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Growth of a Pleistocene giant carbonate vein and nearby thermogene travertine deposits at Semproniano, southern Tuscany, Italy: Estimate of CO2leakage

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Abstract

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 volcano-tectonic domain; (2) implications in terms of the CO_2 release; and (3) possible relationships with Quaternary paleoclimate 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 order of 10^{-2} and 10^{-3} mm/a. The giant vein developed mainly during warm humid (interglacial) periods, partially overlapping with the growth of nearby travertine plateaus. Estimated values of CO_2 leakage connected with the vein precipitation are between about $5x10^6$ and $3x10^7$ mol a^{-1} km^{-2}, approximately representing one millionth of the present global CO_2 leakage from volcanic areas. Temperatures estimates as 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 have developed 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.

Keywords: travertine, vein, CO_2 leakage, hydrothermalism, REE, C- O- Sr- Nd- isotopes, Quaternary climate, Tuscany.

Highlights

- Modes and rates for the growth of giant vein in fissure ridge travertines
- Geochemistry and geochronology of CaCO3 mineralizations.
- CO_2 leakage in hydrothermal areas.
- Feedbacks between neotectonics, hydrothermalism and paleoclimate oscillations

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

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Abstract

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 volcano-tectonic domain; (2) implications in terms of the CO_2 release; and (3) possible relationships with Quaternary paleoclimate 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 order of 10^{-2} and 10^{-3} mm/a. The giant vein developed mainly during warm humid (interglacial) periods, partially overlapping with the growth of nearby travertine plateaus. Estimated values of CO_2 leakage connected with the vein precipitation are between about $5x10^6$ and $3x10^7$ mol a^{-1} km^{-2}, approximately representing one millionth of the present global CO_2 leakage from volcanic areas. Temperatures estimates as 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 have developed 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.

Keywords: travertine, vein, CO_2 leakage, hydrothermalism, REE, C- O- Sr- Nd- isotopes, Quaternary climate, Tuscany.

1. Introduction

Thermogene travertines form through precipitation of $CaCO_3$ 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; Crossey et al., 2006). In addition to 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 CO_2 storages (Shipton et al., 2004; Bickle and Kampman, 2013; Burnside et al., 2013; Frery 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).

Travertines can show various deposit morphologies such as cascades, terrace mounds, fissure ridges, plateaus, and towers (Chafetz and Folk, 1984; Altunel and Hancock, 1993a, b; Pentecost, 1995; Pentecost, 2005). These morphologies are only partially dependent on the topography over which the travertines precipitate. Other factors such as (neo)tectonics (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 (Priewisch et al., 2014; Crossey et al., 2015) have been proposed to influence travertine growth and morphology; however, the way how 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 plateaus, which can, nonetheless, form in 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 (Chafetz and Folk 1984; Altunel and Hancock, 1993a,b, 1996; Çakır, 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 banded travertine, which consists of subvertical bands of sparry nonporous carbonate (usually calcite, aragonite, or both) filling large veins that intrude 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 large deposits consisting of sub-horizontal 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).

Tuscany (Fig. 1), central Italy, is a region characterized by Neogene-Quaternary formation of extensional basins, widespread magmatism, associated contact metamorphism, hydrothermalism and 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). 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 CO_2 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 Albegna basin), which is built on top of a hill at an altitude of 620 m. Semproniano is located only about 15 km southward of the Mt Amiata Pleistocene volcanic district and 9 km from the Saturnia thermal spring (Figs. 1 and 2), where active travertine deposition still occurs. The Semproniano village lies on a travertine fissure ridge, a composite carbonate vein (≥50-m-thick) consisting of subvertical banded travertine (Capezzuoli et al., 2013), 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.) as well. 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 $CaCO_3$-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 those carbonates deposits. Using a multidisciplinary approach consisting of geological, structural, geomorphologic, and geochemical methods (including fieldwork, remote observations, U/Th dating, C- Nd- O- and Sr-isotope systematics, rare Earth element (REE) abundances, and fluid inclusion microthermometry), 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 tectonics, volcanisms, and paleoclimate. The main novelty of this work concerns growth modes and rates of the Semproniano fissure ridge and implications for the associated CO_2 leakage. In addition, our results provide insights at regional scale concerning the late Quaternary hydrothermal and tectonic activity of southern Tuscany.

2. Geological setting

Southern Tuscany is located in the inner sector (western) side of the northern Apennine chain (Fig. 1), which is a Cenozoic NW-SE-trending 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 and collapse of the previously formed orogenic belt started in late Miocene time, while, toward the east, the belt was still under a compressional regime (e.g., Malinverno & Ryan, 1986; Dewey 1988; Jolivet et al., 1998; Cavinato and De Celles, 1999; Pauselli et al., 2006). 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) and produced significant crustal thinning (present-day crust thickness is about 22-24 km; Locardi and Nicolich, 1988; Billi et al., 2006) as well as the development of sedimentary basins, magmatic provinces, and diffuse volcanism (Serri et al., 1993; Serri, 1997; Peccerillo, 2003). Fossil and active, structurally-controlled hydrothermal mineralizations are widespread evidence of the interaction between hydrothermal systems and extensional faults (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; Annunziatellis et al., 2008; Brogi, 2008; Liotta et al., 2010; Rossetti et al., 2011; Vignaroli et al., 2014).

Southern Tuscany (Fig. 1) is characterized by main NW-SE-trending and minor NE-SW-trending Miocene-to-Quaternary sedimentary basins 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; Marroni et al., 2015). These structures include the Tevere-Paglia, Siena-Radicofani, and Albegna basins. The Semproniano thick vein and surrounding travertine deposits are located in the Albegna basin, which consists of a NE-SW-trending tectonic depression bounded to the north and southeast by the volcanic districts of the Mt Amiata and Vulsini Mts, respectively (Fig. 1). The magmatic activity (or part of it) of the Mt Amiata district is dated to 300-190 ka according to Cadoux and Pinti (2009) and to 300-225 ka according to Laurenzi et al. (2015), whereas the activity (or part of it) of the Vulsini Mts district is dated to 590-127 ka according to Nappi et al. (1995).

The geological setting of the Albegna basin is characterized by the presence of 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 by basal evaporites followed by shelf carbonates and marls (Tuscan Nappe); (3) Jurassic to Eocene ophiolite-derived clays and marls succession (Ligurian Domain); and (4) Upper Miocene to Pleistocene terrigenous post-orogenic deposits. The latter consist of fluvio-lacustrine deposits and marine clays that deposited in subsiding areas concomitantly with the regional tectonic extension (Zanchi and Tozzi, 1987; Bonazzi et al., 1992; Bossio 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). 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. In particular, Bosi et al. (1996) suggested that the travertines of the Semproniano area deposited during Pliocene time, whereas other authors considered them 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 relationships 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) I Vignacci, (3) Poggio Semproniano, and (4) Poggio i Piani deposits (Figs. 2-5). 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 Apennine 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, unconfomably lie over Pliocene-Quaternary deposits and over the Scaglia Toscana Fmt. of the underlying Tuscan Nappe (Fig. 4a) which host the Semproniano fissure ridge (Fig. 2). The Poggio Semproniano deposit occupies the top portion of a triangular hill that is almost 700 m 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 alluvial and eluvial deposits. The travertine body has dimensions of around 1300 m in the NW-SE direction and 700 m in the N-S direction, and has a maximum vertical thickness 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 cm-thick subvertical veins striking NW-SE, 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 maximum elevation around 630 m. 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 (Figs. 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 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 (Fig. 3). The Semproniano ridge crops out from the top of a NW-SE-elongate domed hill with maximum altitude around 620 m a.s.l. and about 1000 m long and 400 m wide. 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-shaped (Fig. 5e) or crosscutting carbonate bands that are up to about 2 cm thick. The sparry subvertical bands of carbonate form a unique, composite and uninterrupted vein that we call the Semproniano giant vein for its large thickness of more than 50 m. 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 5i). 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 Fmt. (Fig. 5j, k), which is the host rock of the giant vein travertine (Fig. 2).

The I Vignacci deposit crops out about 800 m to the northwest of the Semproniano ridge, exactly along the NW-SE prolongation of the Semproniano hill and ridge (Figs. 2 and 3). I Vignacci travertine is located at an altitude of about 430 m a.s.l., the lowest reached of the studied travertines. I Vignacci travertine deposit is small and it is characterized by banded travertine with subvertical NW-SE-striking bands. These bands cut through the surrounding sub-horizontal beds of the Scaglia Toscana Fmt. 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 ca. E-W and one striking N-S (Figs. 2 and 6). In particular, we recognized that the E-W-striking fault system cuts through the northern portion of the Poggio Semproniano travertine plateau (Fig. 6a). It consists of meter-thick damage zone defined by fault slip surfaces and secondary, subparallel, fracture network (Fig. 6b). A pitch smaller than 15° or greater than 165° have been measured for most slickenlines and abrasive striations occurring on fault planes (Fig. 6c). The kinematic indicators observed on the fault surfaces are mainly represented by synthetic shear fractures within the damage zone (Riedel shear planes) and they are consistent with right-lateral strike-slip movements. The N-S-striking fault system passes along the valley that separates the Poggio Semproniano and Poggio i Piani travertine deposits (Fig. 2). We identified this set of faults as affecting the travertine deposits of the Semproniano ridge and cut through the banded travertine of the Semproniano fissure ridge (Fig. 6a). Within the ridge, the fault system is characterized by a 0.5 m-thick damage zone and several speleothem-filled fracture networks cutting through the banded travertine (Fig. 6d). When observed, abrasive striations on fault planes show a pitch of about 60-70°. Geometrical relationships between faults and secondary fractures are consistent with an extensional movement (associated to a left-lateral movement) lowering the Poggio Semproniano travertine deposit.

3.2. U/Th geochronology

We dated nineteen samples from the $CaCO_3$ 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 analytical methods (α spectrometry and mass spectrometry) are described in the Appendix.

Banded travertine samples from Semproniano Village (SP1) and I Vignacci (VI1) are characterized by a $^{230}Th/^{234}U$ activity ratio higher than 1 and, therefore, by ages higher than the limit of the U/Th method in α spectrometry (c. 350 ka). The bedded travertine exposed on the south-western flank of the Semproniano giant vein (SP11) is characterized by a moderate detrital contamination ($^{230}Th/^{232}Th$ activity ratio = 7.148 ± 0.251) and by a corrected $^{230}Th/^{234}U$ activity ratio of 0.878 ± 0.051, indicating an age of 214 +50/-37 ka. A subordinate carbonate vein (SP16) cutting through the Scaglia Toscana Fmt. (Tuscan Nappe) in the external south-western flank of the Semproniano giant vein is characterized by a $^{230}Th/^{232}Th$ activity ratio of 12.564 ± 1.987 and by a corrected $^{230}Th/^{234}U$ activity ratio of 0.641 ± 0.064. Calculated age for this sample is 104 ± 16 ka. A bedded travertine sample collected in the southern part of Poggio Semproniano plateau (PO2; Fig. 4b) is characterized by a $^{230}Th/^{234}U$ activity ratio of 0.818 ± 0.039. The resulting age is 171 ± 19 ka. Two samples of calcite-filled veins (SP3 and SP10) cutting through the bedded travertine of Poggio Semproniano and the underlying Scaglia Toscana Fmt. are characterized by a $^{230}Th/^{234}U$ 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 $^{230}Th/^{234}U$ activity ratio of 0.857 ± 0.028 and a resulting age of 198 ± 18 ka.

To understand the spatio-temporal growth of the Semproniano giant banded vein, we dated eleven samples from this vein along a 5m 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 (> c. 800 ka). Radiometric 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. 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). The oldest samples have lager errors caused by proximity to secular equilibrium, whereas the youngest ages are characterized by smaller errors (Table 2).

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

We performed $\delta^{13}C$ and $\delta^{18}O$ 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 $\delta^{13}C$ (between 3.2 and 10.5‰) and negative values of $\delta^{18}O$ (between -14.6 and -7.6‰) (Table 3). Results, in particular, are clustered around 8‰ for $\delta^{13}C$ and around -11‰ for $\delta^{18}O$ (Fig. 8b).

Semproniano Village. Samples of banded travertine from the Semproniano veins are characterized by $\delta^{13}C$ values between 3.2 and 10.5‰ (V-PDB) and by $\delta^{18}O$ values between -14.6 and -7.6‰ (V-PDB). Samples from the associated bedded travertine are characterized by $\delta^{13}C$ values between 5.3 and 9.9‰ (V-PDB) and by $\delta^{18}O$ values between -9.8 and -8.2‰ (V-PDB).

I Vignacci. The sample from the banded travertine of I Vignacci (sample VI1) is characterized by a $\delta^{13}C$ of 3.7‰ (V-PDB) and a $\delta^{18}O$ of -9.6‰ (V-PDB).

Poggio Semproniano. Samples of bedded travertine from Poggio Semproniano are characterized by values of $\delta^{13}C$ between 5.7 and 7.1‰ (V-PDB) and values of $\delta^{18}O$ between -11.4 and -8.1‰ (V-PDB). Calcite-filled veins pervading the bedded travertine and the underlying underlying Scaglia Toscana Fmt. (Samples SP3, SP10) at the bottom of the Poggio Semproniano travertine plateau are characterized by $\delta^{13}C$ values between 7.1 and 8.4‰ (V-PDB) and $\delta^{18}O$ values between -11.5 and -10.7‰ (V-PDB).

Poggio i Piani. One sample from the bedded travertine (sample PP1) of Poggio i Piani is characterized by a $\delta^{13}C$ of 6.5‰ (V-PDB) and a $\delta^{18}O$ of -11.6‰ (V-PDB).

We focused particular attention to the Semproniano giant vein by collecting two transects across it (samples SP14/03 to SP14/04 and SP14/08 to SP14/34) and three further samples in the adjacent bedded travertine (samples SP11, SP14/05, SP14/06) (Table 3). Banded travertines collected along the two transects show a wide variability. Samples from the first transect (samples SP14/03 to SP14/16), in particular, are characterized by $\delta^{13}C$ values comprised between 5.3 and 9.7‰ (and $\delta^{18}O$ values comprised between -12.8 and -9.0‰. Samples from the second transect (samples SP14/17 to SP14/34) are characterized by $\delta^{13}C$ values comprised between 3.2 and 10.2‰ and $\delta^{18}O$ values comprised between -12.6 and -7.6‰. Samples from the bedded travertine located along the flanks of the Semproniano giant vein are characterized by $\delta^{13}C$ values comprised between 5.3 and 9.9‰ and $\delta^{18}O$ values comprised between -9.8 and -8.2 ‰. Samples from the two transects don't show any pattern in O and C isotopic values along the Semproniano giant vein.

We calculated the paleo-temperature of the mineralizing parental fluids applying the equation of Kele et al. (2015) to the entire $\delta^{18}O$ dataset (Table 3 and Fig. 8c) and using the present $\delta^{18}O$ of the the Saturnia spring hydrothermal waters (-6.4‰ V-SMOW), whose active source is located 9 km to the south of the Semproniano giant vein. We assume that the oxygen isotope composition of the palaeosprings 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 comprised between 45 and 60 °C. The bedded travertines associated with the giant vein give temperatures between 35 ± 2 and 43 ± 3 °C, whereas the banded travertine sample from I Vignacci sample yields a temperature of 42 ± 3°C. The Poggio Semproniano plateau samples yield temperatures of 36 ± 2 and 53 ± 5 °C, for the bedded travertine, and 49 ± 4 and 53 ± 5 °C, for the calcite veins. The bedded travertine from Poggio I Piani a temperature of 53 ± 5 °C. There is no correlation scheme 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 Yttrium (Y; REE + Yttrium = REY) concentration analysis, and Strontium and Neodymium isotope measurements to understand the subsurface circuit of hydrothermal fluids (e.g., Ederfield and Greaves, 1982; McLennan, 1989; Webb et al., 2000; Uysal et al., 2007; 2009). The analytical procedures and protocols are detailed in the Appendix; results are reported in Tables 4 and S2 and Fig. 9.

We observed a variable Sr concentration, comprised between 105.3 to 4956.3 mg/kg. The mean value (3200 mg/kg) is in the range of Sr contents of most travertines in central Italy (Minissale, 2004). Sr-isotope ratios range from 0.708277 to 0.708527. The banded travertine from the Semproniano giant vein (SP12, SP14/18 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, SP17) and the bedded travertines from Poggio Semproniano (SP9, PO1, PO2) are have the lowest Sr concentrations, between 105.3 and 787.3 mg/kg.

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) show values comprised in a narrow range between 0.512253 and 0.512330 (Table 4).

We determined REY concentrations of the banded travertine from the Semproniano giant vein (SP14/18), of the bedded travertine sample from the flanks of the Semproniano giant vein (SP14/06),of the banded travertine sample from I Vignacci (VI1) of the bedded travertine sample

(PO1) and of calcite vein (SP3) from Poggio Semproniano. We normalized the REY concentrations against PAAS (Post-Archean Austrian Shale; McLennan, 1989; Fig. 9 and Table S2). 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 = 0.1-0.71, 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; (v) consistent negative Ce anomaly (Ce/Ce* = 0.30-0.94; Table S2).

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 travertines are rare (Słowakiewicz 2003; Gibert et al., 2009; El Desouky et al., 2015; Raimondi 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 failing in bubble nucleation upon cooling from the trapping conditions to room temperature (Diamond, 2003); and (3) inclusion anelastic stretching and decrepitation that can cause difficulties in performing microthermometric analyses; (4) double refraction of calcite (Bodnar, 2003).

Unfortunately only one sample contained fluid inclusions suited for microthermometry (Fig. 10a). It 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 structures (Figs. 10b-10d). 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 (Figs. 10c and 10d) and (2) polygonal (Fig. 10b).

As it is shown in Fig 10(f), Tm_{ice} values (i.e., the temperature of ice melting from which salinity is deduced) range between 0.0 and +4.8 °C, but are mostly concentrated around 0-1 °C. Being very small systems, fluid inclusions may exhibit metastable behaviour and metastable ice crystals can persist at temperatures as high as +6,5°C (Roedder, 1967) (Fig. 10f). From these data we can conclude that the fluid consists of pure water. Homogenization temperature (Th) values range between 57 and 105°C, with a maximum around 70-90 °C (Fig. 9g). 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. Our microthermometric results (Fig. 10e) are consistent with the ones obtained by Capezzuoli et al. (2013), who obtained temperatures between 65 and 95 °C and 0.2 wt% NaCl eq.

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 suggest that the Semproniano giant vein represent 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 Semproniano case, although we have no record on the amount of eroded bedded travertine over time (since about 650 ka), the ridge seems to be characterized by a 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 larger than any one we found in the published literature. Thus 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 instance, 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 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 Yilmaz 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).

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 around can be estimated to be 8 x 10^{-2} 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). With distance between the dated samples in each sector and the age difference, we obtain average growth (i.e., thickening) rates of about 7 x 10^{-3}, 2 x 10^{-2}, and 6 x 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 ca. 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^{-2} mm/a; Uysal et al., 2007; Mesci et al., 2008; Gratier et al., 2012; De Filippis e al., 2013a; Frery et a., 2015). This result confirm 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 syntaxial 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 it grew asymmetrically and ataxially (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-seals pulses, which is well supported by the U/Th ages. This growth mode for the Semproniano giant vein 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 diffused fractures within the bedded travertine. The Semproniano giant vein, in fact, defines a singular structure that grew within the same horst 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 $\delta^{13}C$ and negative $\delta^{18}O$ values (Table 3, Fig. 7b), indicating mixing between hydrothermal parental fluids and meteoric waters and with a significant contribution of CO_2 originating from limestone decarbonation (Gonfiantini et al., 1968; Guo et al., 1996: Billi et al., 2007). 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).

$\delta^{13}C$ values of travertines have been used to determinate the original signal of $\delta^{13}C_{CO2}$ 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 $\delta^{13}C_{CO2}$ values are comprised between -6.7 and 2.1 ‰ (V-PDB), while according to the equation of Bottinga (1968), the $\delta^{13}C_{CO2}$ values are comprised between -5.4 and 3.5 ‰ (V-PDB). Those results confirm a mixing between CO_2 originated from limestone decarbonation with CO_2 of igneous origin (e.g. Turi, 1986; Minissale, 2004; Kele et al., 2011).

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 Semproniano 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. 10). This 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 was constituted by almost pure water.

The lack of correlation between ages and precipitation temperatures in the giant vein (Fig. 8d), indicate no systematic and linear cooling of hydrothermal parental fluids with time. This differ from the study of Rimondi et al. (2015), on the Pleistocene Castelnuovo dell'Abate travertines on the northern flank of the Mt. Amiata volcano which showed a cooling of the hydrothermal fluid of about 70 °C in 300-400 ka. Therefore, while the Castelnuovo dell'Abate travertines were strictly and directly connected with the Mt. Amiata geothermal anomaly, the Semproniano system, which is located about 20 km to the south, was influenced not only by the Mt. Amiata geothermal anomaly, but also by further paleoenvironmental and/or paleoclimate factors (see below).

The Sr- and Nd-isotopes as well as the REE patterns help to characterize the origin of the hydrothermal fluids. 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 obtained for the Mesozoic sedimentary units of central Italy (e.g., Barbieri et al., 1979; Cortecci and Lupi, 1994; Barbieri and Morotti, 2003; Gasparrini et al., 2013) and for the hydrothermal springs of Saturnia (Barbagli et al., 2013). This 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). Accordingly, we consider the Mesozoic limestones of the Albegna 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 endogeneous fluids (e.g., Crossey et al., 2009).

4.4. Estimation of CO_2 outflow

Minimum value of total CO_2 volume leaked during the formation of the Semproniano giant vein can be estimated from the volume of $CaCO_3$ precipitated (Crossey et al., 2009; Frery, 2012; Karlstrom, 2013). It has been shown that the volume of leaked CO_2 precipitated in travertine/vein deposits is only a minor part of the total leakage, representing between 6.6% and 10% (Shipton et al., 2005) of the total dissolved CO_2. According to Frery (2012), it is possible to calculate only the minimum value of CO_2 leakage during $CaCO_3$ vein formation for two reasons: (i) the proportion between precipitated CO_2 and total leaked CO_2 includes only the dissolved part of the CO_2 at the surface, thus disregarding the CO_2 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 $CaCO_3$ veins, the total mass of precipitated CO_2 ($m_{CO2}^{precipitated}$) can be calculated using the calcium carbonate precipitation equation:

$$m_{CO2}^{precipitated} = \rho_{CaCO3} \cdot V_{CaCO3} \{M_{CO2} | M_{CaCO3}\} \qquad \text{(Eq. 1)}$$

where ρ_{CaCO3} and$\{M_{CO2} | M_{CaCO3}\}$ are considered as constant parameters: ρ_{CaCO3}= $2.7{\cdot}10^3$ kg/m^3; M_{CO2} = 44g/mol, and M_{CaCO3} = 100.1 g/mol.

Based on field observations, we estimate the volume of the Semproniano giant vein assuming a length of 500 m and a width of 50 m. for the thickness of the vein, we consider two alternative end members: 10 m (the observable vein exposed in the field), and 50 m (estimated through geological cross-sectioning; Fig. 2b). For a thickness of 10 m, the estimated total mass of CO_2 leakage are 3 x 10^6 and 5 x 10^6 tons, for total dissolved CO_2 masses of 10 and 6.6%, respectively. For a depth of 50 m 14 x 10^6 and 22 x 10^6 tons are calculated. Collectively, all these values provide a CO_2 leakage between 5 ton/a and 37 tons/a over the 600 ka longevity of the Semproniano giant vein, corresponding to a CO_2 flux between 5 x 10^6 mol a^{-1} km^{-2} and 3 x 10^7 mol a^{-1} km^{-2}. These estimates are of the same order of magnitude of measured average CO_2 flux discharged by present-day thermal springs in central Italy (between 1 × 10^4 mol a^{-1} km^{-2} and 5×10^7 mol a^{-1} km^{-2}, Minissale, 2004; Frondini et al., 2008) and it is two order of magnitude lower than the CO_2 flux (3.7 × 10^9 mol a^{-1}) in present-day thermal springs on the Colorado Plateau, USA (Crossey et al., 2009). For comparison, the estimated CO_2 flux during the formation of the Semproniano giant vein is about four order of magnitude lower than the deeply sourced (endogenic) CO_2 in non-volcanic areas of Italy (10^{11} mol a^{-1}, Rogie et al., 2000) and represent about one millionth of the present-day CO_2 released from volcanic areas at the global scale (Gerlach, 2011).

4.5. Paleoclimate influence

To determine a possible influence of paleoclimate on the growth of the Sempronaino giant vein, in Fig. 11 we matched our U/Th 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, except for two points, most samples from the giant vein fall within the inter-glacial 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).

The darting, thus suggests that the Sempronaino giant vein formed preferentially during warm and humid climate periods characterized by high stands of the water table promoting a greater 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) for banded travertines precipitated in co-seismic fissures of the Denizli basin (Turkey) which was based on U/Th ages and REE data. These authors, proposed that carbonate precipitation was controlled by seismic-related CO_2 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 precipitation during late Quaternary was not strongly influenced by climatic variation. In particular, we found similarities with Toker et al., (2015) whose recognized that the highest amount 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 Sempronian 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 Albegna basin.

U/Th ages for the bedded travertine samples from the plateaus (Table 2), 171 ± 14 ka for Poggio Semproniano, 198 ± 18 ka for Poggio I Piani) indicate that the formation of the two plateaus was at least in part contemporaneous with that of the Semproniano giant vein. Moreover, also the activity of the nearby Mt. Amiata volcanic district (300-190 ka, Cadoux and Pinti, 2009; 300-225 ka, Laurenzi et al., 2015) was partly contemporaneous with the $CaCO_3$ 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., $CaCO_3$ 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 development 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 mineralising 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 resulted as an epithermal fluid discharge area after convective circulation of the CO_2-enriched hydrothermal fluids (Fig. 12b). In particular, we can assume a fluid pressure cycling 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 well-known N-S-striking fault zone system active during Quaternary time in the Mt Amiata-Albegna basin region (Zanchi and Tozzi, 1987; Brogi, 2004b; Bellani et al., 2004; Brogi and Fabbrini, 2009). In this model, the Semproniano giant vein (i.e., the fissure ridge) is interpreted as an apophysis of a large geothermal field characterized by the deposition of big travertine plateaus.

Conclusions

(1) The thickest continuous vein hitherto documented in the literature (50 m) is found and studied within a fissure ridge travertine exposed in the Semproniano village, in the hydrothermal area surrounding the Pleistocene Mt. Amiata volcano in southern Tuscany, Italy.

(2) The thickness of the Semproniano vein is connected with its probable shallow emplacement and with the unusual longevity of the hydrothermal activity 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 paroxysmal activity of the Mt. Amiata volcano (which is younger than the early growth of the vein), rather with the positive geothermal anomaly associated with its pre-eruptive stages (Cadoux et al., 2009) through structurally-controlled fluid pathways which created and maintained active convection and supply of CO_2-enriched meteoric fluids.

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

(6) Structures such as the Semproniano giant vein can be used to estimate the long-term release of CO_2 from geothermal/volcanic provinces, thus improving our knowledge of the CO_2 cycle on Earth.

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Appendix: geochemical methods

U/Th dating

As reported in Tables 2 and S1, we performed U/Th dating analyses using two different methods, namely (1) through α 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 H_2O and dissolved it gradually with double distilled 14 N HNO_3. After dissolution, we added a ^{229}Th-^{233}U-^{236}U spike (Shen et al., 2003) to the sample, followed by 10-20 drops of $HClO_4$ 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 $^{230}Th/^{232}Th$ ratio of 4 ± 2 ppm. These latter values are the ones typical for a material at secular equilibrium with the crustal $^{232}Th/^{238}U$ 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 HNO_3 and filtered the solution to separate the leachates from the insoluble residue. We heated the leachate at 200 °C after adding a few millilitres of hydrogen peroxide to clear the organic matter, and then spiked the solution with a ^{228}Th-^{232}U 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 ^{230}Th related to detrital ^{232}Th, ages obtained for samples with a $^{230}Th/^{232}Th$ activity ratio less than or equal to 80 required a proper correction, which we performed assuming that all the detrital Th had an average $^{230}Th/^{232}Th$ 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).

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 measurements based on replicated standards was ±0.05‰ for $\delta^{13}C$ and ±0.06‰ for $\delta^{18}O$. The instrument is calibrated with the international standards NBS19 ($\delta^{13}C$= 1.95 and $\delta^{18}O$ = -2.2‰) and NBS18 ($\delta^{13}C$= -5.01 and $\delta^{18}O$ = -23.01‰). The isotope values are reported in the conventional delta notation with respect to VPDB (Vienna Pee Dee Belemnite).

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 thermometer. This empirical equation is expressed as:

$$1000\ln \alpha_{(calcite\text{-}water)} = (20 \pm 2)\ 1000/T - (36 \pm 7) \qquad \text{(Eq.3)}$$

Where (1) $\alpha_{(calcite\text{-}water)} = (\delta^{18}O_{calcite} + 1000) / (\delta^{18}O_{water} + 1000)$, (2) T is the temperature of the mineralizing $CaCO_3$-rich fluids expressed in K and (3) $\delta^{18}O_{calcite}$ and $\delta^{18}O_{water}$ are expressed in parts ‰ relative to V-SMOW. As benchmark ($\delta^{18}O_{water}$), we measured and used the present $\delta^{18}O$ isotopic value from the Saturnia spring hydrothermal waters (-6.4‰ V-SMOW), whose active source is located 9 km to the south of the Semproniano giant vein. We assume that the oxygen isotope composition of the palaeosprings was similar to those of the current springs.

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 mortar and then we dissolved about 200 mg of each sample with ultrapure HNO_3 (3%). 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). We evaporated the aliquot for isotope 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 NH_3 to the solution diluted with MilliΩ 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 4M 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 Geoingegneria – Consiglio nazionale delle Ricerche (IGAG-CNR) laboratory c.o. Dipartimento di Scienze della Terra, Sapienza University of Rome (Italy) using a FINNIGAN MAT 262RPQ 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 $^{86}Sr/^{88}Sr = 0.1194$. We fixed Sr analytical blank at 1ng. Internal precision (“within-run” precision) of a single analytical result is given as two standard error of the mean (2se) and is obtained as a mean of more than 200 ratios collected on each sample with a stable bean of 2.0 V.

Repeated analyses of NIST-987 during the period of the analyses gave a mean value of $^{87}Sr/^{86}Sr$ = 0.710235 ± 9 (n = 20) and La Jolla $^{143}Nd/^{144}Nd$ = 0.511851 ± 10 (n=20), $^{146}Nd/^{144}Nd$ normalized to 0.7219. Total procedural blanks were below 2 ng of Sr and 1 ng of Nd for all the samples. The measured $^{143}Nd/^{144}Nd$ ratios are presented as fractional deviation in parts in 10^4 (ε-units) from $^{143}Nd/^{144}Nd$ in a Chondritic Uniform Reservoir (CHUR) as measured today:

$$\varepsilon_{Nd\,(0)} = [(^{143}Nd/^{144}Nd)_{sample} / (^{143}Nd/^{144}Nd)_{CHUR} - 1] \times 10^4 \qquad \text{(Eq.4)}$$

where $(^{143}Nd/^{144}Nd)_{sample}$ is the ratio measured in the sample today and $(^{143}Nd/^{144}Nd)_{CHUR}$ is the ratio in the reference reservoir today, i.e. 0.511847 (DePaolo and Wasserburg, 1976).

Fluid inclusion analysis

We performed microthermometric measurements at Istituto di Geologia Ambientale e Geoingegneria – 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 THMSG600 (from -196 to +600 °C). The stage is adapted to a Nikon Optiphot-Pol transmitted-light microscope equipped with long-working distance objectives (5X, 10X, 20X, and 40X) and a video camera. We performed the analysis of fluid inclusions on a 150 μm thick double-polished slice of calcite vein (Fig. 9). 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 (Goldtsein and Reynolds, 1994; Bodnar, 2003). A low-temperature sample preparation 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 formation (Bodnar, 2003) were visible, we perform Tm_{ice} measurements separately from Th measurements. Salinity contents (expressed in wt% NaCl eq.) of fluid inclusions has been calculated through the Tm_{ice} 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.

Figure Captions

Figure 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, southern Tuscany) is located. **(b)** Geological map of the southern Tuscany and northern Latium regions showing the main geothermal fields and travertine deposits (including fissure ridges).

Figure 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.

Figure 3. (a) Northward panoramic view of the study area with localization of the studied travertine deposits that are differentiated by morphology. **(b)** Northward panoramic view of the Semproniano ridge (i.e., Semproniano giant vein). Tracks of geological cross-sections (Figs. 2b and 6) are also shown.

Figure 4. (a) Southward panoramic view of Poggio i Piani and Poggio Semproniano travertine plateaus. The Poggio i Piani plateau lies on top of the Scaglia Toscana Fmt. (belonging to the non-metamorphic succession of the Tuscan Domain) whereas the Poggio Semproniano plateau lies on top of Plio-Quaternary marine deposits. **(b)** Southern margin of the Poggio Semproniano travertine plateau. **(c)** Sub-horizontal travertine beds forming the Poggio I Piani plateau. **(d)** Detail of a laminated bedded travertine from Poggio I Piani plateau. **(e)** Close-up view of the bedded travertine occurring at Poggio i Piani.

Figure 5. (a) Panoramic view of the Sempronian giant vein and travertine plateau (Poggio Sempronian). **(b)** Attitude of the sparry bands (banded travertine) forming the Sempronian giant vein (NE flank). This exposure is located below the fortress of the Aldobrandeschi family (X century) in the Sempronian village. **(c)** The Sempronian giant vein (banded travertine) is mainly oriented NW-SE and characterized by high dip values (see the stereoplot: Schmidt net, lower hemisphere, showing poles to travertine subvertical bands forming the giant vein). **(d)** Detail from the Sempronian giant vein (banded travertine) with indication of the vein growth. **(e)** The central part of the Sempronian giant vein shows a V-like shape and is characterized by a rhythmic sequence of crystallized subvertical bands of sparry carbonate. Sample SP12, used for fluid inclusion analysis, was collected here. **(f)** Spatial relationships between banded and bedded travertine along the flank of the Sempronian giant vein. **(g)** Sub-horizontal, bedded travertine exposed on the south-western flank of the Sempronian giant vein. **(h)** Sub-horizontal, bedded travertine cut through by bedded parallel travertine veins (Sempronian village). **(i)** Bedded travertine fabric characterized by laminations, shrubs, and karst-dissolution cavities (Sempronian village). **(j)** and **(k)** Travertine veins cutting through carbonate rocks (Tuscan Domain) along the SW flank of the Sempronian giant vein. Cross-cutting relationships between travertine veins show multiple phases of veining.

Figure 6. (a) Panoramic view of the Sempronian-Poggio Sempronian area where the traces of the main fault systems (*ca*. E-W- and N-S-striking) are indicated. The stereoplots (Schmidt net, lower hemisphere) show attitude of the measured structural features. **(b)** The E-W-striking fault system affecting the bedded travertine at Poggio Sempronian is characterized by meter-thick damage zone and narrowly-spaced fault surfaces. **(c)** Fault surfaces are equipped with oblique- to strike-slip striations (pitch is generally higher than 160° or lesser than 20°; see the stereoplot). Right-lateral strike-slip kinematics has been documented for this fault system. **(d)** The N-S-striking fault across the banded travertine of the Sempronian village is defined by a half-meter-thick damage zone and

secondary fracture network. Extensional kinematics (associated to a left-lateral movement) has been documented for this fault system.

Figure 7. (a) Photomosaic (above) and related line drawing (below) of the Semproniano giant vein as it is exposed in the upper part of the Semproniano village. **(b)** Conceptual cross-sectional sketch of the Semproniano giant vein that is made of an uninterrupted swarm of sparry bands (banded travertine). Sample location and related radiometric ages are shown both in (a) and in (b).

Figure 8. (a) Panoramic view (Google Earth image) with localization of the studied travertine deposits (same as Fig. 3a). **(b)** Combined plot of $\delta^{13}C$ (‰ V-PDB) and $\delta^{18}O$ (‰ V-PDB) isotope values derived from samples of bedded and banded travertines and calcite veins (Table 3). **(c)** Plot of calculated temperatures for the parental fluids of the studied travertines and $CaCO_3$ precipitates (Table 3). **(d)** Combined plot of parental fluid temperatures and U/Th ages determined on the same samples.

Figure 9. Post Archean Australian shale (PAAS) – normalized REY pattern (rare Earth elements + Yttrium) for: the Semproniano giant vein (banded travertine); the bedded travertine flanking the giant vein; bedded travertine and calcite vein from Poggio Semproniano; and banded travertine from I Vignacci. For comparison, REE data from the Tuscan Nappe limestone are also shown (data from Möller et al., 2003).

Figure 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 Tm_{ice} (°C) is the temperature of last melting of ice.

Figure 11. Comparison between U/Th ages of bedded travertine, banded travertine, and calcite veins from the study area and major paleoclimate indicators represented by the deep sea oxygen isotope trend (Zachos et al., 2001) and by the pollen dataset from Valle di Castiglione (Tzedakis et al., 2001). Global glacial/interglacial periods are redrawn and modified after Priewish et al (2014).

Figure 12. (a) Schematic 3D-block diagram interpreting the hydrothermal settingin 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.

Table Captions

Table 1. Samples, sampling sites, and laboratory analyses.

Table 2. U/Th Age of travertines sampled in the study area. See 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 α spectrometry at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University, Italy (errors quoted as 1σ).

Table 3. Stable oxygen and carbon isotope composition, and paleotemperature of banded travertine, bedded travertine, and calcite veins from the study area. Isotope compositions are expressed in ‰ against Vienna Pee Dee Belemnite standard (V-PDB) and in ‰ against Vienna Standard Mean Ocean Water (V-SMOW). Temperature of parental fluids derive from $\delta^{18}O$ through the equation of Kele et al. (2015). $\delta^{13}C_{Co2}$* have been calculated using the empirical equation of Panichi and Tongiorgi. (1976). $\delta^{13}C_{Co2}$** have been calculated using the theoretical equation of Bottinga (1968).

Table 4. Strontium, Strontium isotopes and Neodymium isotopes measured on selected samples from travertines of the study area.

Table S1. Uranium isotopic composition and ^{230}Th ages for travertines of Sempronіano Village, Poggio Semproniano, Poggio I Piani and I Vignacci. Samples marked with * were analysed through MC-ICP-MS. Age correction were calculated using an estimated atomic $^{230}Th/^{232}Th$ ratio of 4 ± 2 ppm. Those are the values for a material at secular equilibrium with the crustal $^{232}Th/^{238}U$ value of 3.8. The errors are arbitrarily assumed to be 50%. Samples marked with ** were analysed through alpha spectrometry. The ($^{230}Th/^{234}U$) was corrected using the crustal thorium mean composition. 0.85 ± 0.36 (Wedephol. 1995), for samples with a $^{230}Th/^{232}Th$ activity ratio lower than 80.

Table S2. Concentration or rare earth elements and yttrium for travertine samples of the study area (in μg/kg).

Table 1
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Table 1. Samples, sampling sites, and laboratory analyses.

Sample	Locality	Rock Type	$\delta^{13}C$ (‰ V-PDB)	$\delta^{18}O$ (‰ V-PDB)	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	REE	U/Th
SP1	Semproniano Village	Banded Travertine	X	X				X
SP5	Semproniano Village	Banded Travertine	X	X				
SP6	Semproniano Village	Banded Travertine	X	X				
SP7	Semproniano Village	Banded Travertine	X	X				
SP8	Semproniano Village	Banded Travertine	X	X				
SP11	Semproniano Village	Bedded Travertine	X	X	X			X
SP12*	Semproniano Village	Banded Travertine	X	X	X			X
SP12B	Semproniano Village	Banded Travertine	X	X				
SP15	Semproniano Village	Banded Travertine	X	X				X
SP16	Semproniano Village	Calcite Vein	X	X				X
SP17	Semproniano Village	Bedded Travertine			X			
SP14/03	Semproniano Village	Banded Travertine	X	X				
SP14/04	Semproniano Village	Banded Travertine	X	X				
SP14/05	Semproniano Village	Bedded Travertine	X	X				
SP14/06	Semproniano Village	Bedded Travertine	X	X	X	X	X	
SP14/08	Semproniano Village	Banded Travertine	X	X				
SP14/09	Semproniano Village	Banded Travertine	X	X				
SP14/10	Semproniano Village	Banded Travertine	X	X				
SP14/11	Semproniano Village	Banded Travertine	X	X				
SP14/11B	Semproniano Village	Banded Travertine	X	X				
SP14/12	Semproniano Village	Banded Travertine	X	X				
SP14/13	Semproniano Village	Banded Travertine	X	X				
SP14/14	Semproniano Village	Banded Travertine	X	X				
SP14/15	Semproniano Village	Banded Travertine	X	X				X
SP14/16	Semproniano Village	Banded Travertine	X	X				
SP14/17	Semproniano Village	Banded Travertine	X	X				
SP14/18	Semproniano Village	Banded Travertine	X	X	X		X	X
SP14/19	Semproniano Village	Banded Travertine	X	X				
SP14/20	Semproniano Village	Banded Travertine	X	X				X
SP14/21	Semproniano Village	Banded Travertine	X	X				
SP14/22	Semproniano Village	Banded Travertine	X	X				
SP14/23	Semproniano Village	Banded Travertine	X	X				X
SP14/24	Semproniano Village	Banded Travertine	X	X				
SP14/25	Semproniano Village	Banded Travertine	X	X				X
SP14/26	Semproniano Village	Banded Travertine	X	X				
SP14/27	Semproniano Village	Banded Travertine	X	X				
SP14/28	Semproniano Village	Banded Travertine	X	X	X			X
SP14/29	Semproniano Village	Banded Travertine	X	X				
SP14/30	Semproniano Village	Banded Travertine	X	X				X
SP14/31	Semproniano Village	Banded Travertine	X	X				
SP14/32	Semproniano Village	Banded Travertine	X	X				X
SP14/33	Semproniano Village	Banded Travertine	X	X				
SP14/34	Semproniano Village	Banded Travertine	X	X				X
VI1	I Vignacci	Banded Travertine	X	X	X	X	X	X
SP3	Poggio Semproniano	Calcite Vein	X	X	X	X	X	X
SP9	Poggio Semproniano	Bedded Travertine	X	X	X			
SP10	Poggio Semproniano	Calcite Vein	X	X	X			X
PS1	Poggio Semproniano	Bedded Travertine	X	X				
PS2	Poggio Semproniano	Bedded Travertine	X	X				
PS3	Poggio Semproniano	Bedded Travertine	X	X				
PO1	Poggio Semproniano	Bedded Travertine	X	X	X		X	
PO2	Poggio Semproniano	Bedded Travertine	X	X	X			X
PP1	Poggio i Piani	Bedded Travertine	X	X				X

* In addition to the reported analyses, geothermometric determinations through fluid inclusion and clumped isotope analyses were done on this sample (SP12).

Table 2

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Table 2. U/Th Age of travertines sampled in the study area. See 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 α spectrometry at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University, Italy (errors quoted as 1σ).

Sample	Location	Rock type	Age corrected (ka)
SP15*	Semproniano Village	banded travertine	**347 ± 22**
SP14/15*	Semproniano Village	banded travertine	**>800**
SP14/18*	Semproniano Village	banded travertine	**86 ± 1**
SP14/20*	Semproniano Village	banded travertine	**231 ± 9**
SP14/23*	Semproniano Village	banded travertine	**314 ± 11**
SP14/25*	Semproniano Village	banded travertine	**419 ± 39**
SP14/28*	Semproniano Village	banded travertine	**613 ± 200**
SP14/30*	Semproniano Village	banded travertine	**105 ± 1**
SP14/32*	Semproniano Village	banded travertine	***646***
SP14/34*	Semproniano Village	banded travertine	**495 ± 99**
SP1**	Semproniano Village	banded travertine	**>350**
SP12**	Semproniano Village	banded travertine	**128 ± 19**
SP16**	Semproniano Village	calcite vein	**104 ± 16**
SP11**	Semproniano Village	bedded travertine	**214 +50/-37**
SP3**	Poggio Semproniano	calcite vein	**43 ± 8**
SP10**	Poggio Semproniano	calcite vein	**39 ± 4**
PO2**	Poggio Semproniano	bedded travertine	**171 ± 19**
PP1**	Poggio i Piani	bedded travertine	**198 ± 18**
VI1**	Vignacci	banded travertine	**>350**

Table 3

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Table 3. Stable oxygen and carbon isotope composition, and paleotemperature of banded travertine, bedded travertine, and calcite veins from the study area. Isotope compositions are expressed in ‰ against Vienna Pee Dee Belemnite standard (V-PDB) and in ‰ against Vienna Standard Mean Ocean Water (V-SMOW). Temperature of parental fluids derive from $\delta^{18}O$ through the equation of Kele et al. (2015). $\delta^{13}C_{Co2}$* have been calculated using the empirical equation of Panichi and Tongiorgi. (1976). $\delta^{13}C_{Co2}$** have been calculated using the theoretical equation of Bottinga (1968).

Sample	Locality	Rock Type	$\delta^{13}C$ (‰ V-PDB)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{18}O$ (‰ V-SMOW)	$T_{calculated}$ (°C)	$\delta^{13}C_{Co2}$* (‰ V-PDB)	$\delta^{13}C_{Co2}$** (‰ V-PDB)
SP1	Semproniano Village	Banded Travertine	9.5	-12.7	17.8	60 ± 6	0.9	3.2
SP5	Semproniano Village	Banded Travertine	8.9	-10.8	19.8	49 ± 4	0.2	1.5
SP6	Semproniano Village	Banded Travertine	10.0	-12.2	18.3	57 ± 5	1.4	3.3
SP7	Semproniano Village	Banded Travertine	10.5	-11.6	19.0	53 ± 5	2.1	3.5
SP8	Semproniano Village	Banded Travertine	9.7	-12.3	18.2	58 ± 5	1.2	3.1
SP11	Semproniano Village	Bedded Travertine	9.9	-8.2	22.4	36 ± 2	1.4	1.1
SP12	Semproniano Village	Banded Travertine	4.9	-14.6	15.9	71 ± 7	-4.6	-0.5
SP12B	Semproniano Village	Banded Travertine	4.7	-13.5	17.0	64 ± 6	-4.9	-1.3
SP16	Semproniano Village	Calcite Vein	8.9	-12.0	18.6	56 ± 5	0.2	2.1
SP14/03	Semproniano Village	Banded Travertine	9.6	-12.3	18.2	58 ± 5	1.0	3.0
SP14/04	Semproniano Village	Banded Travertine	9.2	-12.7	17.8	60 ± 5	0.6	2.9
SP14/05	Semproniano Village	Bedded Travertine	5.8	-9.7	20.9	44 ± 3	-3.5	-2.2
SP14/06	Semproniano Village	Bedded Travertine	5.3	-9.8	20.9	44 ± 3	-4.2	-2.7
SP14/08	Semproniano Village	Banded Travertine	6.0	-9.8	20.8	44 ± 3	-3.3	-1.9
SP14/09	Semproniano Village	Banded Travertine	9.8	-11.1	19.5	51 ± 4	1.2	2.5
SP14/10	Semproniano Village	Banded Travertine	9.3	-10.9	19.7	50 ± 4	0.7	1.9
SP14/11	Semproniano Village	Banded Travertine	7.1	-11.1	19.5	51 ± 4	-2.1	-0.2
SP14/11B	Semproniano Village	Banded Travertine	6.0	-11.6	19.0	54 ± 5	-3.3	-1.0
SP14/12	Semproniano Village	Banded Travertine	9.2	-12.8	17.7	60 ±6	0.6	2.9
SP14/13	Semproniano Village	Banded Travertine	8.6	-12.3	18.3	57 ± 5	-0.2	2.0
SP14/14	Semproniano Village	Banded Travertine	7.7	-9.0	21.6	40 ± 3	-1.2	-0.7
SP14/15	Semproniano Village	Banded Travertine	8.0	-11.3	19.3	52 ± 5	-0.9	0.9
SP14/16	Semproniano Village	Banded Travertine	9.7	-10.1	20.5	46 ± 4	1.1	1.9
SP14/17	Semproniano Village	Banded Travertine	10.2	-10.7	19.9	49 ± 4	1.7	2.7
SP14/18	Semproniano Village	Banded Travertine	9.9	-10.6	20.0	48 ± 4	1.3	2.4
SP14/19	Semproniano Village	Banded Travertine	8.5	-10.7	19.9	49 ± 4	-0.3	1.1
SP14/20	Semproniano Village	Banded Travertine	8.2	-9.6	21.0	43 ± 3	-0.6	0.1
SP14/21	Semproniano Village	Banded Travertine	8.4	-12.1	18.5	56 ± 5	-0.4	1.7
SP14/22	Semproniano Village	Banded Travertine	10.1	-12.0	18.5	56 ± 5	1.6	3.3
SP14/23	Semproniano Village	Banded Travertine	7.0	-11.6	19.0	53 ± 5	-2.1	0.0

SP14/24	Semproniano Village	Banded Travertine	6.8	-11.3	19.2	52 ± 5	-2.3	-0.3
SP14/25	Semproniano Village	Banded Travertine	8.9	-9.9	20.7	45 ± 3	0.2	1.0
SP14/26	Semproniano Village	Banded Travertine	6.7	-11.4	19.2	52 ± 5	-2.5	-0.4
SP14/27	Semproniano Village	Banded Travertine	8.8	-10.7	19.9	49 ± 4	0.1	1.3
SP14/28	Semproniano Village	Banded Travertine	7.6	-10.0	20.6	45 ± 3	-1.4	-0.2
SP14/29	Semproniano Village	Banded Travertine	3.2	-8.8	21.8	39 ± 3	-6.7	-5.4
SP14/30	Semproniano Village	Banded Travertine	8.6	-11.2	19.4	51 ± 4	-0.2	1.4
SP14/31	Semproniano Village	Banded Travertine	6.5	-11.1	19.5	51 ± 4	-2.7	-0.8
SP14/32	Semproniano Village	Banded Travertine	9.0	-10.1	20.5	46 ± 4	0.3	1.2
SP14/33	Semproniano Village	Banded Travertine	6.3	-7.6	23.1	34 ± 2	-2.9	-2.9
SP14/34	Semproniano Village	Banded Travertine	6.5	-12.6	17.9	59 ± 5	-2.7	0.0
VI1	I Vignacci	Banded Travertine	3.7	-9.6	21.0	43 ± 3	-6.0	-4.4
SP3	Poggio Semproniano	Calcite Vein	7.1	-11.5	19.0	53 ± 5	-2.0	0.0
SP9	Poggio Semproniano	Bedded Travertine	6.8	-9.6	21.0	43 ± 3	-2.4	-1.3
SP10	Poggio Semproniano	Calcite Vein	8.4	-10.7	19.9	49 ± 4	-0.5	0.9
PS1	Poggio Semproniano	Bedded Travertine	6.9	-10.2	20.4	46 ± 4	-2.2	-0.8
PS2	Poggio Semproniano	Bedded Travertine	6.7	-8.1	22.6	36-± 2	-2.5	-2.3
PS3	Poggio Semproniano	Bedded Travertine	5.8	-10.1	20.5	46 ± 4	-3.6	-2.0
PO1	Poggio Semproniano	Bedded Travertine	5.6	-11.4	19.2	53 ± 5	-3.8	-1.5
PO2	Poggio Semproniano	Bedded Travertine	7.1	-9.8	20.8	44 ± 3	-2	-0.8
PP1	Poggio i Piani	Bedded Travertine	6.5	-11.6	19.0	53 ± 5	-2.7	-0.5

***(Panichi and Tongiorgi. 1976)**

**** (Bottinga, 1968)**

Table 4
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Table 4. Strontium, Strontium isotopes and Neodymium isotopes measured on selected samples from travertines of the study area.

Sample	Locality	Rock Type	Sr (mg/kg)	$^{87}Sr/^{86}Sr$ ± 2se*	$^{143}Nd/^{144}Nd$ ± 2se*	$\varepsilon_{Nd\ i}$ **
SP12	Semproniano Village	Banded travertine	1189.46	0.708277 ± 11		
SP14/18	Semproniano Village	Banded travertine	1223.70	0.708395 ± 9		
SP14/28	Semproniano Village	Banded travertine	1125.91	0.708368 ± 10		
SP11	Semproniano Village	Bedded travertine	105.31	0.708491 ± 10		
SP14/06	Semproniano Village	Bedded travertine	652.35	0.708470 ± 5	0.512253 ± 18	-6.50
SP17	Semproniano Village	Bedded travertine	592.74	0.708437 ± 6		
SP9	Poggio Semproniano	Bedded travertine	734.74	0.708326 ± 7		
PO1	Poggio Semproniano	Bedded travertine	502.19	0.708334 ± 5		
PO2	Poggio Semproniano	Bedded travertine	787.25	0.708366 ± 7		
SP3	Poggio Semproniano	Calcite Vein	4763.20	0.708527 ± 7	0.512330 ± 39	-2.41
SP10	Poggio Semproniano	Calcite Vein	4154.77	0.708488 ± 9		
VI1	I Vignacci	Banded travertine	4956.30	0.708456 ± 6	0.512275 ± 20	-9.93

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

** ε_{Nd} has been calculated at 200Ma

Figure 1
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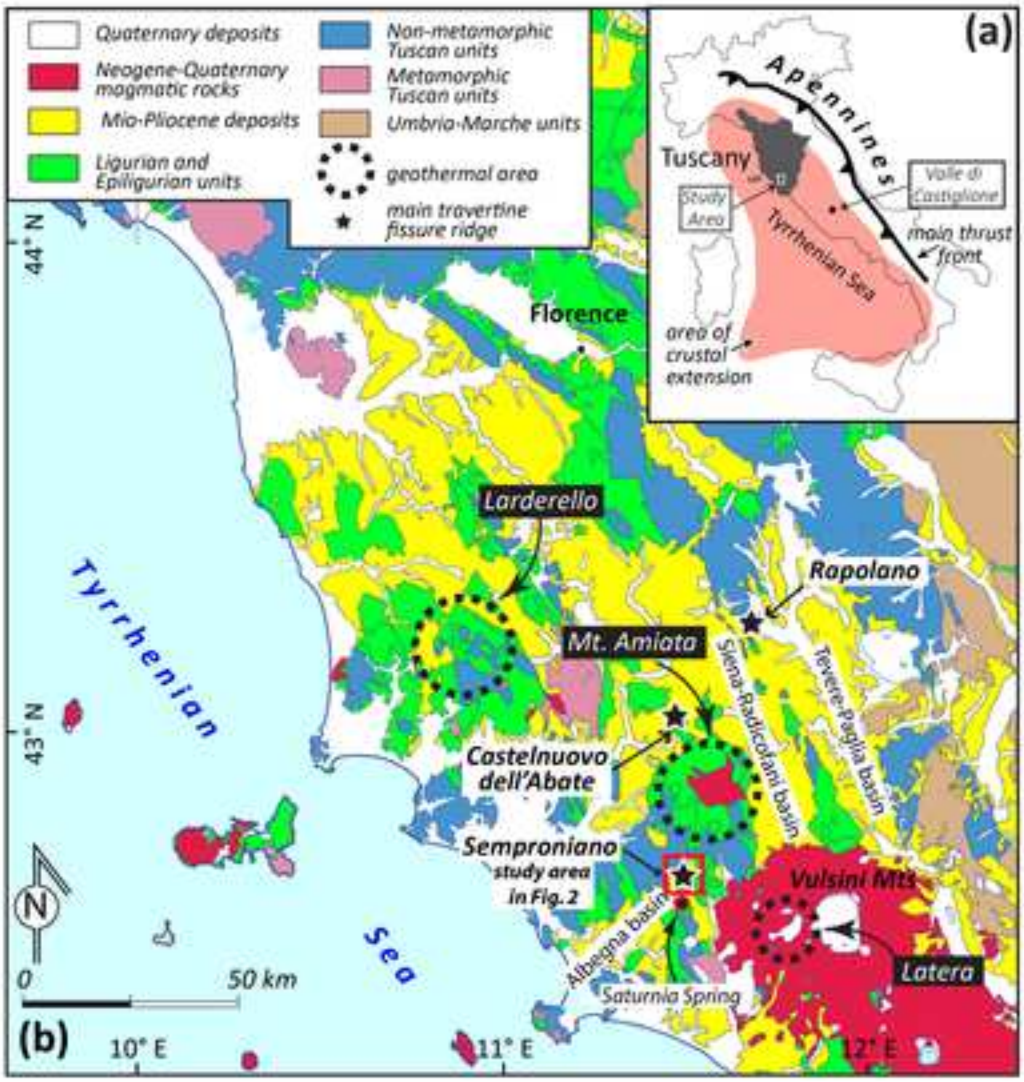

Figure 1. (a) Schematic map of Italy showing the Apennines fold-thrust belt and the area affected by crustal extension at the rear (west) of the belt. This latter area includes Tuscany, where the study area (Semproniano, upper Albegna basin, southern Tuscany) is located. **(b)** Geological map of the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

Figure 2
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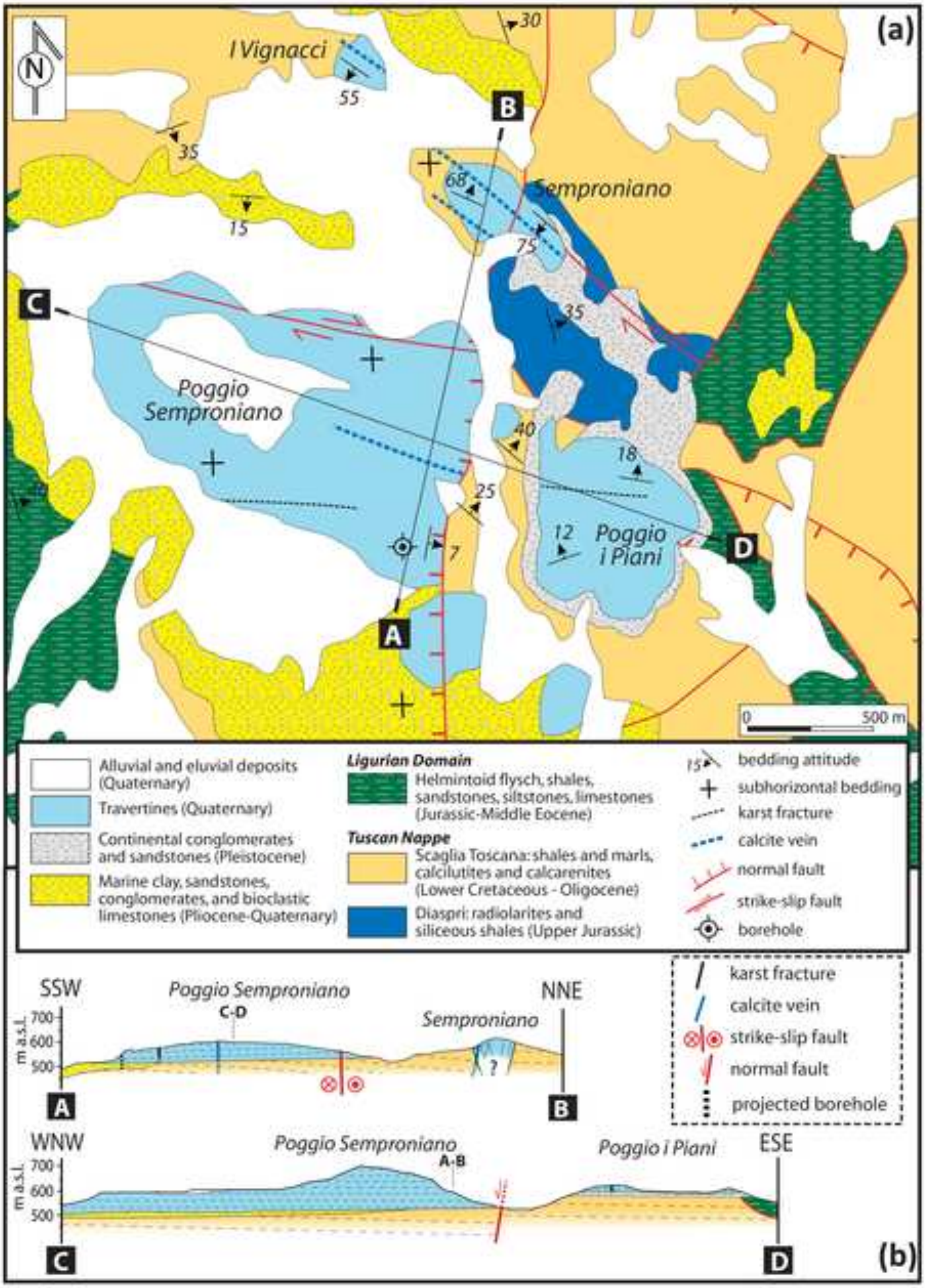

Figure 2. **(a)** Structural geological map of the study area (Sempironiano area in the upper Albegna basin) and **(b)** related geological cross-sections. The map is based on and partly redrawn from the geological map at the 1:10,000 scale available online at www.regione.toscana.it/-/geologia.

Figure 3

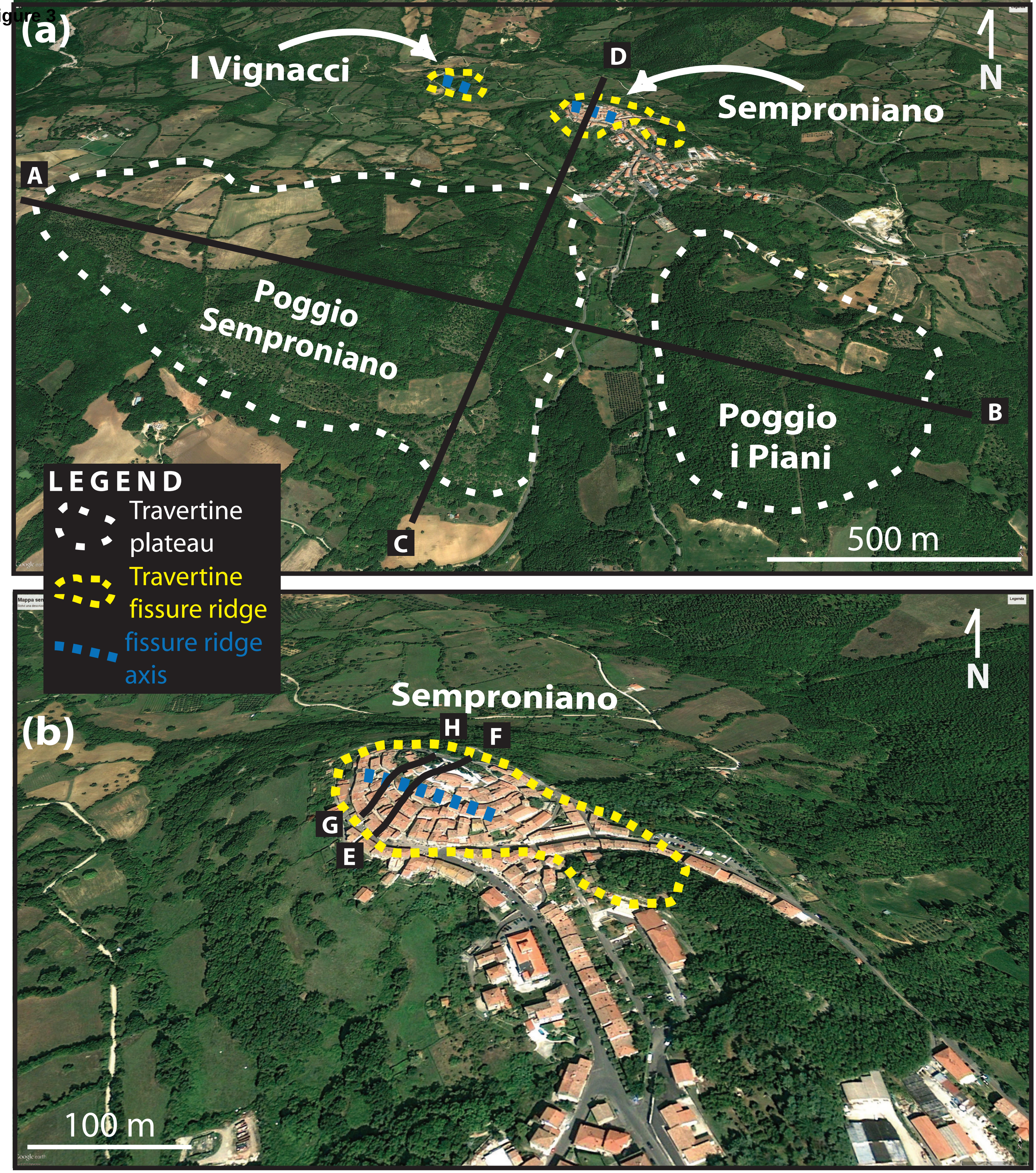

Figure 3. (a) Northward panoramic view of the study area with localization of the studied travertine deposits that are differentiated by morphology. **(b)** Northward panoramic view of the Semproniano ridge (i.e., Semproniano giant vein). Tracks of geological cross-sections (Figs. 2b and 6) are also shown.

Figure 4
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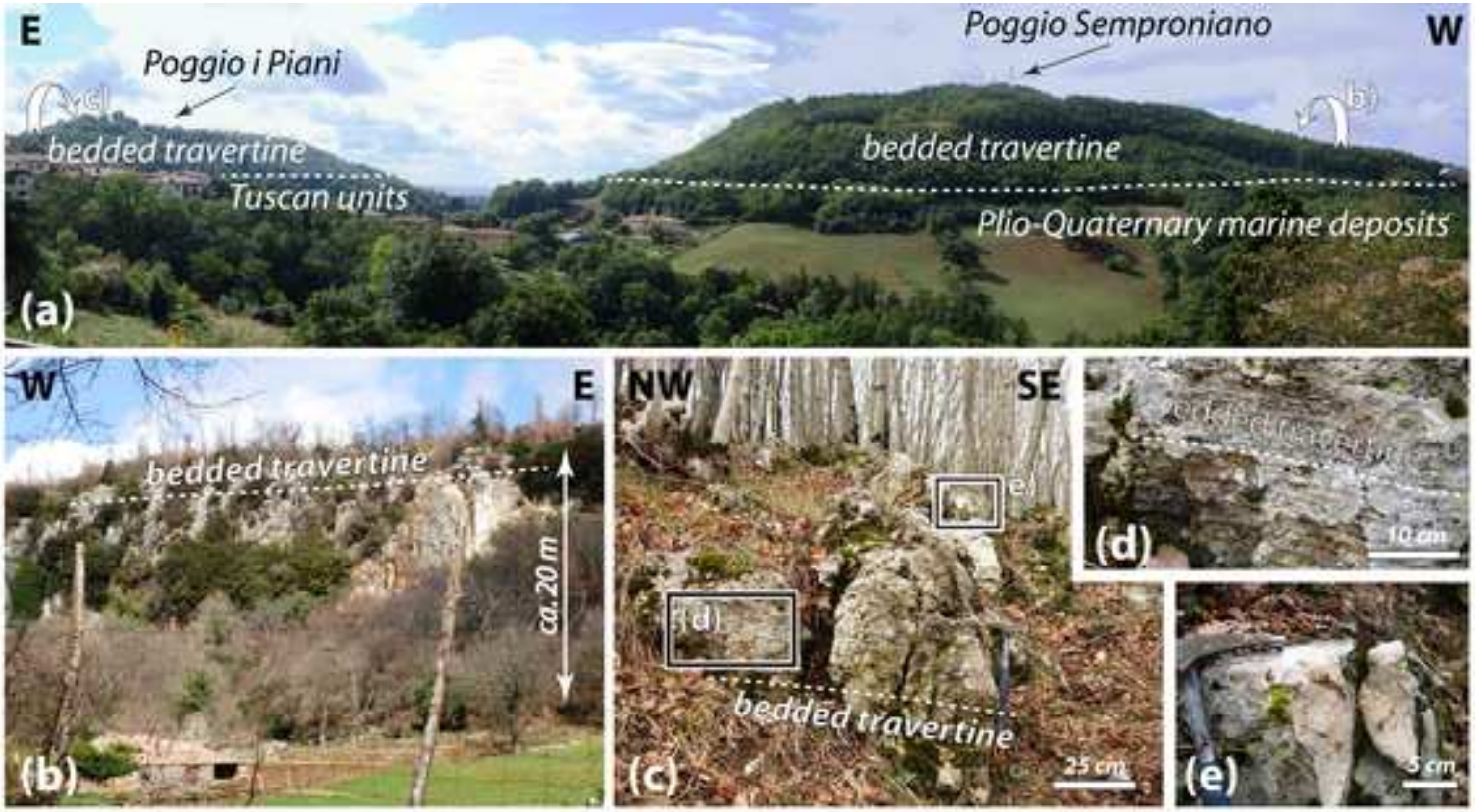

Figure 4. **(a)** Southward panoramic view of Poggio i Piani and Poggio Semproniano travertine plateaus. The Poggio i Piani plateau lies on top of the Scaglia Toscana Fmt. (belonging to the non-metamorphic succession of the Tuscan Domain) whereas the Poggio Semproniano plateau lies on top of Plio-Quaternary marine deposits. **(b)** Southern margin of the Poggio Semproniano travertine plateau. **(c)** Sub-horizontal travertine beds forming the Poggio I Piani plateau. **(d)** Detail of a laminated bedded travertine from Poggio I Piani plateau. **(e)** Close-up view of the bedded travertine occurring at Poggio i Piani.

Figure 5
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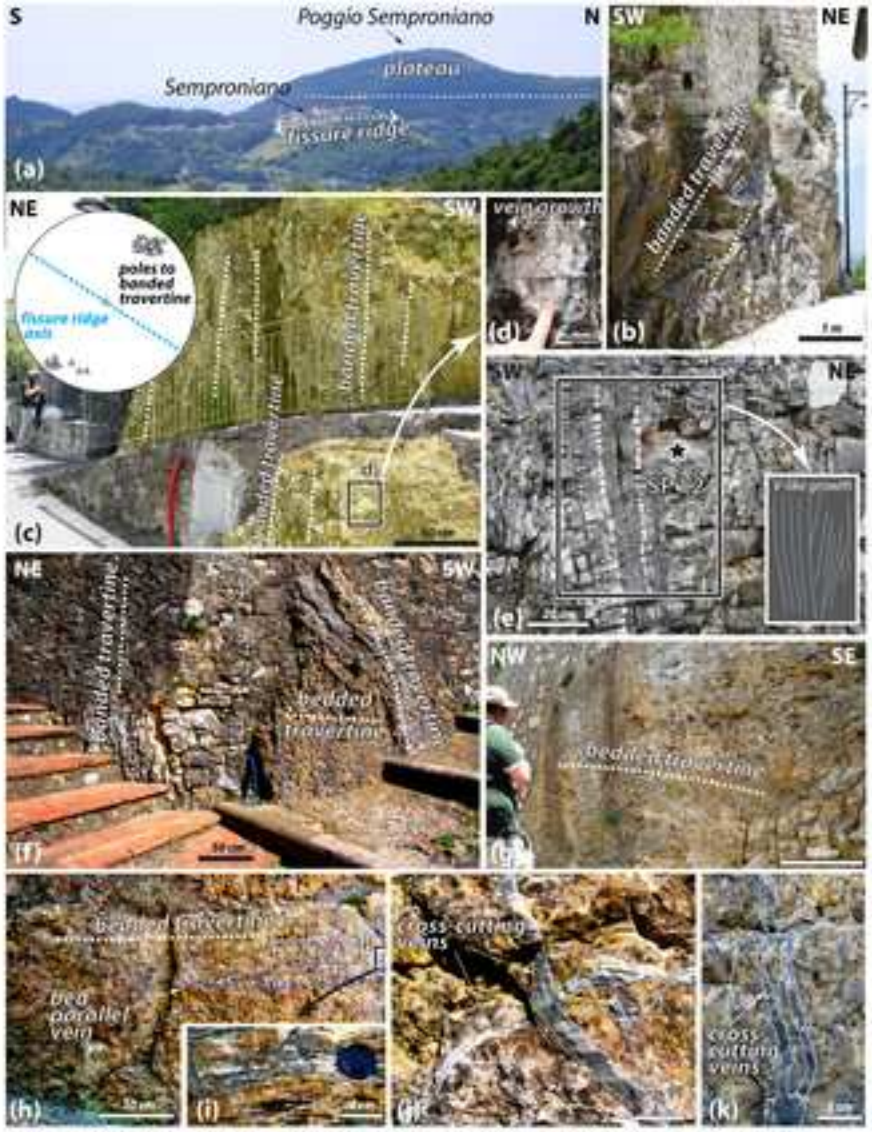

Figure 5. (a) Panoramic view of the Semproniano giant vein and travertine plateau (Poggio Semproniano). **(b)** Attitude of the sparry bands (banded travertine) forming the Semproniano giant vein (NE flank). This exposure is located below the fortress of the Aldobrandeschi family (X century) in the Semproniano village. **(c)** The Semproniano giant vein (banded travertine) is mainly oriented NW-SE and characterized by high dip values (see the stereoplot: Schmidt net, lower hemisphere, showing poles to travertine subvertical bands forming the giant vein). **(d)** Detail from the Semproniano giant vein (banded travertine) with indication of the vein growth. **(e)** The central part of the Semproniano giant vein shows a V-like shape and is characterized by a rhythmic sequence of crystallized subvertical bands of sparry carbonate. Sample SP12, used for fluid inclusion analysis, was collected here. **(f)** Spatial relationships between banded and bedded travertine along the flank of the Semproniano giant vein. **(g)** Sub-horizontal, bedded travertine exposed on the south-western flank of the Semproniano giant vein. **(h)** Sub-horizontal, bedded travertine cut through by bedded parallel travertine veins (Semproniano village). **(i)** Bedded travertine fabric characterized by laminations, shrubs, and karst-dissolution cavities (Semproniano village). **(j)** and **(k)** Travertine veins cutting through carbonate rocks (Tuscan Domain) along the SW flank of the Semproniano giant vein. Cross-cutting relationships between travertine veins show multiple phases of veining.

Figure 6
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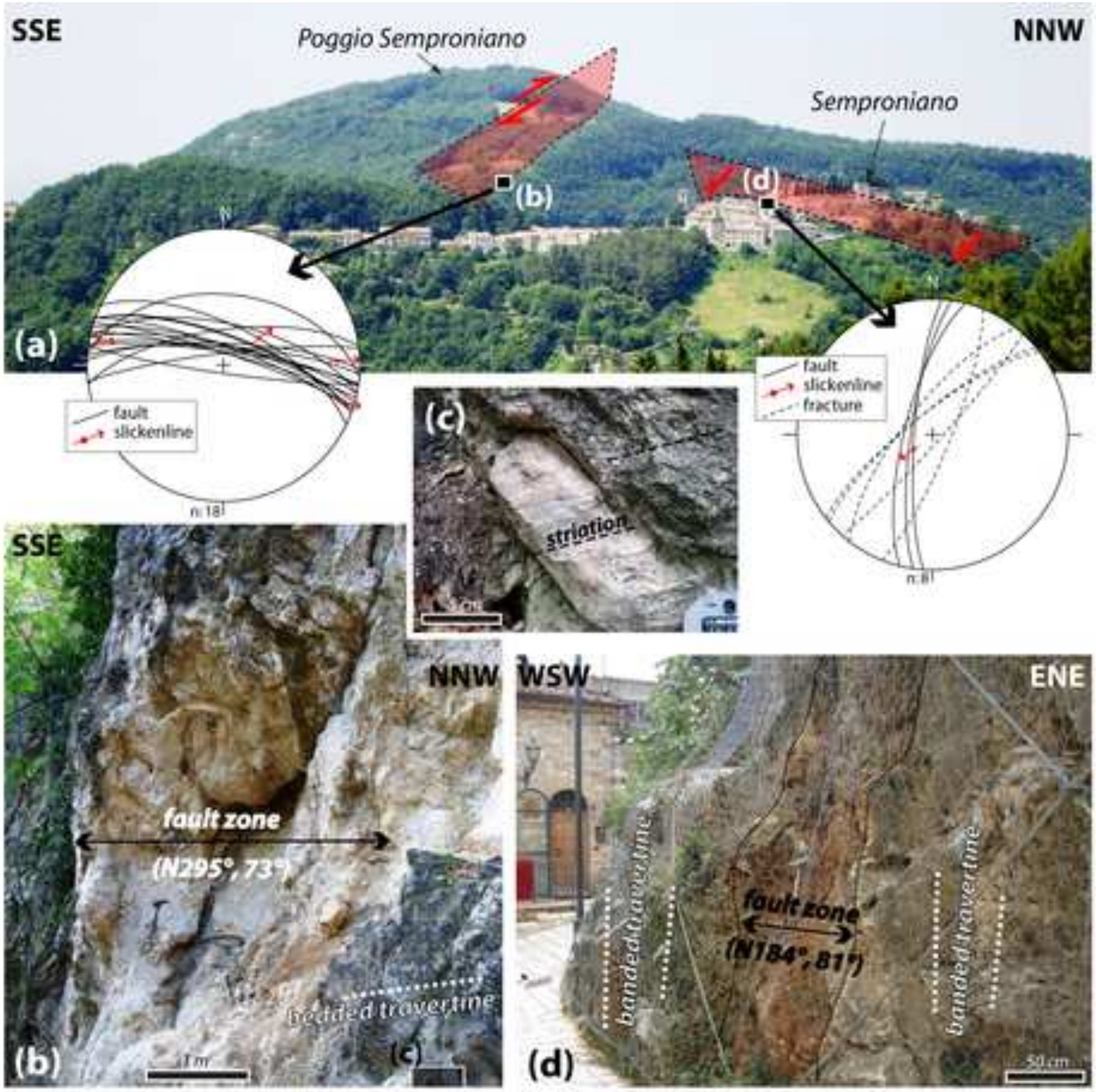

Figure 6. **(a)** Panoramic view of the Semproniano-Poggio Semproniano area where the traces of the main fault systems (*ca.* E-W- and N-S-striking) are indicated. The stereoplots (Schmidt net, lower hemisphere) show attitude of the measured structural features. **(b)** The E-W-striking fault system affecting the bedded travertine at Poggio Semproniano is characterized by meter-thick damage zone and narrowly-spaced fault surfaces. **(c)** Fault surfaces are equipped with oblique- to strike-slip striations (pitch is generally higher than 160° or lesser than 20°; see the stereoplot). Right-lateral strike-slip kinematics has been documented for this fault system. **(d)** The N-S-striking fault across the banded travertine of the Semproniano village is defined by a half-meter-thick damage zone and secondary fracture network. Extensional kinematics (associated to a left-lateral movement) has been documented for this fault system.

Figure 7
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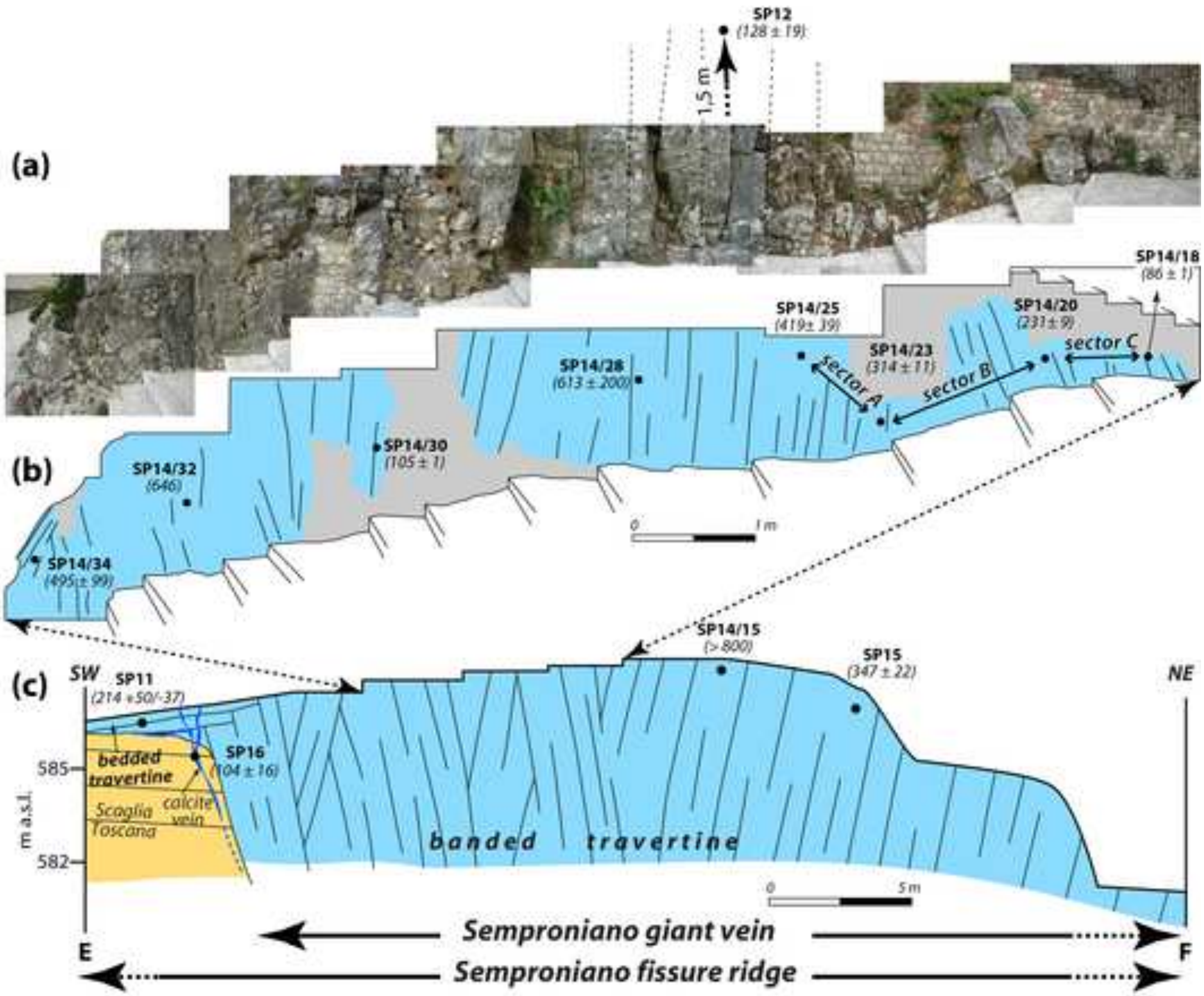

Figure 7. (a) Photomosaic (above) and related line drawing (below) of the Semproniano giant vein as it is exposed in the upper part of the Semproniano village. **(b)** Conceptual cross-sectional sketch of the Semproniano giant vein that is made of an uninterrupted swarm of sparry bands (banded travertine). Sample location and related radiometric ages are shown both in (a) and in (b).

Figure 8

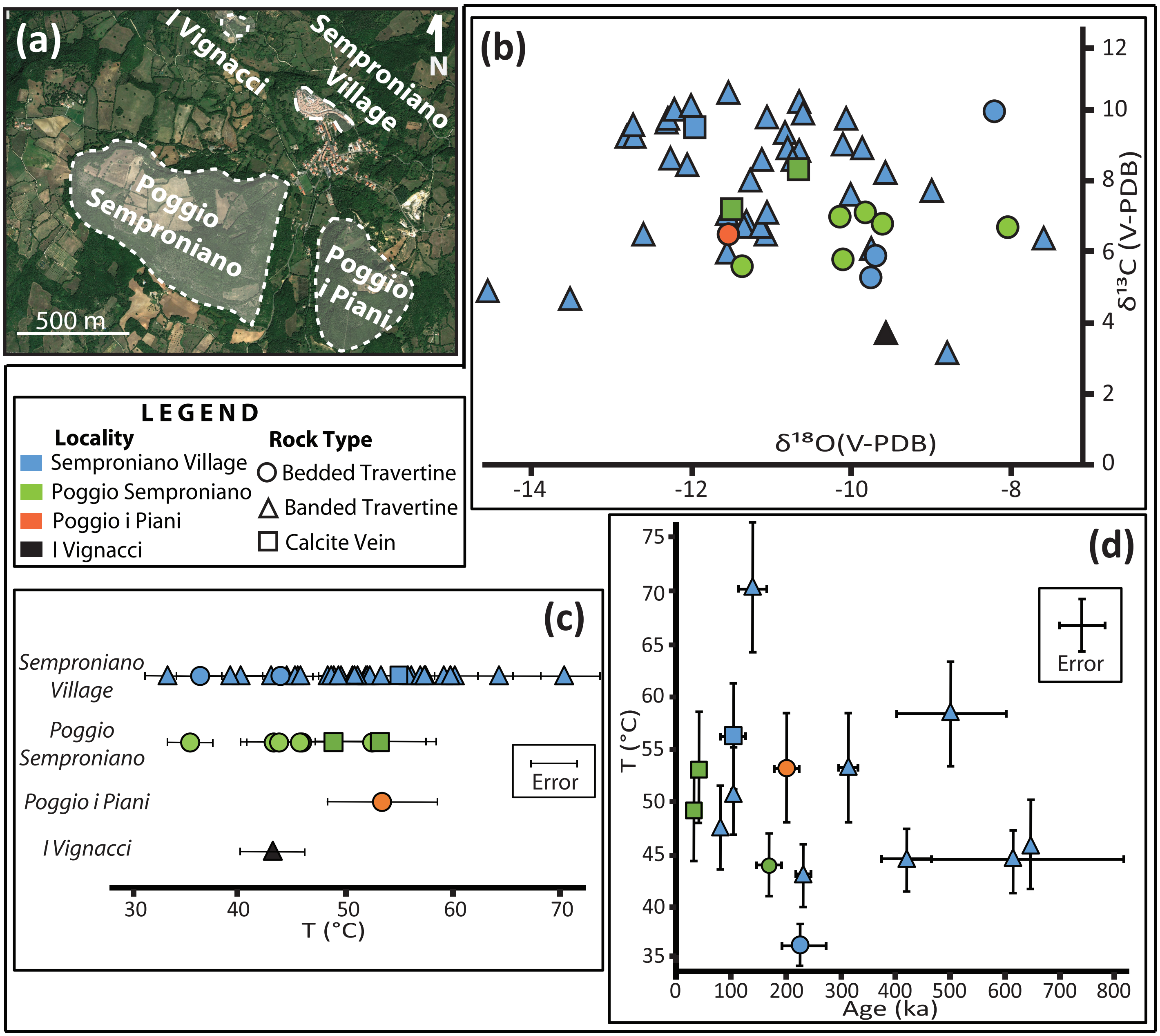

Figure 8. (a) Panoramic view (Google Earth image) with localization of the studied travertine deposits (same as Fig. 3a). **(b)** Combined plot of $\delta^{13}C$ (‰ V-PDB) and $\delta^{18}O$ (‰ V-PDB) isotope values derived from samples of bedded and banded travertines and calcite veins (Table 3). **(c)** Plot of calculated temperatures for the parental fluids of the studied travertines and $CaCO_3$ precipitates (Table 3). **(d)** Combined plot of parental fluid temperatures and U/Th ages determined on the same samples.

Figure 9

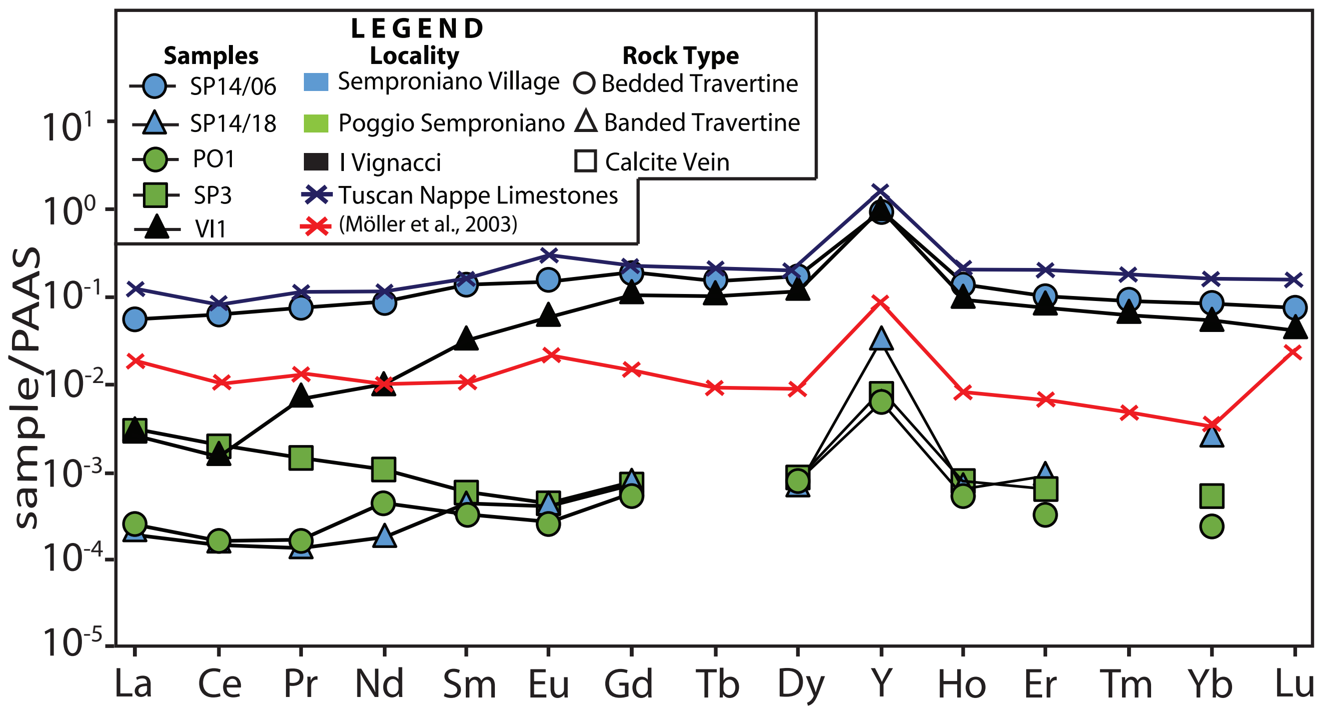

Figure 9. Post Archean Australian shale (PAAS) – normalized REY pattern (rare Earth elements + Yttrium) for: the Semproniano giant vein (banded travertine); the bedded travertine flanking the giant vein; bedded travertine and calcite vein from Poggio Semproniano; and banded travertine from I Vignacci. For comparison, REE data from the Tuscan Nappe limestone are also shown (data from Möller et al., 2003).

Figure 10

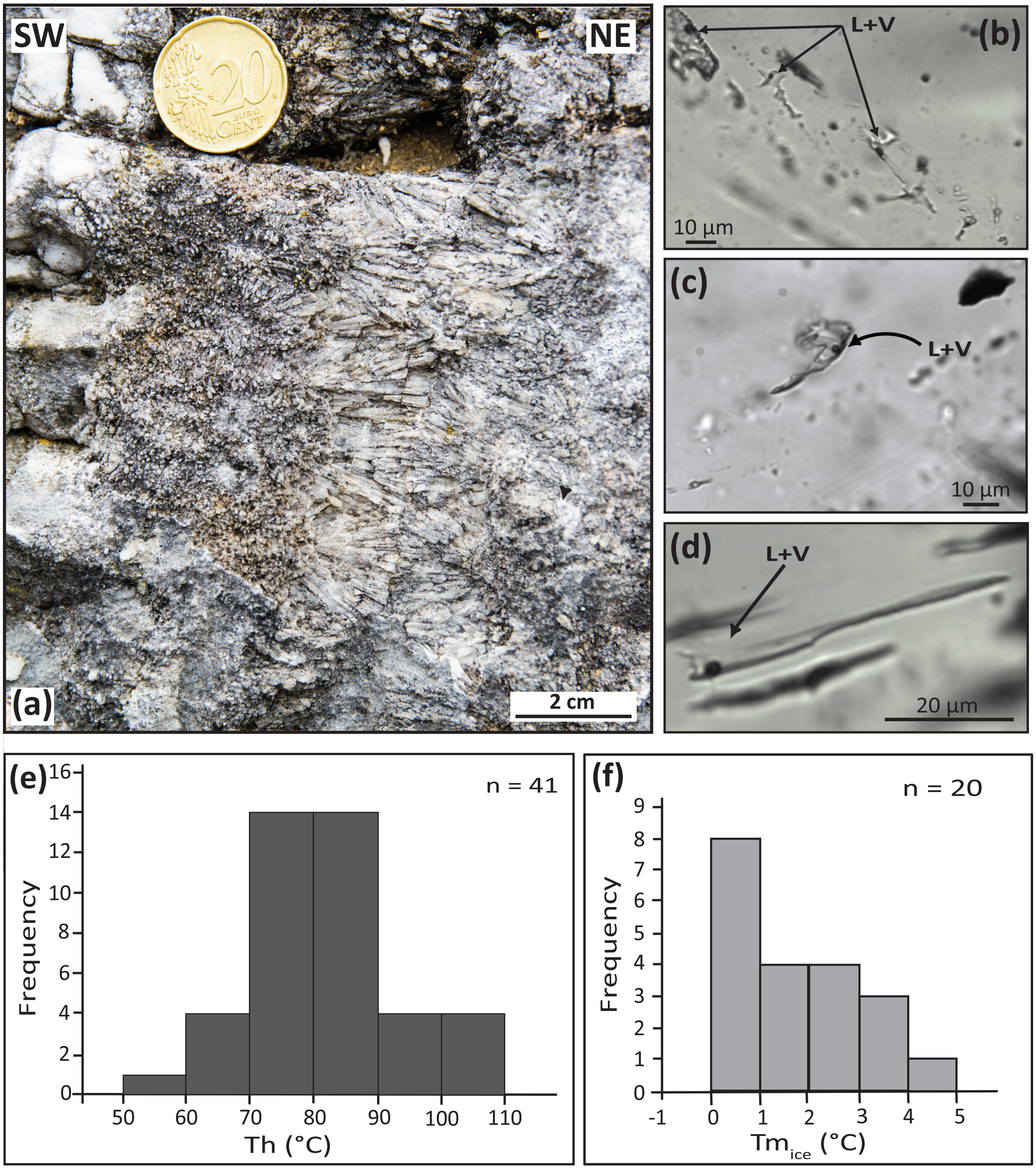

Figure 10. (a) Close up photograph of banded travertine from the central part of the Semproniano giant vein. The sample studied for fluid inclusions comes exactly from the spot shown in the photograph. **(b)**, **(c)**, and **(d)** Microphotographs (transmitted light, parallel nicols) of liquid-rich 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 Tm_{ice} (°C) is the temperature of last melting of ice.

Figure 11
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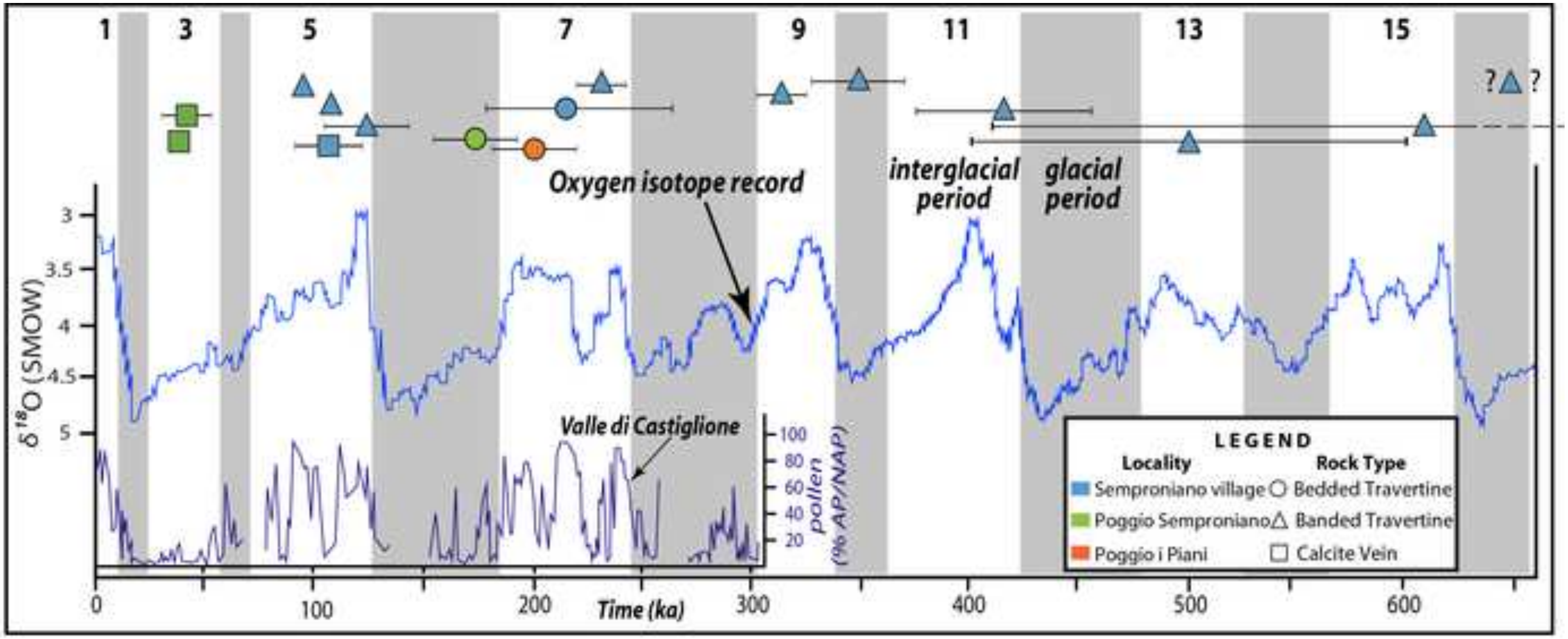

Figure 11. Comparison between U/Th ages of bedded travertine, banded travertine, and calcite veins from the study area and major paleoclimate indicators represented by the deep sea oxygen isotope trend (Zachos et al., 2001) and by the pollen dataset from Valle di Castiglione (Tzedakis et al., 2001). Global glacial/interglacial periods are redrawn and modified after Priewish et al (2014).

Figure 12
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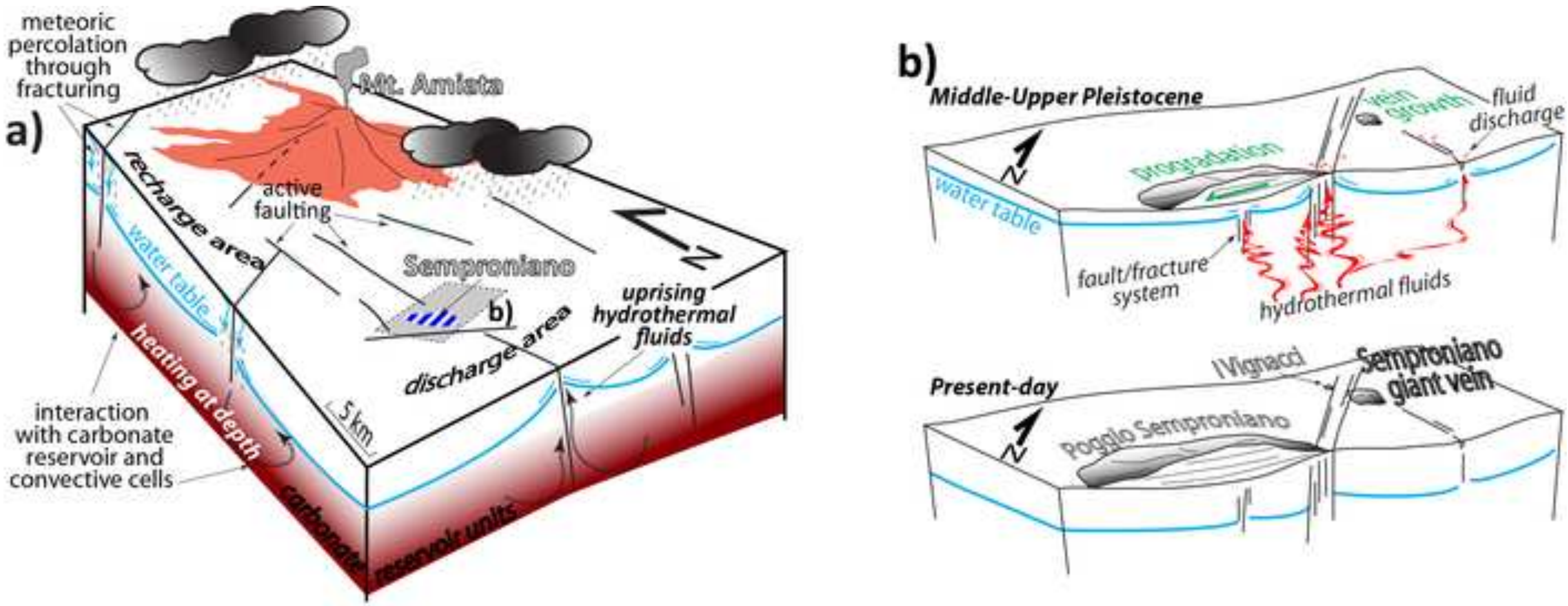

Figure 12. (a) Schematic 3D-block diagram interpreting the hydrothermal settingin the Mt. Amiata-Semproniano area. Active faulting and related fracturation have primary role in controlling meteoric percolation within the carbonate reservoir at depth, and the uprise of hydrothermal fluids. **(b)** Two-step 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.

Table S1

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Table S2

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