pliocene time. Other authors considered these latter travertines as early Pleistocene in age (Zanchi and Tozzi, 1987). The lack of absolute radiometric ages restricts the full understanding of these travertine deposits and their relation ships with the hydrothermal and tectonic activity in the Albegna basin.

3. Methods and results

3.1. Geology and geomorphology

We performed a field based study on the geology, geomorphology, and structural setting of the travertine deposits located in the Semproniano area, namely: the (1) Semproniano ridge, (2) Vignacci,
We focused this study on the recognition of different travertine morphotypes (e.g., plateaus vs. fissure ridge travertines), on the relationships between travertine deposits and host rocks, and on the deformation features affecting the travertine deposits.

The study area is characterized by a set of post-orogenic Pliocene Quaternary continental and marine sedimentary deposits (including the studied travertines) that unconformably rest on top of the Apennines stacked units (e.g., Bonciani et al., 2005; Brogi, 2008; Brogi and Fabbrini, 2009). The travertine plateaus (Poggio Semproniano and Poggio i Piani), in particular, unconformably lie over Pliocene deposits and over the late Cretaceous Eocene Scaglia Toscana Fm. of the Tuscan Nappe (Fig. 4a), which hosts the Semproniano fissure ridge (Fig. 2; Carmignani et al., 2013). The Poggio Semproniano deposit occupies the top portion of a triangular hill that is almost 700 m a.s.l. (above sea level) high (Fig. 3). The hill is tabular with a terrace-like top surface marked by a peripheral rim that runs all around the terraced deposit and delimits the terrace itself from the steep flanks of the hill. At the foot of these escarpments, the contact between the travertine deposit and the surrounding units is often covered by debris constituted by

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Fig. 2. (a) Structural geological map of the study area (Semproniano area in the upper Albegna basin) and (b) related geological cross-sections. The map is based on and partly redrawn from the geological map at the 1:10,000 scale available online at www.regione.toscana.it/-/geologia and on numerous previous papers including Bettelli et al. (1990), Brogi (2004a), Bonciani et al. (2005); Carmignani et al. (2013), and Guastaldi et al. (2014).
The semproniano (Fig. Poggio i Piani hills) deposit characterized a maximum of about 200 m (Figs. 2 and 3). The travertine depositional fabric consists of piano parallel centimeters thick beds of whitish lime mudstone with homogeneous porosity due to the presence of microbialites. Millimeter to centimeter sized karst dissolution cavities are also present (Fig. 4c). On the eastern flank, the travertine beds of the Poggio Semproniano plateau and the underlying marly deposits of the Tuscan Nappe are pervaded by a set of NW SE striking cm thick subvertical veins filled by white sparry carbonate.

The Poggio i Piani deposit is very similar to the one of Poggio Semproniano. Poggio i Piani is a terraced triangular hill with a maximum elevation of about 530 m a.s.l. Also here, the travertine deposit is characterized by an outer sharp rim that runs all around the terraced deposit and delimits the terrace itself with the steep flanks of the hill. The deposit is tabular and sub horizontal with sedimentary features similar to the ones described for Poggio Semproniano (Fig. 4c, d, e). The dimensions of the Poggio i Piani travertine plateau are about 500 m in the NW SE direction and 450 m in the N S direction with a maximum thickness of 35 m (Fig. 2). A narrow N10° trending valley with a minimum elevation of about 500 m a.s.l. separates the Poggio Semproniano and Poggio i Piani hills (Fig. 3).

The Semproniano ridge is separated from the Poggio Semproniano and Poggio i Piani deposits by a narrow NW SE trending valley with a minimum elevation of about 500 m a.s.l. (Fig. 3). The Semproniano ridge crops out from the top of a NW SE elongated domed hill about 1000 m long and 400 m wide with a maximum altitude around 600 m a.s.l. The central part of the Semproniano ridge, constituted by banded sparry travertine with a total thickness of more than 50 m, is characterized by complex geometries such as V like shapes (Fig. 5e) or crosscut ting carbonate bands that are up to about 2 cm thick. The sparry subvertical bands of carbonate form a unique, composite and uninter rupted vein that we call the Semproniano giant vein for its thickness (see below). The southwestern flank of the ridge is characterized by the presence of sub horizontal bedded travertine leaning over the sub vertical banded travertine (Fig. 5f). The bedded travertine is characterized by sub horizontal brownish centimeters thick beds (Fig. 5g), shrubs, and laminations affected, in places, by millimeters to centimeters sized cavities of depositional and post depositional (karst) origin. In some cases, the porous bedded travertine appears to be pervaded by bed parallel veins (Fig. 5h and i). In the external part of the southwestern flank of the giant vein, at an altitude of about 580 m a.s.l., a set of sub vertical centimeters thick carbonate veins cut through the marly carbonates of the Scaglia Toscana Fm., which is the host rock of the giant vein (Figs. 2 and 5j k).
The I Vignacci deposit crops out about 1 km to the northwest of the NW striking Semproniano ridge (Figs. 2 and 3). I Vignacci travertine deposit is located at an altitude of about 430 m a.s.l. that is the lowest alti tude reached by the studied travertines. The deposit consists of banded travertine with subvertical NW SE striking bands. These bands cut through the surrounding sub horizontal beds of the Scaglia Toscana Fm. Geometrical attitude and location of I Vignacci outcrop suggest a structural and geometric continuity with the Semproniano ridge (Figs. 2 and 3).

From a tectonic point of view, the travertine deposits are cross cut by two main subvertical fault systems, one striking WNW ESE and one striking c. N S (Figs. 2 and 6). The WNW ESE striking fault system cuts through the northern portion of the Poggio Semproniano travertine plateau (Fig. 6a). It consists of a meter thick damage zone defined by fault slip surfaces and a secondary, subparallel, fracture network (Fig. 6b). A pitch angle smaller than 15° or greater than 165° was mea sured for most slickenlines occurring on the fault surfaces (Fig. 6c). The kinematic indicators within the fault damage zone are mainly provided by synthetic shear fractures (Riedel shears), consistent with a right lateral slip. The N S striking fault system runs along the valley that sep arates the Poggio Semproniano and Poggio i Piani travertine deposits (Fig. 2). We recognized this set of faults as affecting the banded trave tine deposits of the Semproniano ridge and cutting through the banded travertine of the Semproniano fissure ridge (Fig. 6a). Within the ridge, the N S striking fault system is characterized by a 0.5 m thick damage zone, overprinted by several speleothem filled fracture networks (Fig. 6d). When present, abrasive striations on fault surfaces are char ac terized by a pitch angle ranging between 50 and 70°. Geometrical rela tionships between faults and secondary fractures are consistent with an oblique extensional kinematics. This fault system is responsible for block faulting affecting and lowering the Poggio Semproniano trave tine deposit (Fig. 2).

3.2. U/Th geochronology

We dated nineteen samples from the CaCO3 mineralizations in the study area (Tables 1, 2, and S1), namely from Semproniano (thirteen samples from the giant banded vein, bedded travertines, and one subordinate vein), I Vignacci (one sample from the banded travertine), Poggio Semproniano (three samples from bedded travertines and veins), and Poggio i Piani (one sample from bedded travertines). The an alytical methods (α spectrometry and mass spectrometry) are de scribed in the Appendix.

Banded travertine samples from Semproniano Village (SP1) and I Vignacci (V11) are characterized by a \(^{230}\text{Th}/^{234}\text{U}\) activity ratio higher than 1 and, therefore, by ages higher than the limit of the U/Th method in \(\alpha\) spectrometry (c. 350 ka). The banded travertine exposed on the south western flank of the Semproniano giant vein (SP11) is character ized by a moderate detrital contamination \(^{230}\text{Th}/^{232}\text{Th}\) activity ratio = 7.148 ± 0.251) and by a corrected \(^{230}\text{Th}/^{234}\text{U}\) activity ratio of 0.878 ± 0.051, indicating an age of 214 ± 50/−37 ka. A subordinate carbonate vein (SP16) cutting through the host rocks of the Scaglia Toscana Fm. in the external south western flank of the Semproniano giant vein is characterized by a \(^{230}\text{Th}/^{232}\text{Th}\) activity ratio of 12.564 ± 1.987 and by a corrected \(^{230}\text{Th}/^{234}\text{U}\) activity ratio of 0.641 ± 0.064. Calculated age for this sample is 104 ± 16 ka. A banded travertine sample collected in the southern part of Poggio Semproniano plateau (PO2; Fig. 4b) is characterized by a \(^{230}\text{Th}/^{234}\text{U}\) activity ratio of 0.81 ± 0.039. The resulting age is 171 ± 19 ka. Two samples of calcite filled veins (SP3 and SP10) cutting through the banded travertine of Poggio Semproniano and the underlying Scaglia Toscana Fm. are characterized by a \(^{230}\text{Th}/^{234}\text{U}\) activity ratio of 0.340 ± 0.052 and 0.299 ± 0.023, respectively. The related ages are 43 ± 8 ka and 39 ± 4 for the SP3 and SP10 samples, respectively. A sample of bedded travertine from Poggio i Piani plateau (PP1; Fig. 4e) is characterized by a \(^{230}\text{Th}/^{234}\text{U}\) activity ratio of 0.857 ± 0.028 and a resulting age of 198 ± 18 ka.

To understand the spatial temporal and metric growth of the Semproniano giant banded vein, we dated eleven samples along a transect across the vein (Fig. 6), and one sample (SP12) from the upper part of the transect (Figs. 5e and 7) by mass spectrometry (Fig. 7 and Tables 2 and S1). We obtained, ages between 86 ka to 646 ka (Fig. 7), with only one sample being older than the resolution of the method (>800 ka). Radium ages along the transect do not vary systematically. In other words, the oldest samples are not located within the inner or external portions of the vein to indicate its antitaxial or syntaxial growth, respec tively. The three oldest samples (i.e., c. 646, 613, and >800 ka) occur in
separate inner portions of the vein and are divided by younger carbonates (Fig. 7).

3.3. C and O isotopes and parental fluid thermometry from O isotopes

We performed δ¹³C and δ¹⁸O analyses on fifty one samples (banded and bedded travertines, calcite veins) from the Semproniano area (Tables 1 and 3). Details on the analytical procedure are provided in the Appendix. Oxygen and carbon isotopes are reported with respect to V PDB. All analyzed samples are characterized by positive values of δ¹³C (between 3.2 and 10.5‰) and negative values of δ¹⁸O (between −14.6 and −7.6‰) (Table 3). Results, in particular, are clustered around 8‰ for δ¹³C and around −11‰ for δ¹⁸O (Fig. 8b).
3.3.1. Semproniano Village

Samples of banded travertine from the Semproniano veins are characterized by δ13C values between 3.2 and 10.5‰ (V PDB) and by δ18O values between −14.6 and −7.6‰ (V PDB). Samples from the associated banded travertine are characterized by δ13C values between 5.3 and 9.9‰ (V PDB) and by δ18O values between −9.8 and −8.2‰ (V PDB).

3.3.2. I Vignacci

The sample from the banded travertine of I Vignacci (sample VI1) is characterized by a δ13C of 3.7‰ (V PDB) and a δ18O of −9.6‰ (V PDB).

3.3.3. Poggio Semproniano

Samples of bedded travertine from Poggio Semproniano are characterized by values of δ13C between 5.7 and 7.1‰ (V PDB) and values of δ18O between −11.4 and −8.1‰ (V PDB). Calcite filled veins pervading the bedded travertine and the underlying Scaglia Toscana Fm. (Samples SP3, SP10) are characterized by δ13C values between 7.1 and 8.4‰ (V PDB) and δ18O values between −11.5 and −10.7‰ (V PDB).

3.3.4. Poggio i Piani

One sample from the bedded travertine (sample PP1) of Poggio i Piani is characterized by a δ13C of 6.5‰ (V PDB) and a δ18O of −11.6‰ (V PDB).

We focused particular attention to the Semproniano giant vein by performing a detailed sampling along two NE-SW trending transects perpendicular to the vein (samples SP14/03 to SP14/04 and SP14/08 to SP14/34; Figs. 3b and 7) and collecting three further samples in the adjacent bedded travertine (samples SP11, SP14/05, SP14/06) (Table 3). Samples from the banded travertine deposits do not show any systematic pattern in the O and C isotope values along the Semproniano giant vein: (i) samples from the first transect (samples SP14/03 to SP14/16; transect G-H in Fig. 3b) are characterized by δ13C values ranging between 5.3 and 9.7‰ and δ18O values between −12.8 and −9.0‰; (ii) samples from the second transect (samples SP14/17 to SP14/34; transect E-F in Fig. 3b) are characterized by δ13C values ranging between 3.2 and 10.2‰ and δ18O values between −12.6 and −7.6‰. Samples from the bedded travertine located along the flanks of the Semproniano giant vein are characterized by δ13C values ranging between 5.3 and 9.9‰ and δ18O values ranging between −9.8 and −8.2‰.
We calculated the paleo temperature of the mineralizing parental fluids applying the equation of Kele et al. (2015) to the entire δ18O dataset (Table 3 and Fig. 8c), using as benchmark the present δ18O of the Saturnia spring hydrothermal waters (−6.4‰ V-SMOW), whose active source is located c. 10 km to the south of the Semproniano giant vein. We assume that the oxygen isotope composition of the palaepsprings was similar to those of the current Saturnia spring. The banded travertines of the Semproniano giant vein yield temperatures between 34 ± 2 and 71 ± 7°C, with the majority in the range between 45 and 60°C. The banded travertines associated with the giant vein give temperatures between 35 ± 2 and 43 ± 3°C, whereas the banded travertine sample from I Vignacci yields a temperature of 42 ± 3°C. The Poggio Semproniano plateau samples yield temperatures of 36 ± 2 and 53 ± 5°C, for the banded travertine, and 49 ± 4 and 53 ± 5°C, for the calcite veins. The banded travertine from Poggio i Piani yields a temperature of 53 ± 5°C. There is no correlation between ages and temperature of precipitation (Fig. 8d). In particular, there is no systematic trend of decreasing temperature with younger ages of deposition.

### 3.4 Sr and Nd isotopes and rare earth elements

We performed Strontium, REE, and Ytrrium (Y; REE + Ytrrium = REY) concentration analysis, and Strontium and Neodymium isotope measurements on carbonate fraction of samples to understand the sub-surface circuit of hydrothermal fluids (e.g., Ederfield and Greaves, 1982; McLennan, 1989; Webb and Kamber, 2000; Uysal et al., 2007, 2009). The analytical procedures and protocols are explained in the Appendix. Results are reported in Tables 4 and S2 and Fig. 9.

We observed a variable Sr concentration comprised between 105.3 and 4956.3 mg/kg, with the mean value (3200 mg/kg) in the range of Sr contents for most travertines in central Italy (Minissale, 2004). The banded travertine from the Semproniano giant vein (SP12, SP14/18, SP...
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Rock type</th>
<th>Age corrected (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP15**</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>347 ± 22</td>
</tr>
<tr>
<td>SP14/15*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>&gt; 800</td>
</tr>
<tr>
<td>SP14/18*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>86 ± 1</td>
</tr>
<tr>
<td>SP14/20*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>231 ± 9</td>
</tr>
<tr>
<td>SP14/23*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>314 ± 11</td>
</tr>
<tr>
<td>SP14/25*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>419 ± 39</td>
</tr>
<tr>
<td>SP14/28*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>613 ± 200</td>
</tr>
<tr>
<td>SP14/30*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>105 ± 1</td>
</tr>
<tr>
<td>SP14/32*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>646</td>
</tr>
<tr>
<td>SP14/34*</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>495 ± 99</td>
</tr>
<tr>
<td>SP15**</td>
<td>Semproniano Village</td>
<td>Calcite vein</td>
<td>&gt; 350</td>
</tr>
<tr>
<td>SP12**</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>128 ± 19</td>
</tr>
<tr>
<td>SP16**</td>
<td>Semproniano Village</td>
<td>Calcite vein</td>
<td>104 ± 16</td>
</tr>
<tr>
<td>SP11**</td>
<td>Semproniano Village</td>
<td>Bedded travertine</td>
<td>214 ± 50/ 37</td>
</tr>
<tr>
<td>SP13**</td>
<td>Poggio Semproniano</td>
<td>Calcite vein</td>
<td>43 ± 8</td>
</tr>
<tr>
<td>SP10**</td>
<td>Poggio Semproniano</td>
<td>Calcite vein</td>
<td>39 ± 4</td>
</tr>
<tr>
<td>PO2**</td>
<td>Poggio Semproniano</td>
<td>Bedded travertine</td>
<td>171 ± 19</td>
</tr>
<tr>
<td>PP1**</td>
<td>Poggio i Piani</td>
<td>Bedded travertine</td>
<td>198 ± 18</td>
</tr>
<tr>
<td>VI1**</td>
<td>Vignacci</td>
<td>Banded travertine</td>
<td>&gt; 350</td>
</tr>
</tbody>
</table>

and SP14/28), the banded travertine from I Vignacci (VI1), and the calcite vein from Poggio Semproniano (SP3 and SP10) are characterized by the highest Sr concentrations, between 1125.9 and 4956.3 mg/kg. On the contrary, the bedded travertine from the flanks of the Semproniano giant vein (SP11, SP14/06, and SP17) and the bedded travertines from Poggio Semproniano (SP9, PO1, and PO2) are characterized by the lowest Sr concentrations, between 105.3 and 787.3 mg/kg. Sr isotope ratios from the same selected samples range from 0.708277 to 0.708527 (Table 4).

The Nd isotope composition of one bedded travertine from the flanks of the Semproniano giant vein (SP14/06), one banded travertine from I Vignacci (VI1), and one calcite vein from Poggio Semproniano (SP3) are characterized by values comprised in a narrow 0.512253-0.512330 range (Table 4).

We determined REY concentrations for the banded travertine from the Semproniano giant vein (SP14/18), the bedded travertine sample from the flanks of the Semproniano giant vein (SP14/06), the banded travertine sample from I Vignacci (VI1), and the bedded travertine sample (PO1) and calcite vein (SP3) from Poggio Semproniano. We normalized the REY concentrations against PAAS (Post Archean Austrian Shale; McLennan, 1989; Fig. 9 and Table S2) following the recommendations by Bau and Möller (1992) concerning the study of (shallow) crustal processes. The REY concentrations are highly variable (ΣREE = 0.08-18.6), resulting significantly lower than PAAS (Fig. 9). The main features of REY patterns are (Fig. 9): (i) relative depletion of the light rare Earth elements (LREE = NdN/YbN = 0.71, with the exclusion of sample VI1); (ii) variable enrichment of the heavy rare Earth elements (HREE as NdN/YbN = 1.9-0.07, according to Webb and Kamber, 2000); (iii) strongly superchondritic Y/Ho ratio (38.3 221.3) characterized by a huge positive Y spike in the pattern; (iv) positive Gd anomaly for sample SP14/06 and VI1; and (v) consistent negative Ce anomaly (Ce/Ce* = 0.30-0.94; Table S2).

Table S1 for a complete list of data. Samples indicated with * were analyzed through MC-ICP-MS at the HISPEC lab of the National Taiwan University (errors quoted as 2σ), whereas samples indicated with ** were analyzed through o-spectrometry at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University, Italy (errors quoted as 1σ).
Unfortunately, only one of our samples contained fluid inclusions suited for microthermometry (Fig. 10a). This sample consists of elongate calcite crystals containing numerous two-phase (liquid + vapor or L + V) liquid-rich fluid inclusions 5 to 50 μm long and a constant V/L ratio for all the analyzed inclusions (Figs. 10b d). Fluid inclusions occur both as primary isolated and as pseudosecondary in small planes that do not cross the crystal rims. The inclusion shape is variable. We recognized, in particular, two main types of inclusions: (1) flat irregular (Fig. 10c and d) and (2) polygonal (Fig. 10b).

Temperature values (i.e., the temperature of last ice melting from which salinity is deduced) range between 0.0 and +4.8 °C, but are mostly centered around 0 ± 1 °C (Fig. 10f). Being very small systems, fluid inclusions may exhibit metastable behavior and metastable ice crystals.

### 3.5. Fluid Inclusion microthermometry

Fluid inclusion microthermometry is the best direct technique to understand and reconstruct the physical and chemical properties of the mineralizing fluids; however, fluid inclusion studies on travertine are rare (Słowiakiewicz, 2003; Gibert et al., 2009; El Desouky et al., 2015; Rimondi et al., 2015) due to some difficulties inherent to travertines such as: (1) scarce occurrence and small size of inclusions (Pentecost, 2005); (2) inclusion metastability often causing failure in bubble nucleation upon cooling from the trapping conditions to room temperature (Diamond, 2003); (3) stretching and de crepitation making microthermometric analyses unreliable; and (4) double refraction of calcite (Bodnar, 2003).
can persist at temperatures as high as +6.5 °C (Roedder, 1967) (Fig. 10f). Based on these data, we deduce that the fluid consists of almost pure water. Homogenization temperature (Tθ) values range between 57 and 105 °C, with a maximum around 70-90 °C (Fig. 10e). No pressure correction is required for these homogenization temperature values as the analyzed sample precipitated in a very shallow environment represented by the giant vein (e.g., De Filippis and Billi, 2012).

4. Discussion

4.1. A long lived giant vein

The thick and continuous sequence of travertine sparry subvertical bands (the giant vein) in the Semproniano village accompanied by bedded travertine on its flanks and by veins in the Tuscan Nappe host rock suggests that the Semproniano giant vein represents the central portion of a fossil fissure ridge travertine larger than but similar to those known in several other hydrothermal areas such as Turkey (e.g. Denizli Basin; Altunel and Hancock, 1993a, 1993b, 1996; Uysal et al., 2007, 2009; De Filippis et al., 2012, 2013a), U.S.A. (e.g. Mammoth Hot Springs and Bridgeport; Hancock et al., 1999; De Filippis and Billi, 2012), Italy (e.g. Rapolano, Castelnuovo dell’Abate, and Tivoli; Guo and Riding, 1999; Brogi, 2004a; Brogi and Capezzuoli, 2009; De Filippis et al., 2013b; Rimondi et al., 2015), and elsewhere (De Filippis et al., 2012). Most fissure ridge travertines are volumetrically dominated by bedded travertines occurring mainly along the flanks and partially along the axial portion of the ridges, whereas the banded travertine is normally confined within a narrow band along the ridge axis. In the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Rock type</th>
<th>Sr (mg/kg)</th>
<th>Δ⁶⁸Sr/⁶⁹Sr ± 2σ</th>
<th>εNd ¹⁴⁴Nd/¹⁴⁴Nd ± 2σ</th>
<th>εSr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP12</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>1189.46</td>
<td>0.708277 ± 11</td>
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<tr>
<td>SP14/18</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>1223.70</td>
<td>0.708395 ± 9</td>
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<tr>
<td>SP14/28</td>
<td>Semproniano Village</td>
<td>Banded travertine</td>
<td>1123.91</td>
<td>0.708368 ± 10</td>
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<tr>
<td>SP11</td>
<td>Semproniano Village</td>
<td>Bedded travertine</td>
<td>105.31</td>
<td>0.708491 ± 10</td>
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<tr>
<td>SP14/06</td>
<td>Semproniano Village</td>
<td>Bedded travertine</td>
<td>652.35</td>
<td>0.708470 ± 5</td>
<td>0.512253 ± 18</td>
<td>6.50</td>
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<tr>
<td>SP17</td>
<td>Semproniano Village</td>
<td>Bedded travertine</td>
<td>592.74</td>
<td>0.708437 ± 6</td>
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<tr>
<td>SP9</td>
<td>Poggio Semproniano</td>
<td>Bedded travertine</td>
<td>734.74</td>
<td>0.708326 ± 7</td>
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<tr>
<td>PO1</td>
<td>Poggio Semproniano</td>
<td>Bedded travertine</td>
<td>502.19</td>
<td>0.708334 ± 5</td>
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<td></td>
</tr>
<tr>
<td>PO2</td>
<td>Poggio Semproniano</td>
<td>Bedded travertine</td>
<td>787.25</td>
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<tr>
<td>SP3</td>
<td>Poggio Semproniano</td>
<td>Calcite vein</td>
<td>4763.20</td>
<td>0.708527 ± 7</td>
<td>0.512330 ± 39</td>
<td>2.41</td>
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<tr>
<td>SP10</td>
<td>Poggio Semproniano</td>
<td>Calcite vein</td>
<td>4154.77</td>
<td>0.708488 ± 9</td>
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</tr>
<tr>
<td>V11</td>
<td>I Vignacci</td>
<td>Banded travertine</td>
<td>4096.30</td>
<td>0.708456 ± 6</td>
<td>0.512275 ± 20</td>
<td>9.93</td>
</tr>
</tbody>
</table>

* Uncertainties are 2σ mean, within-run precision and refer to the last digits.

* εNd has been calculated at 200 Ma.
Semproniano case, although we have no record on the amount of eroded banded travertine over time (since about 650 ka), the ridge seems to be characterized by a volumetric predominance of banded travertine (i.e., the giant vein) with only small slabs (at present) of bedded travertine on its flanks.

We consider the Semproniano vein as a giant structure characterized by a minimum thickness of 50 m, which is a thickness larger than any one we found in the published literature. Hence, the Semproniano giant vein is probably the thickest continuous vein (i.e., no relics of host rock are interspersed across the Semproniano giant vein) so far documented in the geological literature. Very thick veins (i.e., banded travertine) are common in many fissure ridge travertines (e.g., Uysal et al., 2007, 2009; De Filippis et al., 2012), but their thickness (at least that of the continuous portion of banded travertine) is normally at least one order of magnitude smaller than that of Semproniano. For in stance, the Akköy fissure ridge in the Denizli basin (Turkey) is known as one of the largest and thickest fissure ridges on the Earth. This fossil structure is very well visible in its inner portion thanks to the presence of numerous quarries. In the quarries, the Akköy ridge is characterized by inner veins that are less than 10 m thick (i.e., considering only continuous veins; De Filippis et al., 2012).

Very thick veins pervading rocks are common in different settings (e.g., metamorphic rocks), but all these occurrences are characterized by non continuous veins, with relics of host rock interspersed across the veins. Quartz veins of a thickness comparable to the one of Semproniano were described by Bons (2001) and Yılmaz et al. (2014). In both instances, the veins have thicknesses close to 50 m but, unlike the Semproniano structure, these quartz veins are characterized by wall rock inclusions.

We interpret the giant thickness of the Semproniano vein as due to two main factors: (1) the shallow emplacement of this vein and therefore the limited confining pressure, which would have otherwise limited the lateral expansion of the vein in a deeper case. Although we do not know the exact depth of formation, most veins along fissure ridge travertines are typically formed only at a few meters depth at the most (De Filippis et al., 2012, 2013a); (2) the second factor is the unique longevity of the hydrothermal activity, which lasted at least 600 ka. This is much longer than what is reported by other studies of fissure ridge travertines which are typically around 10^4 a (e.g., Altunel and Karabacak, 2005; Uysal et al., 2007, 2009).

Although the Semproniano giant vein is located on top of the Semproniano ridge, we did not observe any evidence of gravity driven overturning of the peripheral blocks of the vein as observed, for instance, by De Filippis et al. (2012) in the case of the Akköy fissure ridge, Turkey; however, the occurrence of V-like growth patterns in the Semproniano giant vein (Fig. 5e) suggests that the hypothesis of a gravity influenced emplacement of the vein (e.g., De Filippis et al., 2012) cannot be excluded. Moreover, some fissure ridges can represent the surface emergence of normal or oblique extensional faults (e.g., Brogi and Capuzzo, 2009). We think that this is not the case for the Semproniano fissure ridge, as the related exposures are characterized by no evidence of faulting (Figs. 5 and 7); however, it is worth noting that the NW striking Semproniano vein formation is compatible with an orthogonal (NE-SW) maximum extension that is in turn compatible with the right lateral movement along the ENE striking main fault occurring 500 m to the south of the Semproniano ridge (Figs. 2 and 6b). We therefore infer that the travertine deposition in the Semproniano area may have been structurally controlled.

4.2. Rate and mode of vein growth

The Semproniano giant vein grew between about 650 and 85 ka. Considering 50 m as the vein total thickness, the average growth rate can be estimated to be around 8 × 10^{-3} mm/a. The three inner sectors of the giant vein can also be considered separately according to age groups: sector A, between samples SP14/25 and SP14/23; sector B, between samples SP14/23 and SP14/20; and sector C, between samples SP14/20 and SP14/18 (Fig. 7b). Considering the distance between the dated samples in each sector and the related age difference, we obtain average growth (i.e., thickening) rates of about 7 × 10^{-3}, 2 × 10^{-2}, and 6 × 10^{-3} mm/a for sectors A, B, and C, respectively. We therefore assume that the Semproniano giant vein grew with average rates ranging between 10^{-2} and 10^{-3} mm/a. These rates are consistent with previously estimated rates for banded travertines within fissure ridges located elsewhere (about 10^{-3} mm/a; Uysal et al., 2007; Mesci et al., 2008; Gratier et al., 2012; De Filippis et al., 2013a; Frery et al., 2015). This result confirms that the giant thickness of the Semproniano vein is not related to a fast growth rate but rather to the duration of hydrothermal activity, which is significantly larger than veins in other fissure ridges (e.g., Altunel and Karabacak, 2005; Uysal et al., 2007, 2009).

The age distribution along the transect shows that the oldest samples are located neither at the lateral ends of the giant vein nor at its central part, indicating that the vein did not grow in a pure syntactical or antitaxial fashion (Bons et al., 2012). The three oldest samples (i.e., c. 646, 613, and ~800 ka; Fig. 7b) occur in separate inner portions of the vein showing that the vein grew asymmetrically and antitaxially (Passchier and Trouw, 1996; Bons et al., 2012) with no systematic growth direction and no systematic age sequence. Based on our data, we hypothesize an accordion like mode of growth through multiple events of crack and seal pulses. Such a growth mode is well supported.
by the U/Th ages and is somewhat different from models proposed for fissure ridge structures (e.g., Hancock et al., 1999; Brogi and Capezzuoli, 2009) characterized by banded travertine forming injection veins and sill like structures filling diffuse fractures within the bedded travertine. The Semproniano giant vein, in fact, defines a single structure that grew within the same host rock over a long time, maintaining the same orientation.

4.3. Hydrothermal parental fluids

C and O isotope data show that the Semproniano giant vein is of thermogene origin (Pentecost, 2005). All analyzed samples are characterized by positive δ13C and negative δ18O values (Table 3, Fig. 7b), indicating mixing between hydrothermal parental fluids and mete oric waters, with a significant contribution of CO2 originating from limestone decarbonation (Gonfiantini et al., 1968; Guo et al., 1996; Billi et al., 2007). Moreover, our stable isotope data are in the range typical of thermogene travertines deposited by present day thermal springs of central Italy (Minissale, 2004; Gandin and Capezzuoli, 2008).

δ13C values of travertines have been used to determine the original signal of δ13C CO2 applying the empirical equation of Panichi and Tongiorgi (1976) and the theoretical equation of Bottinga (1968) (Table 3). According to the equation of Panichi and Tongiorgi (1976), the δ13C CO2 values are comprised between −6.7 and 2.1‰ (V PDB), while according to the equation of Bottinga (1968), the δ13C CO2 values are comprised between −5.4 and 3.5‰ (V PDB). These results confirm a mixing between CO2 originated from limestone decarbonation with CO2 of igneous origin (e.g. Turi, 1986; Minissale, 2004; Kele et al., 2011). In interpreting our stable isotope data, we assume equilibrium fractionation (Bottinga, 1968; Panichi and Tongiorgi, 1976); however, it is important to note that CO2 degassing and calcite precipitation could lead to the preferential loss of isotopically light C and O bearing species (i.e. CO2 and HCO3−; e.g. Kampman et al., 2012).

Fig. 10. (a) Close up photograph of banded travertine from the central part of the Semproniano giant vein. The sample studied for fluid inclusions comes exactly from the spot shown in the photograph. (b), (c), and (d) Microphotographs (transmitted light, parallel nicols) of liquid-rich fluid inclusions hosted in the banded travertine shown in the previous close-up photograph. L and V are for liquid and vapor phases, respectively, within the studied inclusions. (e) and (f) Results of microthermometry on fluid inclusions hosted in elongate calcite crystals. Th is the temperature (°C) of homogenization whereas Tmice (°C) is the temperature of last melting of ice.
The O isotope composition allowed us to estimate the parental fluid temperatures using the water oxygen isotopic composition of modern springs. In the case of the Semporniano giant vein, calculated temperatures span between about 34 ± 2 and 71 ± 7 °C, with the majority of data comprised between 46 and 60 °C (Table 3, Fig. 8c). The validity of these temperature estimates are confirmed by the fluid inclusion microthermometric data on sample SP12 yielding temperatures between 70 and 90 °C (Fig. 10e), which are also consistent with the 65.95 °C temperature range obtained by Capezzuoli et al. (2013). This evidence supports the assumption that the oxygen isotope composition of the hydrothermal fluid did not change substantially through time. Fluid inclusion data also show that the giant vein parental fluid (at least that trapped within the crystal inclusions) was constituted by almost pure water. Similar results were obtained by Capezzuoli et al. (2013), who found salinity values of 0.2 wt.% NaCl equivalent in the Semporniano fissure ridge, by Ronchi and Cruciani (2015), who found salinity values of about 0.3 wt.% NaCl equivalent in travertines from the Pianetti and Pian di Palma quarries in the southern Alibegna basin, and by Rimondi et al. (2015), who found maximum salinity value of 1.4 wt.% NaCl in the Castelnuovo dell’Abate travertines located on the northern flank of the Mt. Amiata volcano. Rimondi et al. (2015), in particular, explained the low salinity values as due to the lithological nature of the fluid reservoir mainly constituted by poorly soluble anhydrites (i.e., Triassic evaporites).

The lack of correlation between ages and precipitation temperatures in the giant vein (Fig. 8d) indicates no systematic and linear cooling of hydrothermal parental fluids with time. This hypothesis differs from that of Rimondi et al. (2015), who showed a cooling of the hydrothermal fluid of about 70 °C in 300-400 ka for the Castelnuovo dell’Abate travertines. We infer that the Semporniano travertines, which are located about 30 km to the south of Castelnuovo dell’Abate travertines, were influenced by paleoenvironmental and/or palaeoclimatic factors (see below) in addition to the Mt Amiata geothermal anomaly.

The rather homogeneous Sr and Nd isotope values are indicative of a unique reservoir for the deposition of travertines and calcite veins. Sr and Nd isotope values are different from isotopic signature of Mt. Amiata volcanic rocks (Conticelli et al., 2015). In particular, our Sr isotope values are in the range of those previously obtained for the Mesozoic sedimentary units of central Italy (e.g., Barbieri et al., 1979; Corteci and Lupi, 1994; Barbieri and Morotti, 2003) and for the hydrothermal springs of Saturnia (Barbagli et al., 2013). This evidence suggests no contamination through volcanic units during underground circulation of these fluids. This interpretation is compatible with the REE patterns that are similar to those obtained from the Tuscan Nappe limestone from the Larderello Travale geothermal area (Möller et al., 2003; Fig. 9).

Although the number of samples analyzed for the REE is limited, all samples are characterized by similar La and Gd anomalies, superchondritic Y/Ho ratio, and negative Ce anomaly. This evidence suggests a REE provenance from a marine source, possibly related to the meteoric water circulation through the Mesozoic limestones (Tuscan Nappe) and consequent leaching of REE from these rocks. In such a scenario, the enrichment of HREE relative to MREE and LREE may be related to carbonate complexation, a process activated during fluid rock interaction. Accordingly, REE distribution, Sr isotope data and field data. Accordingly, we consider the Mesozoic limestones of the Alibegna area (e.g., Bonciani et al., 2005; Brogi, 2008; Guastaldi et al., 2014) as the main reservoir of the hydrothermal system and the probable source for the chemical signature of the studied carbonates. Eventually, the best scenario explaining the entire hydrothermal fluid circuit should involve variable mixing of meteoric waters with fluids characterized by water rock isotopic exchange similar to the broad field of endogenous fluids (e.g., Crossey et al., 2009).

4.4. Estimate of CO₂ outflow

Minimum value of total CO₂ volume leaked during the formation of the Semporniano giant vein can be estimated from the volume of CaCO₃ precipitated (e.g., Crossley et al., 2009, 2016; Frey, 2012; Karlstrom et al., 2013; Lee et al., 2016). It has been shown that the volume of leaked CO₂ precipitated in travertine/vein deposits is only a minor part of the total leakage, i.e., between 6.6% and 10% (Shipton et al., 2005) of the total dissolved CO₂. According to Frey (2012), it is possible to calculate only the minimum value of CO₂ leakage during CaCO₃ vein formation for two reasons: (i) the proportion between precipitated CO₂ and total leaked CO₂ includes only the dissolved part of the CO₂ at the surface, thus disregarding the CO₂ escaping as free phase (i.e., degassing); (ii) after formation, the vein or travertine deposit may have undergone erosional processes, which are difficult to accurately quantify.

For fossil travertines or CaCO₃ veins, the total mass of precipitated CO₂ (\(m_{\text{CO}_2}^{\text{precipitated}}\)) can be calculated using the calcium carbonate precipitation equation:

\[
m_{\text{CO}_2}^{\text{precipitated}} = \rho_{\text{CaCO}_3} \cdot V_{\text{CaCO}_3} \cdot M_{\text{CO}_2} / M_{\text{CaCO}_3}
\]

where \(\rho_{\text{CaCO}_3}\) and \(M_{\text{CO}_2} / M_{\text{CaCO}_3}\) are considered as constant parameters; \(\rho_{\text{CaCO}_3} = 2.7 \times 10^3\) kg/m³; \(M_{\text{CO}_2} = 44\) mol/mol, and \(M_{\text{CaCO}_3} = 100.1\) g/mol.

Based on field observations, we estimate the volume of the Semporniano giant vein assuming a horizontal length of 500 m and a horizontal thickness of 50 m. For its vertical depth, we consider two alternative endmembers: 10 m (the observable vein depth exposed in the field), and 50 m (estimated through geological cross-sectioning: Fig. 2b). For a depth of 10 m, the estimated total mass of CO₂ leakage is \(5 \times 10^6\) and \(3 \times 10^6\) for total dissolved CO₂ masses of 6.6 and 10%, respectively. For a depth of 50 m, \(22 \times 10^6\) and \(14 \times 10^6\) tons are calculated for total dissolved CO₂ masses of 6.6 and 10%, respectively. Collectively, all these values provide a CO₂ leakage between 5 and 37 t/a for the Semporniano giant vein, corresponding to a CO₂ flux between \(5 \times 10^6\) mol a⁻¹ km⁻² and \(3 \times 10^6\) mol a⁻¹ km⁻². These estimates are of the same order of magnitude of measured average CO₂ flux discharged by present day thermal springs in central Italy (between \(1 \times 10^6\) mol a⁻¹ km⁻² and \(5 \times 10^6\) mol a⁻¹ km⁻²; Minissale, 2004; Frondini et al., 2008) and it is two order of magnitude lower than the CO₂ flux \(3.7 \times 10^6\) mol a⁻¹) in some present day thermal springs of the Colorado Plateau, USA (Crossey et al., 2009). For comparison, the estimated CO₂ flux during the formation of the Semporniano giant vein (on the order of \(10^6\) 10⁷ mol a⁻¹ km⁻²) is about four orders of magnitude lower than the deeply sourced (endogenic) CO₂ in non volcanic areas of Italy \((10^4\) mol a⁻¹, Rogie et al., 2000) and represents about one millionth of the present day CO₂ released from volcanic areas at the global scale (Gerlach, 2011).

4.5. Paleoclimate influence

To determine a possible influence of paleoclimatic on the growth of the Semporniano giant vein, in Fig. 11, we matched our U/T ages (Tables 2 and S1) with Quaternary glacial cycles, using the curve extracted from the deep sea oxygen isotope trend elaborated by Zachos et al. (2001), and the pollen record of the Valle di Castiglione, located about 150 km to the south of the study area (Fig. 1a), elaborated by Tzedakis et al. (2001).

We note that most samples from the giant vein fall within the interglacial stages. Also the host rock of the giant vein and the bedded travertine on the vein flanks match well with interglacial stages (Fig. 11). It is noteworthy that six samples fall within marine isotope stages MIS 5 and MIS 7, which are suggested to be humid times by the pollen curve (Fig. 11).
Our geochronological data therefore suggest that the Semproniano giant vein formed preferentially during warm and humid climatic periods characterized by high stands of the water table promoting a great fluid discharge. Similar patterns have been suggested for other Quaternary travertine deposits (e.g., Dramis et al., 1999; Frank et al., 2000; Rihs et al., 2000; Soligo et al., 2002; Pentecost, 2005; Luque and Julià, 2007; Faccenna et al., 2008; Kampman et al., 2012; Priewisch et al., 2014). This scenario is different from the one proposed by Uysal et al. (2007, 2009) on the basis of U/Th ages and REE data for banded travertines precipitated in co seismic fissures of the Denizli basin (Turkey). These authors proposed that carbonate precipitation was con trolled by seismic related CO₂ exsolution from a depressed water table during glacial stages. Ages obtained for Turkish travertines by Özkul et al. (2013) and Toker et al. (2015) show that deposition was active during glacial and interglacial time, indicating that travertine precipita tion during late Quaternary was not strongly influenced by climatic var iation. In particular, we found similarities with Toker et al. (2015) whose recognized that the highest amount of travertine precipitation in Kocabas (Denizli basin, Turkey) occurred during MIS 5 (interglacial) and proposed that active fault systems favored the rise of hydrothermal fluids and travertine deposition. Finally, our results for the Semproniano giant vein suggest that high stand of the water table was a primary influencing factor in the vein formation.

4.6. Relationships between the giant vein and nearby travertine deposits: the fluid circuit

The Poggio Semproniano and Poggio i Piani travertine plateaus constitute the largest travertine deposits in the Semproniano area (Fig. 3a). Although the dataset for these deposits is smaller than that of the giant vein, the C and O isotope values are comparable (Fig. 8b), showing that the hydrothermal parental fluids were very similar. The Sr , Nd isotopes, and REE data (Table 4 and Fig. 9) confirm that the parental fluid circuit and reservoir was mainly the Mesozoic limestones of the Albenga basin.

U/Th ages for the bedded travertine samples from the plateaus (171 ± 14 ka for Poggio Semproniano, 198 ± 18 ka for Poggio i Piani; Table 2) indicate that the formation of the two plateaus was at least in part contemporaneous with that of the Semproniano giant vein. More over, also the activity of the nearby Mt Amiata volcanic district (300 190 ka, Cadoux and Pinti, 2008; 300 225 ka, Laurenzi et al., 2015) was partly contemporaneous with the CaCO₃ mineralizations of the Semproniano area, with the giant vein being partly older and partly younger than the volcanic district.

From previous studies we know that while fissure ridges such as the Semproniano giant vein are aggradational systems that tend to grow vertically due to the scarcity of feeding fluids (i.e., CaCO₃ precipitates contributing to the vertical grow of the deposit), travertine plateaus are progradational systems where the abundance of feeding fluids contribute to the horizontal grow (progradation) of the deposit (Faccenna et al., 2008; De Filippis et al., 2013a). We also know that fissure ridges and plateaus can coexist, in space and time, in geothermal areas where the abundance of geothermal fluids primarily feeds the plateau whereas the fissure ridge(s) constitutes a remote apophysis of the plateau with a scarcity of fluids that provokes the aggradation develop ment of the fissure ridge (e.g., Tivoli travertines; De Filippis et al., 2013b).

The possible scenario for the genesis of the Semproniano giant travertine vein is a structurally controlled pathway (faults and fractures) for the circulating mineralizing fluids during the Quaternary. Dominant meteoric fluids interacted with the carbonate reservoir of the Mt Amiata volcano and were heated at depth, where the heat source is maintained by the regional geothermal anomaly (Fig. 12a). In this scenario, the Semproniano giant vein grew in correspondence of an epithermal fluid discharge area induced by CO₂ enriched heated convective groundwater (Fig. 12b). In particular, we can assume a fluid pressure cy cling in a long lived fault valve behavior setting (Cox et al., 2001; Sibson, 2004; Cox, 2010) assisted by fracture network generation and maintenance that could have been provided by the strike slip tectonics active during Quaternary time in the Mt Amiata and Albenga basin regions (Zanchi and Tozzi, 1987; Brogi, 2004b; Bellani et al., 2004; Brogi and Fabbrini, 2009; this study). In this model, the Semproniano giant vein (i.e., the fissure ridge) is interpreted as an apophysis of a large hydrothermal field characterized by the deposition of big travertine plateaus. As sealing of fracture enhanced secondary permeability tends to occur over time when hydrothermal fluids flow through the fractured media (e.g., Curewitz and Karson, 1997), prolonged hydrothermal circulation, as is the case for the Semproniano giant vein, can be maintained only when faulting and fracturing are persistent through time, thus opening new conduits that favour fluid flow (e.g., Rihs et al., 2000; Sibson, 2004; Brogi et al., 2012; Nishikawa et al., 2012). It follows that the depositional and mineralization history of travertine systems may reveal much on the age of Quaternary tectonics in the southern Tuscan region.

5. Conclusions

(1) The thickest continuous vein hitherto documented in the literature (≥50 m) is found and studied within a fissure ridge.
Fig. 12. (a) Schematic 3D-block diagram interpreting the hydrothermal setting in the Mt Amiata-Semproniano area. Active faulting and related fracturation have primary role in controlling meteoric percolation within the carbonate reservoir at depth, and the uprise of hydrothermal fluids. (b) Two-step scenario illustrating the mode of travertine deposition (by veining at Semproniano fissure ridge and by dominant progradation at the Poggio Semproniano plateau) supplied by hydrothermal fluid discharge at the fault/fracture tips. The fault architecture is indicative.

travertine exposed in the Semproniano village, to the south of the active Mt Amiata geothermal area in southern Tuscany, Italy.

(2) The thickness of the Semproniano vein is the likely consequence of its shallow emplacement and of the unusual longevity of the hydrothermal feeding system, spanning between at least 650 and 85 ka.

(3) The epithermal fluid supply feeding the Semproniano giant vein is not directly connected with the main volcanic activity of the Pleistocene Mt Amiata volcano (which is younger than the early growth of the vein). Rather, it was likely connected with the positive geothermal anomaly associated with its pre eruptive stages (Cadoux and Pinti, 2009).

(4) Geochemical and isotope signatures of the travertine suggest that the hydrothermal fluids responsible for the travertine precipitation derived from a confined reservoir mainly located in the Mesozoic limestones, which resulted impervious to most fluid inputs from the adjacent Mt Amiata volcanic area.

(5) The hydrothermal circuit was assisted by structurally controlled fluid pathways, which maintained active convection and the supply of CO₂ enriched meteoric fluids.

(6) The growth of the Semproniano giant vein was probably also modulated by Pleistocene climate oscillations, with warm humid interglacial periods being the preferential phases of vein accretion due to high fluid discharge.

(7) Structures such as the Semproniano giant vein can be used to estimate the long term release of CO₂ from geothermal/volcanic provinces, thus improving our knowledge of the CO₂ cycle on Earth.

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Appendix A. Geochemical methods

A.1. U/Th dating

As reported in Tables 2 and S1, we performed U/Th dating analyses using two different methods, namely (1) through a spectrometry performed at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University (Italy), or (2) through a Thermo Electron Neptune multi collector inductively coupled mass spectrometer (MC ICP MS) (Shen et al., 2012) hosted at the High Precision Mass Spectrometry and Environment Change Laboratory (HISPEC) of the National Taiwan University, Taipei (Taiwan ROC).

For MC ICP MS dating, we covered about 0.05 g of each sample with H₂O₂ and dissolved it gradually with double distilled 14 N HNO₃. After dissolution, we added a 229 Th–234 U spike (Shen et al., 2003) to the sample, followed by 10–20 drops of HClO₄ to clear the organic matter. We then followed the chemical procedure described in Shen et al. (2003) for the separation of uranium and thorium. We calculated the age correction using an estimated atomic 230Th/232Th ratio of 4 ± 2 ppm. These latter values are the ones typical for a material at secular equilibrium with the crustal 232Th/238U value of 3.8. We arbitrarily assumed a 50% error.

For α spectrometry dating, we dissolved about 60 g of each sample in 7 N HNO₃ and filtered the solution to separate the leachates from the insoluble residue. We heated the leachate at 200 °C after adding a few milliliters of hydrogen peroxide to clear the organic matter, and then spiked the solution with a 228Th–232U tracer. We extracted the isotopic complexes of U and Th following the procedure described in Edwards et al. (1988) and then analyzed the solution by an alpha counted using high resolution ion implanted Ortec silicon surface barrier detectors. Due to the presence of non radiogenic 230Th related to detrital 238Th, ages obtained for samples with a 230Th/232Th activity ratio less than or equal to 80 required a proper correction, which we performed assuming that all the detrital Th had an average 230Th/232Th activity ratio of 0.85 ± 0.36 (Wedepohl, 1995), which is the crustal thorium mean composition. We then calculated the ages using ISOPLOT, a plotting and regression program for radiogenic isotope data (Ludwig, 2003).

A.2. C and O isotope determination

The isotopic composition of carbonate was measured according to the method described in detail in Breitenbach and Bernasconi (2011). Briefly, approximately 100 μg of powder were filled in 12 ml Exetainers (Labco, High Wycombe, UK) and flushed with pure Helium. The samples
were reacted with 3 5 drops of 100% phosphoric acid at 70 °C with a ThermoFisher GasBench device connected to a ThermoFisher Delta V mass spectrometer. The average long term reproducibility of the measurement was ± 0.05% for δ13C and ± 0.06% for δ18O. The instrument is calibrated with the international standards NBS19 (δ13C = 1.95 and δ18O = −2.2%) and NBS18 (δ13C = −2.51 and δ18O = 23.01%). The isotope values are reported in the conventional delta notation with respect to VPDB (Vienna Pee Dee Belemnite).

A.3. Thermometry of mineralizing parental fluids from O isotopes

We calculated the paleo temperature of mineralizing parental fluids using the equation of Kele et al. (2015) specifically developed for travertine parental fluids and calibrated through clumped isotope thermometry. This empirical equation is expressed as:

\[ T = \frac{T_{water}}{(1 + C_{calcite} \times 100)} \times (36 ± 7) \]

where \( C_{calcite} = \frac{\delta^{18}O_{calcite} - 1000}{\delta^{18}O_{water} - 1000} \)

\( T \) is the temperature of the mineralizing CaCO3-rich fluids expressed in K and \( \delta^{18}O_{calcite} \) and \( \delta^{18}O_{water} \) are expressed in parts ‰ relative to SMOW. As benchmark, we measured and used the present \( \delta^{18}O \) isotopic value from the Saturna spring hydrothermal waters (−6.4% SMOW), whose active source is located 9 km to the south of the Semproniano giant vein. We assumed that the oxygen isotope composition of the palaesprings was similar to those of the current springs.

A.4. Sr and Nd isotope and REE determination

We determined the strontium (Sr) and neodymium (Nd) isotope ratios as well as strontium, rare earth elements (REE) and yttrium (Y) concentrations on fragments of handpicked travertine and vein samples. We crushed the chips of travertine in a stainless steel mortor and then dissolved about 200 mg of each sample with ultrapure HNO3 (3%). After dissolution, the residue was separated by filtration and then evaporated to dryness. Residuals were lastly dissolved with 1 M HNO3. We splitted 100 ml of solution from each sample into two aliquots. We used one of the two aliquots for REE, Y, and Sr concentrations and the other aliquot for Sr and Nd isotopes. The aliquot for REE, Y, and Sr concentration were analyzed via ICP MS (Agilent mod. 7500ce) equipped with collision cell at the Chemical Laboratory of Istituto di Chimica Agraria ed Ambientale, Catholic University of Piacenza and Cremona (Italy). In this laboratory, the analytical precision is verified by replicate measurements (three injections of a single sample). In our analyses, the RSDs values result always below 10% for microelements. Analytical precision and trueness were checked by using Certified Reference Material. We evaporated the aliquot for isolate analysis, converted it into chloride form, and loaded it onto standard Bio Rad AG50W X12 cation exchange resin to separate Sr from matrix. The very low REE and Y (REY) contents in travertine required the procedure of Sharma and Wasserburg (1996): we added ultrapure NH3 to the solution diluted with MilliQ water up to ionic strength of about 1.0 to shift pH to 9.0 for precipitating REY with Fe oxide hydroxides. We then mixed both the precipitate and the supernatant with a vortex overnight and separated from each other by filtration. We dissolved the oxide hydroxides with 4 M HCl and separated them from the matrix via ion exchange chromatography. We separated Nd from the other REE with Ln Spec resin (Triskem international) following the procedure of Pin and Zalduegui (1997).

We carried out the isotopic analyses at Istituto di Geologia Ambientale e Geogeoingegneria Consiglio Nazionale delle Ricerche (IGAG CNR) laboratory c/o Dipartimento di Scienze della Terra, Sapienza University of Rome (Italy) using a FINNIGAN MAT 282R PQ multicollector mass spectrometer. We loaded all samples on a Re double filament as nitrate and analyzed them in static mode. We normalized Sr analyses to 87Sr/86Sr = 0.1194. We fixed Sr analytical blank at 1 ng. In internal precision (“within run” precision) of a single analytical result is given as two standard error of the mean (2σe) and is obtained as a mean of more than 200 ratios collected on each sample with a stable beam of 2.0 V.

Repeated analyses of NIST 987 during the period of the analyses gave a mean value of 87Sr/86Sr = 0.710235 ± 9 (n = 20) and La Jolla 143Nd/144Nd = 0.511851 ± 0.000007 (n = 20), 146Nd/144Nd normalized to 0.7219. Total procedural blanks were below 2 ng of Sr and 1 ng of Nd for all the samples. The measured 143Nd/144Nd ratios are presented as fractional deviation in parts in 10^5 (%) units from 143Nd/144Nd in a Chondritic Uniform Reservoir (CHUR) as measured today:

\[ \frac{143Nd}{144Nd}_{\text{sample}} = \frac{143Nd}{144Nd}_{\text{CHUR}} \times \left( \frac{143Nd}{144Nd}_{\text{sample}} - 1 \right) \times 10^4 \]  

where \( 143Nd/144Nd_{\text{sample}} \) is the ratio measured in the sample today and \( 143Nd/144Nd_{\text{CHUR}} \) is the ratio in the reference reservoir today, i.e. 0.518847 (DePaolo and Wasserburg, 1976).

A.5. Fluid inclusion analysis

We performed microthermometric measurements at Istituto di Geologia Ambientale e Geogeoingegneria Consiglio nazionale delle Ricerche (IGAG CNR) Fluid Inclusion Laboratory c/o Dipartimento di Scienze della Terra, Sapienza University of Rome (Italy), using a freezing heating stage Linkam THMS 600 (from −196 to +600 °C). The stage is adapted to a Nikon Optiphot Pol transmitted light microscope equipped with long working distance objectives (5×, 10×, 20×, 40×) and a video camera. We performed the analysis of fluid inclusions on a 150 μm thick double polished slice of calcite vein (Fig. 10). Due to the physical properties of calcite minerals, we took particular care in maintaining as low as possible the temperature during grinding, polishing, and, in general, during all the sample preparation (Goldstein and Reynolds, 1994; Bodnar, 2003). A low temperature sample prepa ration is fundamental to avoid phenomena of stretching and decrepitation of the inclusions, which may affect the microthermometric measurements. In those fluid inclusions where decrepitation and stretching phenomena due to the volume expansion during ice forma tion (Bodnar, 2003) were visible, we performed Tm_rec measurements separately from TH measurements. Salinity contents (expressed in wt.% NaCl eq.) of fluid inclusions has been calculated through the Tm_rec values using the equation proposed by Bodnar and Vityk (1994). Data reproducibility is of ±0.2 °C for cooling runs and of ±1 °C for heating runs.

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