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Growth of a Pleistocene giant carbonate vein and nearby thermogene travertine deposits at Semproniano, southern Tuscany, Italy: Estimate of CO<sub>2</sub>leakage

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## **Abstract**

A giant carbonate vein ( $\geq 50$  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<sub>2</sub> 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<sub>2</sub> leakage connected with the vein precipitation are between about  $5 \times 10^6$  and  $3 \times 10^7$  mol a<sup>-1</sup> km<sup>-2</sup>, approximately representing one millionth of the present global CO<sub>2</sub> 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<sub>2</sub> 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 CaCO<sub>3</sub> mineralizations.
- CO<sub>2</sub> leakage in hydrothermal areas.
- Feedbacks between neotectonics, hydrothermalism and paleoclimate oscillations

1 **Growth of a Pleistocene giant carbonate vein and nearby**  
2 **thermogene travertine deposits at Semproniano, southern**  
3 **Tuscany, Italy**  
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48

49 **Abstract**

50

51 A giant carbonate vein ( $\geq 50$  m thick; fissure ridge travertines) and nearby travertine plateaus in the  
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53 multidisciplinary approach, including field and laboratory geochemical analyses (U/Th  
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73 **Keywords:** travertine, vein, CO<sub>2</sub> leakage, hydrothermalism, REE, C- O- Sr- Nd- isotopes,  
74 Quaternary climate, Tuscany.

## 75 **1. Introduction**

76 Thermogene travertines form through precipitation of  $\text{CaCO}_3$  from supersaturated fluids usually  
77 generated and discharged in volcano-tectonic settings, often deposited in proximity of active  
78 geothermal springs or along open fissures (Pentecost, 1995; Ford and Pedley, 1996; Pentecost,  
79 2005; Crossey et al., 2006). In addition to being important decorative and construction stones since  
80 at least the Roman time (Calvo and Regueiro, 2010), a renewed world-wide interest for thermogene  
81 travertine deposits resides in their importance to be potential analogs of long-term outflow from  
82 artificial  $\text{CO}_2$  storages (Shipton et al., 2004; Bickle and Kampman, 2013; Burnside et al., 2013;  
83 Frery et al., 2015). Moreover, recent discoveries of large hydrocarbon reserves in subsalt porous  
84 microbial and travertine-like rocks along the Brazilian and Angolan margins of the Atlantic Ocean  
85 place thermogene travertines among the best exposed analogs of these hydrocarbon-reservoir rocks,  
86 which are hitherto known only from seismic data and well cores (e.g., Beasley et al., 2010; Rezende  
87 and Pope, 2015; Ronchi and Cruciani, 2015; Soete et al., 2015).

88 Travertines can show various deposit morphologies such as cascades, terrace mounds, fissure  
89 ridges, plateaus, and towers (Chafetz and Folk, 1984; Altunel and Hancock, 1993a, b; Pentecost,  
90 1995; Pentecost, 2005). These morphologies are only partially dependent on the topography over  
91 which the travertines precipitate. Other factors such as (neo)tectonics (Altunel and Hancock, 1996;  
92 Hancock et al., 1999; Brogi, 2004a; Brogi and Capezzuoli, 2009; Brogi et al., 2010, 2012; De  
93 Filippis et al., 2013a; Ricketts et al., 2014; Maggi et al., 2015), climate oscillations (Sturchio et al.,  
94 1994, Rihs et al., 2000; Faccenna et al., 2008, De Filippis et al., 2012), earthquakes (Uysal et al.,  
95 2007, 2009; Brogi et al., 2014; Gradziński et al., 2014), and hydrological regimes (Priewisch et al.,  
96 2014; Crossey et al., 2015) have been proposed to influence travertine growth and morphology;  
97 however, the way how these and other factors control the travertine development and shape is still  
98 uncertain. It is, in particular, unclear what are the factors controlling travertine deposits, that are  
99 completely different in morphology and volume such as travertine fissure ridges and plateaus,

100 which can, nonetheless, form in close proximity during the same time span (e.g., [De Filippis et al.,](#)  
101 [2013b](#)).

102 In this paper, we address the growth of travertine fissure ridges and plateaus. Fissure ridges are  
103 deposits of travertines with an elongate mound shape characterized by a length between a few  
104 meters and over 2000 m, and a main crestal fissure from which the travertine-feeding fluids gush  
105 out ([Chafetz and Folk 1984](#); [Altunel and Hancock, 1993a,b, 1996](#); [Çakır, 1999](#); [Hancock et al.,](#)  
106 [1999](#); [Uysal et al., 2007, 2009](#); [De Filippis et al., 2012, 2013a](#)). Fissure ridges are usually formed by  
107 two main travertine types: (1) the bedded travertine, which consists of a porous and stratified  
108 deposit constituting the flanks (often clinostratified) and the bulk of the fissure ridge and (2) the  
109 banded travertine, which consists of subvertical bands of sparry nonporous carbonate (usually  
110 calcite, aragonite, or both) filling large veins that intrude the axial region of the fissure ridge. In  
111 places, these veins can also develop as sill-like structures along the beds of the bedded travertine or  
112 host rocks ([Uysal et al., 2007](#); [Gratier et al., 2012](#)). Travertine plateaus, in contrast, are  
113 characterized by massive and large deposits consisting of sub-horizontal to gently-clinostratified  
114 travertine beds usually filling a tectonic or morphological depression and producing no prominent  
115 topography ([Faccenna et al., 2008](#); [De Filippis et al., 2013a](#)).

116 Tuscany ([Fig. 1](#)), central Italy, is a region characterized by Neogene-Quaternary formation of  
117 extensional basins, widespread magmatism, associated contact metamorphism, hydrothermalism  
118 and ore mineralization, and also numerous thermogene travertine deposits ([Marinelli et al., 1993](#);  
119 [Serri et al., 1993](#); [Barberi et al., 1994](#); [Carmignani et al., 1994](#); [Dini et al., 2005](#); [Gandin and](#)  
120 [Capezzuoli, 2008](#); [Brogi and Capezzuoli, 2009](#); [Rossetti et al., 2008, 2011](#)). Travertine deposition in  
121 Tuscany has occurred near highly-productive geothermal areas (Larderello-Travale and Mt. Amiata;  
122 [Batini et al., 2003](#)), where endogenous fluids permeate Meso-Cenozoic carbonate reservoirs and  
123 mix before feeding thermal springs and CO<sub>2</sub> emission centers (e.g., [Minissale, 2004](#)). Both  
124 travertine fissure ridges and plateaus are documented in Tuscany. In particular, studied fissure  
125 ridges are exposed in the Rapolano Terme (e.g., [Brogi and Capezzuoli, 2009](#); [Guo and Riding,](#)

126 1999) and Castelnuovo dell'Abate (Rimondi et al., 2015) localities (Fig. 1b), where banded  
127 travertine forms centimeters-to-meters thick veins within meters-sized elongate mounds accreted  
128 over a restricted time interval between Pleistocene and Holocene times.

129 We focus our study on travertines exposed in the village of Semproniano (northern Albegna  
130 basin), which is built on top of a hill at an altitude of 620 m. Semproniano is located only about 15  
131 km southward of the Mt Amiata Pleistocene volcanic district and 9 km from the Saturnia thermal  
132 spring (Figs. 1 and 2), where active travertine deposition still occurs. The Semproniano village lies  
133 on a travertine fissure ridge, a composite carbonate vein ( $\geq 50$ -m-thick) consisting of subvertical  
134 banded travertine (Capezzuoli et al., 2013), which crops up from the surrounding host carbonate  
135 rocks (Paleogene). Other travertine deposits or carbonate mineralizations, including travertine  
136 plateaus, small veins, and bedded travertines, are exposed within a few kilometers from the  
137 Semproniano village (Fig. 3a). The origin and growth modes of these deposits and mineralizations  
138 in the Semproniano area are unknown and the main driving factors (e.g., tectonics, paleohydrology,  
139 paleoclimate, etc.) as well. Moreover, absolute dating of these travertines is missing, thus making  
140 very difficult the regional correlation among these deposits as well as between the deposits  
141 themselves and the dated tectonic, volcanic, and paleoclimate events in the region.

142 The coexistence of different nearby  $\text{CaCO}_3$ -mineralizations and travertine deposits in a region  
143 of recent tectonic and volcanic activity makes the Semproniano area an excellent case study to  
144 understand the nature of those carbonates deposits. Using a multidisciplinary approach consisting of  
145 geological, structural, geomorphologic, and geochemical methods (including fieldwork, remote  
146 observations, U/Th dating, C- Nd- O- and Sr-isotope systematics, rare Earth element (REE)  
147 abundances, and fluid inclusion microthermometry), this study is aimed at understanding the  
148 development of the different travertine bodies (vein and plateau type), their mutual relationships,  
149 and the feedback relationships between travertine deposition and driving factors such as tectonics,  
150 volcanisms, and paleoclimate. The main novelty of this work concerns growth modes and rates of  
151 the Semproniano fissure ridge and implications for the associated  $\text{CO}_2$  leakage. In addition, our

152 results provide insights at regional scale concerning the late Quaternary hydrothermal and tectonic  
153 activity of southern Tuscany.

154

## 155 **2. Geological setting**

156 Southern Tuscany is located in the inner sector (western) side of the northern Apennine chain  
157 (Fig. 1), which is a Cenozoic NW-SE-trending orogenic belt developed through a general eastward  
158 migration of thrust sheets in a classical piggy back sequence toward the Adriatic foreland (e.g.,  
159 Patacca et al., 1990; Cipollari and Cosentino, 1995; Massoli et al., 2006). In Tuscany, post-orogenic  
160 extension and collapse of the previously formed orogenic belt started in late Miocene time, while,  
161 toward the east, the belt was still under a compressional regime (e.g., Malinverno & Ryan, 1986;  
162 Dewey 1988; Jolivet et al., 1998; Cavinato and De Celles, 1999; Pauselli et al., 2006). The  
163 extensional process generated normal faults that dismantled the previously-formed fold-thrust belt  
164 (e.g. Carmignani et al., 1994; Keller et al., 1994; Barchi et al., 1998; Jolivet et al., 1998; Collettini  
165 et al., 2006) and produced significant crustal thinning (present-day crust thickness is about 22-24  
166 km; Locardi and Nicolich, 1988; Billi et al., 2006) as well as the development of sedimentary basins,  
167 magmatic provinces, and diffuse volcanism (Serri et al., 1993; Serri, 1997; Peccerillo, 2003). Fossil  
168 and active, structurally-controlled hydrothermal mineralizations are widespread evidence of the  
169 interaction between hydrothermal systems and extensional faults (e.g., Barberi et al., 1994;  
170 Buonasorte et al., 1988; Chiarabba et al., 1995; Gianelli et al., 1997; Batini et al., 2003; Bellani et  
171 al., 2004; Annunziatellis et al., 2008; Brogi, 2008; Liotta et al., 2010; Rossetti et al., 2011;  
172 Vignaroli et al., 2014).

173 Southern Tuscany (Fig. 1) is characterized by main NW-SE-trending and minor NE-SW-  
174 trending Miocene-to-Quaternary sedimentary basins formed during post-orogenic extensional  
175 processes and bounded by extensional-to-transensional structures (Martini and Sagri, 1993; Liotta,  
176 1994; Pascucci et al., 2006; Brogi and Liotta, 2008; Brogi, 2011; Brogi et al., 2013; 2014; 2015;  
177 Marroni et al., 2015). These structures include the Tevere-Paglia, Siena-Radicofani, and Albegna

178 basins. The Semproniano thick vein and surrounding travertine deposits are located in the Albegna  
179 basin, which consists of a NE-SW-trending tectonic depression bounded to the north and southeast  
180 by the volcanic districts of the Mt Amiata and Vulsini Mts, respectively (Fig. 1). The magmatic  
181 activity (or part of it) of the Mt Amiata district is dated to 300-190 ka according to Cadoux and  
182 Pinti (2009) and to 300-225 ka according to Laurenzi et al. (2015), whereas the activity (or part of  
183 it) of the Vulsini Mts district is dated to 590-127 ka according to Nappi et al. (1995).

184 The geological setting of the Albegna basin is characterized by the presence of metamorphic  
185 and non-metamorphic tectonic units stacked during the formation of the Apennines fold-thrust belt.  
186 From bottom to top, these units are as follows (e.g., Carmignani et al., 2013): (1) low-grade  
187 metamorphic rocks of the Tuscan Metamorphic Complex; (2) Upper Triassic to Oligocene  
188 kilometers-thick sedimentary succession composed by basal evaporites followed by shelf  
189 carbonates and marls (Tuscan Nappe); (3) Jurassic to Eocene ophiolite-derived clays and marls  
190 succession (Ligurian Domain); and (4) Upper Miocene to Pleistocene terrigenous post-orogenic  
191 deposits. The latter consist of fluvio-lacustrine deposits and marine clays that deposited in subsiding  
192 areas concomitantly with the regional tectonic extension (Zanchi and Tozzi, 1987; Bonazzi et al.,  
193 1992; Bossio et al., 2004).

194 In the Albegna basin, travertine deposits unconformably lie on top of the Neogene-Pleistocene  
195 deposits (Zanchi and Tozzi, 1987; Martelli et al., 1989; Bosi et al., 1996). The travertine deposition  
196 occurred in distinct phases and over a long time interval (Bosi et al., 1996). In particular, based on  
197 the travertine morphological and stratigraphic characters, Bosi et al. (1996) proposed a travertine  
198 deposition spanning from Messinian to Holocene times. In particular, Bosi et al. (1996) suggested  
199 that the travertines of the Semproniano area deposited during Pliocene time, whereas other authors  
200 considered them as early Pleistocene in age (Zanchi and Tozzi, 1987). The lack of absolute  
201 radiometric ages restricts the full understanding of these travertine deposits and their relationships  
202 with the hydrothermal and tectonic activity in the Albegna basin.

203

## 204 **3. Methods and Results**

### 205 **3.1. Geology and geomorphology**

206 We performed a field-based study on the geology, geomorphology, and structural setting of the  
207 travertine deposits located in the Semproniano area, namely: the (1) Semproniano ridge, (2) I  
208 Vignacci, (3) Poggio Semproniano, and (4) Poggio i Piani deposits (Figs. 2-5). We focused this  
209 study on the recognition of different travertine morphotypes (e.g., plateaus vs. fissure ridge  
210 travertines), on the relationships between travertine deposits and host rocks, and on the deformation  
211 features affecting the travertine deposits.

212 The study area is characterized by a set of post-orogenic Pliocene-Quaternary continental and  
213 marine sedimentary deposits (including the studied travertines) that unconformably rest on top of  
214 the Apennine stacked units (e.g., Bonciani et al., 2005; Brogi, 2008; Brogi and Fabbrini, 2009). The  
215 travertine plateaus (Poggio Semproniano and Poggio i Piani), in particular, unconformably lie over  
216 Pliocene-Quaternary deposits and over the Scaglia Toscana Fmt. of the underlying Tuscan Nappe  
217 (Fig. 4a) which host the Semproniano fissure ridge (Fig. 2). The Poggio Semproniano deposit  
218 occupies the top portion of a triangular hill that is almost 700 m high (Fig. 3). The hill is tabular  
219 with a terrace-like top surface marked by a peripheral rim that runs all around the terraced deposit  
220 and delimits the terrace itself from the steep flanks of the hill. At the foot of these escarpments, the  
221 contact between the travertine deposit and the surrounding units is often covered by debris  
222 constituted by alluvial and eluvial deposits. The travertine body has dimensions of around 1300 m  
223 in the NW-SE direction and 700 m in the N-S direction, and has a maximum vertical thickness of  
224 about 200 m (Figs. 2 and 3). The travertine depositional fabric consists of piano-parallel  
225 centimeters-thick beds of whitish lime-mudstone with homogeneous porosity due to the presence of  
226 microbialites. Millimeter to centimeter-sized karst dissolution cavities are also present (Fig. 4c). On  
227 the eastern flank, the travertine beds of the Poggio Semproniano plateau and the underlying marly  
228 deposits of the Tuscan Nappe are pervaded by a set of cm-thick subvertical veins striking NW-SE,  
229 filled by white sparry carbonate.

230 The Poggio i Piani deposit is very similar to the one of Poggio Semproniano. Poggio i Piani is a  
231 terraced triangular hill with maximum elevation around 630 m. Also here, the travertine deposit is  
232 characterized by an outer sharp rim that runs all around the terraced deposit and delimits the terrace  
233 itself with the steep flanks of the hill. The deposit is tabular and sub-horizontal with sedimentary  
234 features similar to the ones described for Poggio Semproniano (Figs. 4c, d, e). The dimensions of  
235 the Poggio i Piani travertine plateau are about 500 m in the NW-SE direction and 450 m in the N-S  
236 direction with a maximum thickness of 35 m (Fig. 2). A narrow N10°-trending valley with a  
237 minimum elevation of about 500 m separates the Poggio Semproniano and Poggio i Piani hills (Fig.  
238 3).

239 The Semproniano ridge is separated from the Poggio Semproniano and Poggio I Piani deposits  
240 by a narrow NW-SE-trending valley with a minimum elevation of about 500 m (Fig. 3). The  
241 Semproniano ridge crops out from the top of a NW-SE-elongate domed hill with maximum altitude  
242 around 620 m a.s.l. and about 1000 m long and 400 m wide. The central part of the Semproniano  
243 ridge, constituted by banded sparry travertine with a total thickness of more than 50 m, is  
244 characterized by complex geometries such as V-like-shaped (Fig. 5e) or crosscutting carbonate  
245 bands that are up to about 2 cm thick. The sparry subvertical bands of carbonate form a unique,  
246 composite and uninterrupted vein that we call the Semproniano giant vein for its large thickness of  
247 more than 50 m. The southwestern flank of the ridge is characterized by the presence of sub-  
248 horizontal bedded travertine leaning over the sub-vertical banded travertine (Fig. 5f). The bedded  
249 travertine is characterized by sub-horizontal brownish centimeters-thick beds (Fig. 5g), shrubs, and  
250 laminations affected, in places, by millimeters-to-centimeters-sized cavities of depositional and  
251 post-depositional (karst) origin. In some cases, the porous bedded travertine appears to be pervaded  
252 by bed-parallel veins (Fig. 5h and 5i). In the external part of the southwestern flank of the giant vein,  
253 at an altitude of about 580 m a.s.l, a set of sub-vertical centimeters-thick carbonate veins cut  
254 through the marly carbonates of the Scaglia Toscana Fmt. (Fig. 5j, k), which is the host rock of the  
255 giant vein travertine (Fig. 2).

256 The I Vignacci deposit crops out about 800 m to the northwest of the Semproniano ridge,  
257 exactly along the NW-SE prolongation of the Semproniano hill and ridge (Figs. 2 and 3). I Vignacci  
258 travertine is located at an altitude of about 430 m a.s.l., the lowest reached of the studied travertines.  
259 I Vignacci travertine deposit is small and it is characterized by banded travertine with subvertical  
260 NW-SE-striking bands. These bands cut through the surrounding sub-horizontal beds of the Scaglia  
261 Toscana Fmt. Geometrical attitude and location of I Vignacci outcrop suggest a structural and  
262 geometric continuity with the Semproniano ridge (Figs. 2 and 3).

263 From a tectonic point of view, the travertine deposits are cross-cut by two main subvertical fault  
264 systems, one striking ca. E-W and one striking N-S (Figs. 2 and 6). In particular, we recognized that  
265 the E-W-striking fault system cuts through the northern portion of the Poggio Semproniano  
266 travertine plateau (Fig. 6a). It consists of meter-thick damage zone defined by fault slip surfaces and  
267 secondary, subparallel, fracture network (Fig. 6b). A pitch smaller than 15° or greater than 165°  
268 have been measured for most slickenlines and abrasive striations occurring on fault planes (Fig. 6c).  
269 The kinematic indicators observed on the fault surfaces are mainly represented by synthetic shear  
270 fractures within the damage zone (Riedel shear planes) and they are consistent with right-lateral  
271 strike-slip movements. The N-S-striking fault system passes along the valley that separates the  
272 Poggio Semproniano and Poggio i Piani travertine deposits (Fig. 2). We identified this set of faults  
273 as affecting the travertine deposits of the Semproniano ridge and cut through the banded travertine  
274 of the Semproniano fissure ridge (Fig. 6a). Within the ridge, the fault system is characterized by a  
275 0.5 m-thick damage zone and several speleothem-filled fracture networks cutting through the  
276 banded travertine (Fig. 6d). When observed, abrasive striations on fault planes show a pitch of  
277 about 60-70°. Geometrical relationships between faults and secondary fractures are consistent with  
278 an extensional movement (associated to a left-lateral movement) lowering the Poggio Semproniano  
279 travertine deposit.

280

### 281 **3.2. U/Th geochronology**

282 We dated nineteen samples from the CaCO<sub>3</sub> mineralizations in the study area (Tables 1, 2, and  
283 S1), namely from Semproniano (thirteen samples from the giant banded vein, bedded travertines,  
284 and one subordinate vein), I Vignacci (one sample from the banded travertine), Poggio  
285 Semproniano (three samples from bedded travertines and veins), and Poggio I Piani (one sample  
286 from bedded travertines). The analytical methods ( $\alpha$  spectrometry and mass spectrometry) are  
287 described in the Appendix.

288 Banded travertine samples from Semproniano Village (SP1) and I Vignacci (VI1) are  
289 characterized by a  $^{230}\text{Th}/^{234}\text{U}$  activity ratio higher than 1 and, therefore, by ages higher than the  
290 limit of the U/Th method in  $\alpha$  spectrometry (c. 350 ka). The bedded travertine exposed on the south-  
291 western flank of the Semproniano giant vein (SP11) is characterized by a moderate detrital  
292 contamination ( $^{230}\text{Th}/^{232}\text{Th}$  activity ratio =  $7.148 \pm 0.251$ ) and by a corrected  $^{230}\text{Th}/^{234}\text{U}$  activity  
293 ratio of  $0.878 \pm 0.051$ , indicating an age of  $214 +50/-37$  ka. A subordinate carbonate vein (SP16)  
294 cutting through the Scaglia Toscana Fmt. (Tuscan Nappe) in the external south-western flank of the  
295 Semproniano giant vein is characterized by a  $^{230}\text{Th}/^{232}\text{Th}$  activity ratio of  $12.564 \pm 1.987$  and by a  
296 corrected  $^{230}\text{Th}/^{234}\text{U}$  activity ratio of  $0.641 \pm 0.064$ . Calculated age for this sample is  $104 \pm 16$  ka. A  
297 bedded travertine sample collected in the southern part of Poggio Semproniano plateau (PO2; Fig.  
298 4b) is characterized by a  $^{230}\text{Th}/^{234}\text{U}$  activity ratio of  $0.818 \pm 0.039$ . The resulting age is  $171 \pm 19$  ka.  
299 Two samples of calcite-filled veins (SP3 and SP10) cutting through the bedded travertine of Poggio  
300 Semproniano and the underlying Scaglia Toscana Fmt. are characterized by a  $^{230}\text{Th}/^{234}\text{U}$  activity  
301 ratio of  $0.340 \pm 0.052$  and  $0.299 \pm 0.023$ , respectively. The related ages are  $43 \pm 8$  ka and  $39 \pm 4$  for  
302 the SP3 and SP10 samples, respectively. A sample of bedded travertine from Poggio I Piani plateau  
303 (PP1; Fig. 4e) is characterized by a  $^{230}\text{Th}/^{234}\text{U}$  activity ratio of  $0.857 \pm 0.028$  and a resulting age of  
304  $198 \pm 18$  ka.

305 To understand the spatio-temporal growth of the Semproniano giant banded vein, we dated  
306 eleven samples from this vein along a 5m transect across the vein (Fig. 6), and one sample (SP12)  
307 from the upper part of the transect (Figs. 5e and 7) by mass spectrometry (Fig. 7 and Tables 2 and

308 S1). We obtained, ages between 86 ka to 646 ka (Fig. 7), with only one sample being older than the  
309 resolution of the method (> c. 800 ka). Radiometric ages along the transect do not vary  
310 systematically. In other words, the oldest samples are not located within the inner or external  
311 portions of the vein to indicate its antitaxial or syntaxial growth. The three oldest samples (i.e., c.  
312 646, 613, and >800 ka) occur in separate inner portions of the vein and are divided by younger  
313 carbonates. (Fig. 7). The oldest samples have larger errors caused by proximity to secular  
314 equilibrium, whereas the youngest ages are characterized by smaller errors (Table 2).

### 315 316 **3.3. C- and O-isotopes and parental fluid thermometry from O-isotopes**

317 We performed  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analyses on fifty one samples (banded and bedded travertines,  
318 calcite veins) from the Semproniano area (Tables 1 and 3). Details on the analytical procedure are  
319 provided in the Appendix. Oxygen and carbon isotopes are reported with respect to V-PDB. All  
320 analyzed samples are characterized by positive values of  $\delta^{13}\text{C}$  (between 3.2 and 10.5‰) and  
321 negative values of  $\delta^{18}\text{O}$  (between -14.6 and -7.6‰) (Table 3). Results, in particular, are clustered  
322 around 8‰ for  $\delta^{13}\text{C}$  and around -11‰ for  $\delta^{18}\text{O}$  (Fig. 8b).

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

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

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

333 characterized by  $\delta^{13}\text{C}$  values between 7.1 and 8.4‰ (V-PDB) and  $\delta^{18}\text{O}$  values between -11.5 and -  
334 10.7‰ (V-PDB).

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

337 We focused particular attention to the Semproniano giant vein by collecting two transects across  
338 it (samples SP14/03 to SP14/04 and SP14/08 to SP14/34) and three further samples in the adjacent  
339 bedded travertine (samples SP11, SP14/05, SP14/06) (Table 3). Banded travertines collected along  
340 the two transects show a wide variability. Samples from the first transect (samples SP14/03 to  
341 SP14/16), in particular, are characterized by  $\delta^{13}\text{C}$  values comprised between 5.3 and 9.7‰ (and  
342  $\delta^{18}\text{O}$  values comprised between -12.8 and -9.0‰. Samples from the second transect (samples  
343 SP14/17 to SP14/34) are characterized by  $\delta^{13}\text{C}$  values comprised between 3.2 and 10.2‰ and  $\delta^{18}\text{O}$   
344 values comprised between -12.6 and -7.6‰. Samples from the bedded travertine located along the  
345 flanks of the Semproniano giant vein are characterized by  $\delta^{13}\text{C}$  values comprised between 5.3 and  
346 9.9‰ and  $\delta^{18}\text{O}$  values comprised between -9.8 and -8.2 ‰. Samples from the two transects don't  
347 show any pattern in O and C isotopic values along the Semproniano giant vein.

348 We calculated the paleo-temperature of the mineralizing parental fluids applying the equation of  
349 Kele et al. (2015) to the entire  $\delta^{18}\text{O}$  dataset (Table 3 and Fig. 8c) and using the present  $\delta^{18}\text{O}$  of the  
350 the Saturnia spring hydrothermal waters (-6.4‰ V-SMOW), whose active source is located 9 km to  
351 the south of the Semproniano giant vein. We assume that the oxygen isotope composition of the  
352 palaeosprings was similar to those of the current Saturnia spring. The banded travertines of the  
353 Semproniano giant vein yield temperatures between  $34 \pm 2$  and  $71 \pm 7$  °C, with the majority in the  
354 range comprised between 45 and 60 °C. The bedded travertines associated with the giant vein give  
355 temperatures between  $35 \pm 2$  and  $43 \pm 3$  °C, whereas the banded travertine sample from I Vignacci  
356 sample yields a temperature of  $42 \pm 3$  °C. The Poggio Semproniano plateau samples yield  
357 temperatures of  $36 \pm 2$  and  $53 \pm 5$  °C, for the bedded travertine, and  $49 \pm 4$  and  $53 \pm 5$  °C, for the

358 calcite veins. The bedded travertine from Poggio I Piani a temperature of  $53 \pm 5$  °C. There is no  
359 correlation scheme between ages and temperature of precipitation (Fig. 8d). In particular, there is no  
360 systematic trend of decreasing temperature with younger ages of deposition.

361

### 362 **3.4. Sr- and Nd-Isotopes and rare Earth elements**

363 We performed Strontium, REE, and Yttrium (Y; REE + Yttrium = REY) concentration analysis,  
364 and Strontium and Neodymium isotope measurements to understand the subsurface circuit of  
365 hydrothermal fluids (e.g., Ederfield and Greaves, 1982; McLennan, 1989; Webb et al., 2000; Uysal  
366 et al., 2007; 2009). The analytical procedures and protocols are detailed in the Appendix; results are  
367 reported in Tables 4 and S2 and Fig. 9.

368 We observed a variable Sr concentration, comprised between 105.3 to 4956.3 mg/kg. The mean  
369 value (3200 mg/kg) is in the range of Sr contents of most travertines in central Italy (Minissale,  
370 2004). Sr-isotope ratios range from 0.708277 to 0.708527. The banded travertine from the  
371 Semproniano giant vein (SP12, SP14/18 and SP14/28), the banded travertine from I Vignacci (VII),  
372 and the calcite vein from Poggio Semproniano (SP3 and SP10) are characterized by the highest Sr  
373 concentrations, between 1125.9 and 4956.3 mg/kg. On the contrary, the bedded travertine from the  
374 flanks of the Semproniano giant vein (SP11, SP14/06, SP17) and the bedded travertines from  
375 Poggio Semproniano (SP9, PO1, PO2) are have the lowest Sr concentrations, between 105.3 and  
376 787.3 mg/kg.

377 The Nd-isotope composition of one bedded travertine from the flanks of the Semproniano giant  
378 vein (SP14/06), one banded travertine from I Vignacci (VII), and one calcite vein from Poggio  
379 Semproniano (SP3) show values comprised in a narrow range between 0.512253 and 0.512330  
380 (Table 4).

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

384 (PO1) and of calcite vein (SP3) from Poggio Semproniano. We normalized the REY concentrations  
385 against PAAS (Post-Archean Austrian Shale; [McLennan, 1989](#); [Fig. 9](#) and [Table S2](#)). The REY  
386 concentrations are highly variable ( $\Sigma\text{REE} = 0.08\text{-}18.6$ ), resulting significantly lower than PAAS  
387 ([Fig. 9](#)). The main features of REY patterns are ([Fig. 9](#)): (i) relative depletion of the light rare Earth  
388 elements (LREE = 0.1-0.71, with the exclusion of sample VI1); (ii) variable enrichment of the  
389 heavy rare Earth elements (HREE as NdN/YbN = 1.9- 0.07, according to [Webb and Kamber, 2000](#));  
390 (iii) strongly superchondritic Y/Ho ratio ( 38.3 -221.3) characterized by a huge positive Y spike in  
391 the pattern; (iv) positive Gd anomaly for sample SP14/06 and VI1; (v) consistent negative Ce  
392 anomaly ( $\text{Ce}/\text{Ce}^* = 0.30\text{-}0.94$ ; [Table S2](#)).

393

### 394 **3.5. Fluid inclusion microthermometry**

395 Fluid inclusion microthermometry is the best direct technique to understand and reconstruct the  
396 physical and chemical properties of the mineralizing fluids; however, fluid inclusion studies on  
397 travertines are rare ([Słowakiewicz 2003](#); [Gibert et al., 2009](#); [El Desouky et al., 2015](#); [Raimondi et](#)  
398 [al., 2015](#)) due to some difficulties inherent to travertines such as: (1) scarce occurrence and small  
399 size of inclusions ([Pentecost 2005](#)); (2) inclusion metastability often causing failing in bubble  
400 nucleation upon cooling from the trapping conditions to room temperature ([Diamond, 2003](#)); and  
401 (3) inclusion anelastic stretching and decrepitation that can cause difficulties in performing  
402 microthermometric analyses; (4) double refraction of calcite ([Bodnar, 2003](#)).

403 Unfortunately only one sample contained fluid inclusions suited for microthermometry ([Fig.](#)  
404 [10a](#)). It consists of elongate calcite crystals, containing numerous two-phase (Liquid+Vapor or  
405 L+V) liquid-rich fluid inclusions 5 to 50  $\mu\text{m}$  long and a constant V/L ratio for all the analyzed  
406 structures ([Figs. 10b-10d](#)). Fluid inclusions occur both as primary isolated and as pseudosecondary  
407 in small planes that do not cross the crystal rims. The inclusion shape is variable. We recognized, in  
408 particular, two main types of inclusions: (1) flat irregular ([Figs. 10c and 10d](#)) and (2) polygonal ([Fig.](#)  
409 [10b](#)).

410 As it is shown in Fig 10(f),  $T_{m_{ice}}$  values (i.e., the temperature of ice melting from which salinity  
411 is deduced) range between 0.0 and +4.8 °C, but are mostly concentrated around 0-1 °C. Being very  
412 small systems, fluid inclusions may exhibit metastable behaviour and metastable ice crystals can  
413 persist at temperatures as high as +6,5°C (Roedder, 1967) (Fig. 10f). From these data we can  
414 conclude that the fluid consists of pure water. Homogenization temperature ( $T_h$ ) values range  
415 between 57 and 105°C, with a maximum around 70-90 °C (Fig. 9g). No pressure correction is  
416 required for these homogenization temperature values as the analyzed sample precipitated in a very  
417 shallow environment represented by the giant vein. Our microthermometric results (Fig. 10e) are  
418 consistent with the ones obtained by Capezzuoli et al. (2013), who obtained temperatures between  
419 65 and 95 °C and 0.2 wt% NaCl eq.

420

## 421 **4. Discussion**

### 422 ***4.1. A long-lived giant vein***

423 The thick and continuous sequence of travertine sparry subvertical bands (the giant vein) in the  
424 Semproniano village accompanied by bedded travertine on its flanks and by veins in the Tuscan  
425 Nappe host rock suggest that the Semproniano giant vein represent the central portion of a fossil  
426 fissure ridge travertine larger than, but similar to those known in several other hydrothermal areas  
427 such as Turkey (e.g. Denizli Basin; Altunel and Hancock 1993a,1993b, 1996; Uysal et al.,  
428 2007,2009; De Filippis et al., 2012, 2013a), U.S.A. (e.g. Mammoth Hot Springs and Bridgeport;  
429 Hancock et al., 1999; De Filippis and Billi, 2012), Italy (e.g. Rapolano, Castelnuovo dell'Abate, and  
430 Tivoli; Guo and Riding, 1999; Brogi, 2004a; Brogi and Capezzuoli, 2009; De Filippis et al., 2013b;  
431 Rimondi et al., 2015), and elsewhere (De Filippis et al., 2012). Most fissure ridge travertines are  
432 volumetrically dominated by bedded travertines occurring mainly along the flanks and partially  
433 along the axial portion of the ridges, whereas the banded travertine is normally confined within a  
434 narrow band along the ridge axis. In the Semproniano case, although we have no record on the  
435 amount of eroded bedded travertine over time (since about 650 ka), the ridge seems to be

436 characterized by a predominance of banded travertine (i.e., the giant vein) with only small slabs (at  
437 present) of bedded travertine on its flanks.

438 We consider the Semproniano vein as a giant structure characterized by a minimum thickness of  
439 50 m larger than any one we found in the published literature. Thus the Semproniano giant vein is  
440 probably the thickest continuous vein (i.e., no relics of host rock are interspersed across the  
441 Semproniano giant vein) so far documented in the geological literature. Very thick veins (i.e.,  
442 banded travertine) are common in many fissure ridge travertines (e.g. [Uysal et al., 2007, 2009](#); [De  
443 Filippis et al., 2012](#)), but their thickness (at least that of the continuous portion of banded travertine)  
444 is normally at least one order of magnitude smaller than that of Semproniano. For instance, the  
445 Akköy fissure ridge in the Denizli basin (Turkey) is known as one of the largest and thickest fissure  
446 ridges on the Earth. This fossil structure is well visible in its inner portion thanks to the presence of  
447 numerous quarries. In the quarries, the Akköy ridge is characterized by inner veins that are less than  
448 10 m thick (i.e., considering only continuous veins; [De Filippis et al., 2012](#)).

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

455 We interpret the giant thickness of the Semproniano vein as due to two main factors: (1) the  
456 shallow emplacement of this vein and therefore the limited confining pressure, which would have  
457 otherwise limited the lateral expansion of the vein in a deeper case. Although we do not know the  
458 exact depth of formation, most veins along fissure ridge travertines are typically formed only at a  
459 few meters depth at the most ([De Filippis et al., 2012, 2013a](#)); (2) the second factor is the unique  
460 longevity of the hydrothermal activity, which lasted at least 600 ka. This is much longer than what

461 is reported by other studies of fissure ridge travertines which are typically around  $10^4$  a (e.g.,  
462 [Altunel and Karabacak, 2005](#); [Uysal et al., 2007, 2009](#)).

463

#### 464 **4.2. Rate and mode of vein growth**

465 The Semproniano giant vein grew between about >650 and 85 ka. Considering 50 m as the vein  
466 total thickness, the average growth rate around can be estimated to be  $8 \times 10^{-2}$  mm/a. The three  
467 inner sectors of the giant vein can also be considered separately according to age groups: sector A,  
468 between samples SP14/25 and SP14/23; sector B, between samples SP14/23 and SP14/20; and  
469 sector C, between samples SP14/20 and SP14/18 ([Fig. 7b](#)). With distance between the dated  
470 samples in each sector and the age difference, we obtain average growth (i.e., thickening) rates of  
471 about  $7 \times 10^{-3}$ ,  $2 \times 10^{-2}$ , and  $6 \times 10^{-3}$  mm/a for sectors A, B, and C, respectively. We therefore  
472 assume that the Semproniano giant vein grew with average rates ranging between ca.  $10^{-2}$  and  $10^{-3}$   
473 mm/a. These rates are consistent with previously-estimated rates for banded travertines within  
474 fissure ridges located elsewhere (about  $10^{-2}$  mm/a; [Uysal et al., 2007](#); [Mesci et al., 2008](#); [Gratier et](#)  
475 [al., 2012](#); [De Filippis et al., 2013a](#); [Frery et al., 2015](#)). This result confirm that the giant thickness of  
476 the Semproniano vein is not related to a fast growth rate but rather to the duration of hydrothermal  
477 activity, which is significantly larger than veins in other fissure ridges (e.g., [Altunel and Karabacak,](#)  
478 [2005](#); [Uysal et al., 2007, 2009](#)).

479 The age distribution along the transect shows that the oldest samples are located neither at the  
480 lateral ends of the giant vein nor at its central part indicating that the vein did not grow in a  
481 syntaxial or antitaxial fashion ([Bons et al., 2012](#)). The three oldest samples (i.e., c. 646, 613, and  
482 >800 ka; [Fig. 7b](#)) occur in separate inner portions of the vein showing that it grew asymmetrically  
483 and ataxially ([Passchier and Trouw, 1996](#); [Bons et al., 2012](#)) with no systematic growth direction  
484 and no systematic age sequence. Based on our data, we hypothesize an accordion-like mode of  
485 growth through multiple events of crack-and-seals pulses, which is well supported by the U/Th ages.  
486 This growth mode for the Semproniano giant vein is somewhat different from models proposed for

487 fissure ridge structures (e.g., [Hancock et al., 1999](#); [Brogi and Capezzuoli, 2009](#)) characterized by  
488 banded travertine forming injection veins and sill-like structures filling diffused fractures within the  
489 bedded travertine. The Semproniano giant vein, in fact, defines a singular structure that grew within  
490 the same horst rock over a long time, maintaining the same orientation.

491

#### 492 **4.3. Hydrothermal parental fluids**

493 C- and O-isotope data show that the Semproniano giant vein is of thermogene origin ([Pentecost,](#)  
494 [2005](#)). All analyzed samples are characterized by positive  $\delta^{13}\text{C}$  and negative  $\delta^{18}\text{O}$  values ([Table 3,](#)  
495 [Fig. 7b](#)), indicating mixing between hydrothermal parental fluids and meteoric waters and with a  
496 significant contribution of  $\text{CO}_2$  originating from limestone decarbonation ([Gonfiantini et al., 1968;](#)  
497 [Guo et al., 1996; Billi et al., 2007](#)). Our stable isotope data are in the range typical of thermogene  
498 travertines deposited by present-day thermal springs of central Italy ([Minissale, 2004; Gandin and](#)  
499 [Capezzuoli, 2008](#)).

500  $\delta^{13}\text{C}$  values of travertines have been used to determinate the original signal of  $\delta^{13}\text{C}_{\text{CO}_2}$  applying  
501 the empirical equation of [Panichi and Tongiorgi \(1976\)](#) and the theoretical equation of [Bottinga](#)  
502 [\(1968\)](#) ([Table 3](#)). According to the equation of [Panichi and Tongiorgi \(1976\)](#), the  $\delta^{13}\text{C}_{\text{CO}_2}$  values are  
503 comprised between -6.7 and 2.1 ‰ (V-PDB), while according to the equation of [Bottinga \(1968\)](#),  
504 the  $\delta^{13}\text{C}_{\text{CO}_2}$  values are comprised between -5.4 and 3.5 ‰ (V-PDB). Those results confirm a mixing  
505 between  $\text{CO}_2$  originated from limestone decarbonation with  $\text{CO}_2$  of igneous origin (e.g. [Turi, 1986;](#)  
506 [Minissale, 2004; Kele et al., 2011](#)).

507 The O-isotope composition allowed us to estimate the parental fluid temperatures using the  
508 water oxygen isotopic composition of modern springs. In the case of the Semproniano giant vein,  
509 calculated temperatures span between about  $34 \pm 2$  and  $71 \pm 7^\circ\text{C}$ , with the majority of data  
510 comprised between 46 and  $60^\circ\text{C}$  ([Table 3, Fig. 8c](#)). The validity of these temperature estimates are  
511 confirmed by the fluid inclusion microthermometric data on sample SP12 yielding temperatures  
512 between 70 and  $90^\circ\text{C}$  ([Fig. 10](#)). This supports the assumption that the oxygen isotope composition

513 of the hydrothermal fluid did not change substantially through time. Fluid inclusion data also show  
514 that the giant vein parental fluid was constituted by almost pure water.

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

523 The Sr- and Nd-isotopes as well as the REE patterns help to characterize the origin of the  
524 hydrothermal fluids. The rather homogeneous Sr- and Nd-isotope values are indicative of a unique  
525 reservoir for the deposition of travertines and calcite veins. Sr- and Nd- isotope values are different  
526 from isotopic signature of Mt. Amiata volcanic rocks (Conticelli et al. 2015). In particular, our Sr-  
527 isotope values are in the range of those obtained for the Mesozoic sedimentary units of central Italy  
528 (e.g., Barbieri et al., 1979; Cortecci and Lupi, 1994; Barbieri and Morotti, 2003; Gasparrini et al.,  
529 2013) and for the hydrothermal springs of Saturnia (Barbagli et al., 2013). This suggests no  
530 contamination through volcanic units during underground circulation of these fluids. This  
531 interpretation is compatible with the REE patterns that are similar to those obtained from the  
532 Tuscan Nappe limestone from the Larderello-Travale geothermal area (Möller et al., 2003; Fig. 9).  
533 Accordingly, we consider the Mesozoic limestones of the Albegna area (e.g., Bonciani et al., 2005;  
534 Brogi, 2008; Guastaldi et al., 2014) as the main reservoir of the hydrothermal system and the  
535 probable source for the chemical signature of the studied carbonates. Eventually, the best scenario  
536 explaining the entire hydrothermal fluid circuit should involve variable mixing of meteoric waters  
537 with fluids characterized by water-rock isotopic exchange similar to the broad field of endogeneous  
538 fluids (e.g., Crossey et al., 2009).

539

#### 540 **4.4. Estimation of CO<sub>2</sub> outflow**

541 Minimum value of total CO<sub>2</sub> volume leaked during the formation of the Semproniano giant vein  
542 can be estimated from the volume of CaCO<sub>3</sub> precipitated (Crossey et al., 2009; Frery, 2012;  
543 Karlstrom, 2013). It has been shown that the volume of leaked CO<sub>2</sub> precipitated in travertine/vein  
544 deposits is only a minor part of the total leakage, representing between 6.6% and 10% (Shipton et  
545 al., 2005) of the total dissolved CO<sub>2</sub>. According to Frery (2012), it is possible to calculate only the  
546 minimum value of CO<sub>2</sub> leakage during CaCO<sub>3</sub> vein formation for two reasons: (i) the proportion  
547 between precipitated CO<sub>2</sub> and total leaked CO<sub>2</sub> includes only the dissolved part of the CO<sub>2</sub> at the  
548 surface, thus disregarding the CO<sub>2</sub> escaping as free phase (i.e., degassing); (ii) after formation, the  
549 vein or travertine deposit may have undergone erosional processes, which are difficult to accurately  
550 quantify.

551 For fossil travertines or CaCO<sub>3</sub> veins, the total mass of precipitated CO<sub>2</sub> ( $m_{CO_2}^{precipitated}$ ) can be  
552 calculated using the calcium carbonate precipitation equation:

$$553 \quad m_{CO_2}^{precipitated} = \rho_{CaCO_3} \cdot V_{CaCO_3} \{M_{CO_2} | M_{CaCO_3}\} \quad (\text{Eq. 1})$$

554 where  $\rho_{CaCO_3}$  and  $\{M_{CO_2} | M_{CaCO_3}\}$  are considered as constant parameters:  $\rho_{CaCO_3} = 2.7 \cdot 10^3 \text{ kg/m}^3$ ;  
555  $M_{CO_2} = 44 \text{ g/mol}$ , and  $M_{CaCO_3} = 100.1 \text{ g/mol}$ .

556 Based on field observations, we estimate the volume of the Semproniano giant vein assuming a  
557 length of 500 m and a width of 50 m. for the thickness of the vein, we consider two alternative end  
558 members: 10 m (the observable vein exposed in the field), and 50 m (estimated through geological  
559 cross-sectioning; Fig. 2b). For a thickness of 10 m, the estimated total mass of CO<sub>2</sub> leakage are 3 x  
560 10<sup>6</sup> and 5 x 10<sup>6</sup> tons, for total dissolved CO<sub>2</sub> masses of 10 and 6.6%, respectively. For a depth of 50  
561 m 14 x 10<sup>6</sup> and 22 x 10<sup>6</sup> tons are calculated. Collectively, all these values provide a CO<sub>2</sub> leakage  
562 between 5 ton/a and 37 tons/a over the 600 ka longevity of the Semproniano giant vein,  
563 corresponding to a CO<sub>2</sub> flux between 5 x 10<sup>6</sup> mol a<sup>-1</sup> km<sup>-2</sup> and 3 x 10<sup>7</sup> mol a<sup>-1</sup> km<sup>-2</sup>. These estimates

564 are of the same order of magnitude of measured average CO<sub>2</sub> flux discharged by present-day  
565 thermal springs in central Italy (between  $1 \times 10^4 \text{ mol a}^{-1} \text{ km}^{-2}$  and  $5 \times 10^7 \text{ mol a}^{-1} \text{ km}^{-2}$ , [Minissale,](#)  
566 [2004](#); [Fron dini et al., 2008](#)) and it is two order of magnitude lower than the CO<sub>2</sub> flux ( $3.7 \times 10^9 \text{ mol}$   
567  $\text{a}^{-1}$ ) in present-day thermal springs on the Colorado Plateau, USA ([Crossey et al., 2009](#)). For  
568 comparison, the estimated CO<sub>2</sub> flux during the formation of the Semproniano giant vein is about  
569 four order of magnitude lower than the deeply sourced (endogenic) CO<sub>2</sub> in non-volcanic areas of  
570 Italy ( $10^{11} \text{ mol a}^{-1}$ , [Rogie et al., 2000](#)) and represent about one millionth of the present-day CO<sub>2</sub>  
571 released from volcanic areas at the global scale ([Gerlach, 2011](#)).

572

#### 573 **4.5. Paleoclimate influence**

574 To determine a possible influence of paleoclimate on the growth of the Semproniano giant vein,  
575 in [Fig. 11](#) we matched our U/Th ages ([Tables 2 and S1](#)) with Quaternary glacial cycles, using the  
576 curve extracted from the deep sea oxygen isotope trend elaborated by [Zachos et al. \(2001\)](#), and the  
577 pollen record of the Valle di Castiglione, located about 150 km to the south of the study area ([Fig.](#)  
578 [1a](#)), elaborated by [Tzedakis et al. \(2001\)](#).

579 We note that, except for two points, most samples from the giant vein fall within the inter-glacial  
580 stages. Also the host rock of the giant vein and the bedded travertine on the vein flanks match well  
581 with interglacial stages ([Fig. 11](#)). It is noteworthy that six samples fall within marine isotope stages  
582 MIS 5 and MIS 7, which are suggested to be humid times by the pollen curve ([Fig. 11](#)).

583 The dating, thus suggests that the Semproniano giant vein formed preferentially during warm  
584 and humid climate periods characterized by high stands of the water table promoting a greater fluid  
585 discharge. Similar patterns have been suggested for other Quaternary travertine deposits (e.g.,  
586 [Dramis et al., 1999](#); [Frank et al., 2000](#); [Rihs et al., 2000](#); [Soligo et al., 2002](#); [Pentecost, 2005](#); [Luque](#)  
587 [and Julià, 2007](#); [Faccenna et al., 2008](#); [Kampman et al., 2012](#); [Priewisch et al. 2014](#)).

588 This scenario is different from the one proposed by Uysal et al. (2007, 2009) for banded  
589 travertines precipitated in co-seismic fissures of the Denizli basin (Turkey) which was based on  
590 U/Th ages and REE data. These authors, proposed that carbonate precipitation was controlled by  
591 seismic-related CO<sub>2</sub> exsolution from a depressed water table during glacial stages. Ages obtained  
592 for Turkish travertines by Özkul et al., (2013) and Toker et al., (2015) show that deposition was  
593 active during glacial and interglacial time, indicating that travertine precipitation during late  
594 Quaternary was not strongly influenced by climatic variation. In particular, we found similarities  
595 with Toker et al., (2015) whose recognized that the highest amount travertine precipitation in  
596 Kocabas (Denizli basin, Turkey) occurred during MIS 5 (interglacial) and proposed that active fault  
597 systems favored the rise of hydrothermal fluids and travertine deposition,

598 Finally, our results for the Semproniano giant vein suggest that high stand of the water table was  
599 a primary influencing factor in the vein formation.

600

#### 601 ***4.6. Relationships between the giant vein and nearby travertine deposits: the fluid circuit***

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

608 U/Th ages for the bedded travertine samples from the plateaus (Table 2),  $171 \pm 14$  ka for Poggio  
609 Semproniano,  $198 \pm 18$  ka for Poggio I Piani) indicate that the formation of the two plateaus was at  
610 least in part contemporaneous with that of the Semproniano giant vein. Moreover, also the activity  
611 of the nearby Mt. Amiata volcanic district (300-190 ka, Cadoux and Pinti, 2009; 300-225 ka,  
612 Laurenzi et al., 2015) was partly contemporaneous with the CaCO<sub>3</sub> mineralizations of the

613 Semproniano area, with the giant vein being partly older and partly younger than the volcanic  
614 district.

615 From previous studies we know that while fissure ridges such as the Semproniano giant vein are  
616 aggradational systems that tend to grow vertically due to the scarcity of feeding fluids (i.e., CaCO<sub>3</sub>  
617 precipitates contributing to the vertical grow of the deposit), travertine plateaus are progradational  
618 systems where the abundance of feeding fluids contribute to the horizontal grow (progradation) of  
619 the deposit (Faccenna et al., 2008; De Filippis et al. 2013a). We also know that fissure ridges and  
620 plateaus can coexist, in space and time, in geothermal areas where the abundance of geothermal  
621 fluids primarily feeds the plateau whereas the fissure ridge(s) constitutes a remote apophysis of the  
622 plateau with a scarcity of fluids that provokes the aggradation development of the fissure ridge (e.g.,  
623 Tivoli travertines; De Filippis et al., 2013b).

624 The possible scenario for the genesis of the Semproniano giant travertine vein is a structurally-  
625 controlled pathway (faults and fractures) for the circulating mineralising fluids during the  
626 Quaternary. Dominant meteoric fluids interacted with the carbonate reservoir of the Mt. Amiata  
627 volcano and were heated at depth, where the heat source is maintained by the regional geothermal  
628 anomaly (Fig. 12a). In this scenario, the Semproniano giant vein resulted as an epithermal fluid  
629 discharge area after convective circulation of the CO<sub>2</sub>-enriched hydrothermal fluids (Fig. 12b). In  
630 particular, we can assume a fluid pressure cycling in a long-lived fault-valve behavior setting (Cox  
631 et al., 2001; Sibson, 2004; Cox, 2010), assisted by fracture network generation and maintenance  
632 that could have been provided by the well-known N-S-striking fault zone system active during  
633 Quaternary time in the Mt Amiata-Albegna basin region (Zanchi and Tozzi, 1987; Brogi, 2004b;  
634 Bellani et al., 2004; Brogi and Fabbrini, 2009). In this model, the Semproniano giant vein (i.e., the  
635 fissure ridge) is interpreted as an apophysis of a large geothermal field characterized by the  
636 deposition of big travertine plateaus.

637

638 **Conclusions**

- 639 (1) The thickest continuous vein hitherto documented in the literature (50 m) is found and studied  
640 within a fissure ridge travertine exposed in the Semproniano village, in the hydrothermal area  
641 surrounding the Pleistocene Mt. Amiata volcano in southern Tuscany, Italy.
- 642 (2) The thickness of the Semproniano vein is connected with its probable shallow emplacement and  
643 with the unusual longevity of the hydrothermal activity between at least 650 and 85 ka.
- 644 (3) The epithermal fluid supply feeding the Semproniano giant vein is not directly connected with  
645 the main volcanic paroxysmal activity of the Mt. Amiata volcano (which is younger than the  
646 early growth of the vein), rather with the positive geothermal anomaly associated with its pre-  
647 eruptive stages (Cadoux et al., 2009) through structurally-controlled fluid pathways which  
648 created and maintained active convection and supply of CO<sub>2</sub>-enriched meteoric fluids.
- 649 (5) The growth of the Semproniano giant vein was modulated by by Pleistocene climate oscillations,  
650 with warm humid interglacial periods being the preferential phases of vein accretion, due to the  
651 higher fluid discharge.
- 652 (6) Structures such as the Semproniano giant vein can be used to estimate the long-term release of  
653 CO<sub>2</sub> from geothermal/volcanic provinces, thus improving our knowledge of the CO<sub>2</sub> cycle on  
654 Earth.

655

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664

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1081

1082 **Appendix: geochemical methods**

1083 *U/Th dating*

1084 As reported in [Tables 2](#) and [S1](#), we performed U/Th dating analyses using two different  
1085 methods, namely (1) through  $\alpha$  spectrometry performed at the Laboratorio di Geochimica  
1086 Ambientale e Isotopica of Roma Tre University (Italy), or (2) through a Thermo Electron Neptune  
1087 multi-collector inductively coupled mass spectrometer (MC-ICP-MS) ([Shen et al., 2012](#)) hosted at  
1088 the High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC) of the  
1089 National Taiwan University, Taipei (Taiwan ROC).

1090 For MC-ICP-MS dating, we covered about 0.05 g of each sample with H<sub>2</sub>O and dissolved it  
1091 gradually with double distilled 14 N HNO<sub>3</sub>. After dissolution, we added a <sup>229</sup>Th-<sup>233</sup>U-<sup>236</sup>U spike  
1092 ([Shen et al., 2003](#)) to the sample, followed by 10-20 drops of HClO<sub>4</sub> to clear the organic matter. We  
1093 then followed the chemical procedure described in [Shen et al. \(2003\)](#) for the separation of Uranium  
1094 and Thorium. We calculated the age correction using an estimated atomic <sup>230</sup>Th/<sup>232</sup>Th ratio of  $4 \pm 2$   
1095 ppm. These latter values are the ones typical for a material at secular equilibrium with the crustal  
1096 <sup>232</sup>Th/<sup>238</sup>U value of 3.8. We arbitrarily assumed a 50% error.

1097 For  $\alpha$  spectrometry dating, we dissolved about 60 g of each sample in 7 N HNO<sub>3</sub> and filtered the  
1098 solution to separate the leachates from the insoluble residue. We heated the leachate at 200 °C after  
1099 adding a few millilitres of hydrogen peroxide to clear the organic matter, and then spiked the  
1100 solution with a <sup>228</sup>Th-<sup>232</sup>U tracer. We extracted the isotopic complexes of U and Th following the  
1101 procedure described in [Edwards et al. \(1988\)](#) and then analyzed the solution by an alpha-counted  
1102 using high-resolution ion-implanted Ortec silicon-surface barrier detectors. Due to the presence of  
1103 non-radiogenic <sup>230</sup>Th related to detrital <sup>232</sup>Th, ages obtained for samples with a <sup>230</sup>Th/<sup>232</sup>Th activity  
1104 ratio less than or equal to 80 required a proper correction, which we performed assuming that all the  
1105 detrital Th had an average <sup>230</sup>Th/<sup>232</sup>Th activity ratio of  $0.85 \pm 0.36$  ([Wedepohl, 1995](#)), which is the  
1106 crustal thorium mean composition. We then calculated the ages using ISOPLOT, a plotting and  
1107 regression program for radiogenic-isotope data ([Ludwig, 2003](#)).

1108

1109 ***C- and O-isotope determination***

1110 The isotopic composition of carbonate was measured according to the method described in  
1111 detail in [Breitenbach and Bernasconi \(2011\)](#). Briefly, approximately 100 µg of powder were filled  
1112 in 12 ml Exetainers (Labco, High Wycombe, UK) and flushed with pure Helium. The samples were  
1113 reacted with 3-5 drops of 100% phosphoric acid at 70°C with a ThermoFisher GasBench device  
1114 connected to a ThermoFisher Delta V mass spectrometer. The average long term reproducibility of  
1115 the measurements based on replicated standards was ±0.05‰ for δ<sup>13</sup>C and ±0.06‰ for δ<sup>18</sup>O. The  
1116 instrument is calibrated with the international standards NBS19 (δ<sup>13</sup>C= 1.95 and δ<sup>18</sup>O = -2.2‰) and  
1117 NBS18 (δ<sup>13</sup>C= -5.01 and δ<sup>18</sup>O = -23.01‰). The isotope values are reported in the conventional  
1118 delta notation with respect to VPDB (Vienna Pee Dee Belemnite).

1119

1120 ***Thermometry of mineralizing parental fluids from O-isotopes***

1121 We calculated the paleo-temperature of mineralizing parental fluids using the equation of [Kele](#)  
1122 [et al. \(2015\)](#) specifically developed for travertine parental fluids and calibrated through clumped  
1123 isotope thermometer. This empirical equation is expressed as:

1124

$$1125 \quad 1000 \ln \alpha_{(\text{calcite-water})} = (20 \pm 2) 1000/T - (36 \pm 7) \quad (\text{Eq.3})$$

1126

1127 Where (1)  $\alpha_{(\text{calcite-water})} = (\delta^{18}\text{O}_{\text{calcite}} + 1000) / (\delta^{18}\text{O}_{\text{water}} + 1000)$ , (2) T is the temperature of the  
1128 mineralizing CaCO<sub>3</sub>-rich fluids expressed in K and (3) δ<sup>18</sup>O<sub>calcite</sub> and δ<sup>18</sup>O<sub>water</sub> are expressed in  
1129 parts ‰ relative to V-SMOW. As benchmark (δ<sup>18</sup>O<sub>water</sub>), we measured and used the present δ<sup>18</sup>O  
1130 isotopic value from the Saturnia spring hydrothermal waters (-6.4‰ V-SMOW), whose active  
1131 source is located 9 km to the south of the Semproniano giant vein. We assume that the oxygen  
1132 isotope composition of the palaeosprings was similar to those of the current springs.

1133

1134 ***Sr- and Nd-isotope and REE determination***

1135 We determined the Strontium (Sr) and Neodymium (Nd) isotope ratios as well as Strontium,  
1136 rare Earth elements (REE) and Yttrium (Y) concentrations on fragments of handpicked travertine  
1137 and vein samples. We crushed the chips of travertine in a stainless steel mortar and then we  
1138 dissolved about 200 mg of each sample with ultrapure HNO<sub>3</sub> (3%). We splitted 100 ml of solution  
1139 from each sample into two aliquots. We used one of the two aliquots for REE, Y, and Sr  
1140 concentrations and the other aliquot for Sr and Nd isotopes. The aliquot for REE, Y and Sr  
1141 concentration were analyzed via ICP-MS (Agilent mod. 7500ce) equipped with collision cell at the  
1142 Chemical Laboratory of Istituto di Chimica Agraria ed Ambientale, Catholic University of Piacenza  
1143 and Cremona (Italy). We evaporated the aliquot for isotope analysis, converted it into chloride form,  
1144 and loaded it onto standard Bio-Rad AG50W-X12 cation exchange resin to separate Sr from matrix.  
1145 The very low REE and Y (REY) contents in travertine required the procedure of [Sharma and](#)  
1146 [Wasserburg \(1996\)](#): we added ultrapure NH<sub>3</sub> to the solution diluted with MilliQ water up to ionic  
1147 strength of about 1.0 to shift pH to 9.0 for precipitating REY with Fe oxide-hydroxides. We then  
1148 mixed both the precipitate and the supernatant with a vortex overnight and separated from each  
1149 other by filtration. We dissolved the oxide-hydroxides with 4M HCl and separated them from the  
1150 matrix via ion-exchange chromatography. We separated Nd from the other REE with Ln. Spec resin  
1151 (Triskem-international) following the procedure of [Pin and Zalduegui \(1997\)](#).

1152 We carried out the isotopic analyses at Istituto di Geologia Ambientale e Geoingegneria –  
1153 Consiglio nazionale delle Ricerche (IGAG-CNR) laboratory c.o. Dipartimento di Scienze della  
1154 Terra, Sapienza University of Rome (Italy) using a FINNIGAN MAT 262RPQ multicollector mass  
1155 spectrometer. We loaded all samples on a Re double filament as nitrate and analyzed them in static  
1156 mode. We normalized Sr analyses to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . We fixed Sr analytical blank at 1ng.  
1157 Internal precision (“within-run” precision) of a single analytical result is given as two standard error  
1158 of the mean (2se) and is obtained as a mean of more than 200 ratios collected on each sample with a  
1159 stable beam of 2.0 V.

1160 Repeated analyses of NIST-987 during the period of the analyses gave a mean value of  
1161  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710235 \pm 9$  (n = 20) and La Jolla  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511851 \pm 10$  (n=20),  $^{146}\text{Nd}/^{144}\text{Nd}$   
1162 normalized to 0.7219. Total procedural blanks were below 2 ng of Sr and 1 ng of Nd for all the  
1163 samples. The measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are presented as fractional deviation in parts in  $10^4$  ( $\epsilon$ -  
1164 units) from  $^{143}\text{Nd}/^{144}\text{Nd}$  in a Chondritic Uniform Reservoir (CHUR) as measured today:

$$1165 \quad \epsilon_{\text{Nd}(0)} = [({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}} / ({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{CHUR}} - 1] \times 10^4 \quad (\text{Eq.4})$$

1166 where  $({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}}$  is the ratio measured in the sample today and  $({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{CHUR}}$  is the  
1167 ratio in the reference reservoir today, i.e. 0.511847 (DePaolo and Wasserburg, 1976).

1168

### 1169 ***Fluid inclusion analysis***

1170 We performed microthermometric measurements at Istituto di Geologia Ambientale e  
1171 Geoingegneria – Consiglio nazionale delle Ricerche (IGAG-CNR) Fluid Inclusion Laboratory c/o  
1172 Dipartimento di Scienze della Terra, Sapienza University of Rome (Italy), using a freezing-heating  
1173 stage Linkam THMSG600 (from -196 to +600 °C). The stage is adapted to a Nikon Optiphot-Pol  
1174 transmitted-light microscope equipped with long-working distance objectives (5X, 10X, 20X, and  
1175 40X) and a video camera. We performed the analysis of fluid inclusions on a 150  $\mu\text{m}$  thick double-  
1176 polished slice of calcite vein (Fig. 9). Due to the physical properties of calcite minerals, we took  
1177 particular care in maintaining as low as possible the temperature during grinding, polishing, and, in  
1178 general, during all the sample preparation (Goldtsein and Reynolds, 1994; Bodnar, 2003). A low-  
1179 temperature sample preparation is fundamental to avoid phenomena of stretching and decrepitation  
1180 of the inclusions, which may affect the microthermometric measurements. In those fluid inclusions  
1181 where decrepitation and stretching phenomena due to the volume expansion during ice formation  
1182 (Bodnar, 2003) were visible, we perform  $T_{\text{m,ice}}$  measurements separately from  $T_{\text{h}}$   
1183 measurements. Salinity contents (expressed in wt% NaCl eq.) of fluid inclusions has been  
1184 calculated through the  $T_{\text{m,ice}}$  values using the equation proposed by Bodnar and Vityk (1994). Data  
1185 reproducibility is of  $\pm 0.2$  °C for cooling runs and of  $\pm 1$  °C for heating runs.

1186 **Figure Captions**

1187

1188 **Figure 1. (a)** Schematic map of Italy showing the Apennines fold-thrust belt and the area affected  
1189 by crustal extension at the rear (west) of the belt. This latter area includes Tuscany, where the study  
1190 area (Semproniano, upper Albegna basin, southern Tuscany) is located. **(b)** Geological map of the  
1191 southern Tuscany and northern Latium regions showing the main geothermal fields and travertine  
1192 deposits (including fissure ridges).

1193

1194 **Figure 2. (a)** Structural geological map of the study area (Semproniano area in the upper Albegna  
1195 basin) and **(b)** related geological cross-sections. The map is based on and partly redrawn from the  
1196 geological map at the 1:10,000 scale available online at [www.regione.toscana.it/-/geologia](http://www.regione.toscana.it/-/geologia).

1197

1198 **Figure 3. (a)** Northward panoramic view of the study area with localization of the studied travertine  
1199 deposits that are differentiated by morphology. **(b)** Northward panoramic view of the Semproniano  
1200 ridge (i.e., Semproniano giant vein). Tracks of geological cross-sections (Figs. 2b and 6) are also  
1201 shown.

1202

1203 **Figure 4. (a)** Southward panoramic view of Poggio i Piani and Poggio Semproniano travertine  
1204 plateaus. The Poggio i Piani plateau lies on top of the Scaglia Toscana Fmt. (belonging to the non-  
1205 metamorphic succession of the Tuscan Domain) whereas the Poggio Semproniano plateau lies on  
1206 top of Plio-Quaternary marine deposits. **(b)** Southern margin of the Poggio Semproniano travertine  
1207 plateau. **(c)** Sub-horizontal travertine beds forming the Poggio I Piani plateau. **(d)** Detail of a  
1208 laminated bedded travertine from Poggio I Piani plateau. **(e)** Close-up view of the bedded travertine  
1209 occurring at Poggio i Piani.

1210

1211 **Figure 5. (a)** Panoramic view of the Semproniano giant vein and travertine plateau (Poggio  
1212 Semproniano). **(b)** Attitude of the sparry bands (banded travertine) forming the Semproniano giant  
1213 vein (NE flank). This exposure is located below the fortress of the Aldobrandeschi family (X  
1214 century) in the Semproniano village. **(c)** The Semproniano giant vein (banded travertine) is mainly  
1215 oriented NW-SE and characterized by high dip values (see the stereoplot: Schmidt net, lower  
1216 hemisphere, showing poles to travertine subvertical bands forming the giant vein). **(d)** Detail from  
1217 the Semproniano giant vein (banded travertine) with indication of the vein growth. **(e)** The central  
1218 part of the Semproniano giant vein shows a V-like shape and is characterized by a rhythmic  
1219 sequence of crystallized subvertical bands of sparry carbonate. Sample SP12, used for fluid  
1220 inclusion analysis, was collected here. **(f)** Spatial relationships between banded and bedded  
1221 travertine along the flank of the Semproniano giant vein. **(g)** Sub-horizontal, bedded travertine  
1222 exposed on the south-western flank of the Semproniano giant vein. **(h)** Sub-horizontal, bedded  
1223 travertine cut through by bedded parallel travertine veins (Semproniano village). **(i)** Bedded  
1224 travertine fabric characterized by laminations, shrubs, and karst-dissolution cavities (Semproniano  
1225 village). **(j)** and **(k)** Travertine veins cutting through carbonate rocks (Tuscan Domain) along the  
1226 SW flank of the Semproniano giant vein. Cross-cutting relationships between travertine veins show  
1227 multiple phases of veining.

1228

1229 **Figure 6. (a)** Panoramic view of the Semproniano-Poggio Semproniano area where the traces of the  
1230 main fault systems (*ca.* E-W- and N-S-striking) are indicated. The stereoplots (Schmidt net, lower  
1231 hemisphere) show attitude of the measured structural features. **(b)** The E-W-striking fault system  
1232 affecting the bedded travertine at Poggio Semproniano is characterized by meter-thick damage zone  
1233 and narrowly-spaced fault surfaces. **(c)** Fault surfaces are equipped with oblique- to strike-slip  
1234 striations (pitch is generally higher than  $160^\circ$  or lesser than  $20^\circ$ ; see the stereoplot). Right-lateral  
1235 strike-slip kinematics has been documented for this fault system. **(d)** The N-S-striking fault across  
1236 the banded travertine of the Semproniano village is defined by a half-meter-thick damage zone and

1237 secondary fracture network. Extensional kinematics (associated to a left-lateral movement) has been  
1238 documented for this fault system.

1239

1240 **Figure 7.** (a) Photomosaic (above) and related line drawing (below) of the Semproniano giant vein  
1241 as it is exposed in the upper part of the Semproniano village. (b) Conceptual cross-sectional sketch  
1242 of the Semproniano giant vein that is made of an uninterrupted swarm of sparry bands (banded  
1243 travertine). Sample location and related radiometric ages are shown both in (a) and in (b).

1244

1245 **Figure 8.** (a) Panoramic view (Google Earth image) with localization of the studied travertine  
1246 deposits (same as Fig. 3a). (b) Combined plot of  $\delta^{13}\text{C}$  (‰ V-PDB) and  $\delta^{18}\text{O}$  (‰ V-PDB) isotope  
1247 values derived from samples of bedded and banded travertines and calcite veins (Table 3). (c) Plot  
1248 of calculated temperatures for the parental fluids of the studied travertines and  $\text{CaCO}_3$  precipitates  
1249 (Table 3). (d) Combined plot of parental fluid temperatures and U/Th ages determined on the same  
1250 samples.

1251

1252 **Figure 9.** Post Archean Australian shale (PAAS) – normalized REY pattern (rare Earth elements +  
1253 Yttrium) for: the Semproniano giant vein (banded travertine); the bedded travertine flanking the  
1254 giant vein; bedded travertine and calcite vein from Poggio Semproniano; and banded travertine  
1255 from I Vignacci. For comparison, REE data from the Tuscan Nappe limestone are also shown (data  
1256 from Möller et al., 2003).

1257

1258 **Figure 10.** (a) Close up photograph of banded travertine from the central part of the Semproniano  
1259 giant vein. The sample studied for fluid inclusions comes exactly from the spot shown in the  
1260 photograph. (b), (c), and (d) Microphotographs (transmitted light, parallel nicols) of liquid-rich  
1261 fluid inclusions hosted in the banded travertine shown in the previous close-up photograph. L and V  
1262 are for liquid and vapor phases, respectively, within the studied inclusions. (e) and (f) Results of

1263 microthermometry on fluid inclusions hosted in elongate calcite crystals.  $T_h$  is the temperature ( $^{\circ}\text{C}$ )  
1264 of homogenization whereas  $T_{m_{ice}}$  ( $^{\circ}\text{C}$ ) is the temperature of last melting of ice.

1265

1266 **Figure 11.** Comparison between U/Th ages of bedded travertine, banded travertine, and calcite  
1267 veins from the study area and major paleoclimate indicators represented by the deep sea oxygen  
1268 isotope trend (Zachos et al., 2001) and by the pollen dataset from Valle di Castiglione (Tzedakis et  
1269 al., 2001). Global glacial/interglacial periods are redrawn and modified after Priewish et al (2014).

1270

1271 **Figure 12. (a)** Schematic 3D-block diagram interpreting the hydrothermal setting in the Mt. Amiata-  
1272 Semproniano area. Active faulting and related fracturation have primary role in controlling meteoric  
1273 percolation within the carbonate reservoir at depth, and the uprise of hydrothermal fluids. **(b)** Two-  
1274 step scenario illustrating the mode of travertine deposition (by veining at Semproniano fissure ridge  
1275 and by dominant progradation at the Poggio Semproniano plateau) supplied by hydrothermal fluid  
1276 discharge at the fault/fracture tips. The fault architecture is indicative.

1277

1278

## 1279 **Table Captions**

1280

1281 **Table 1.** Samples, sampling sites, and laboratory analyses.

1282

1283 **Table 2.** U/Th Age of travertines sampled in the study area. See Table S1 for a complete list of data.  
1284 Samples indicated with \* were analyzed through MC-ICP-MS at the HISPEC lab of the National  
1285 Taiwan University (errors quoted as  $2\sigma$ ), whereas samples indicated with \*\* were analyzed through  
1286  $\alpha$  spectrometry at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University,  
1287 Italy (errors quoted as  $1\sigma$ ).

1288

1289 **Table 3.** Stable oxygen and carbon isotope composition, and paleotemperature of banded travertine,  
1290 bedded travertine, and calcite veins from the study area. Isotope compositions are expressed in ‰  
1291 against Vienna Pee Dee Belemnite standard (V-PDB) and in ‰ against Vienna Standard Mean  
1292 Ocean Water (V-SMOW). Temperature of parental fluids derive from  $\delta^{18}\text{O}$  through the equation of  
1293 Kele et al. (2015).  $\delta^{13}\text{C}_{\text{CO}_2}$ \* have been calculated using the empirical equation of Panichi and  
1294 Tongiorgi. (1976).  $\delta^{13}\text{C}_{\text{CO}_2}$ \*\* have been calculated using the theoretical equation of Bottinga (1968).

1295

1296 **Table 4.** Strontium, Strontium isotopes and Neodymium isotopes measured on selected samples  
1297 from travertines of the study area.

1298

1299 **Table S1.** Uranium isotopic composition and  $^{230}\text{Th}$  ages for travertines of Semproniano Village,  
1300 Poggio Semproniano, Poggio I Piani and I Vignacci. Samples marked with \* were analysed through  
1301 MC-ICP-MS. Age correction were calculated using an estimated atomic  $^{230}\text{Th}/^{232}\text{Th}$  ratio of  $4 \pm 2$   
1302 ppm. Those are the values for a material at secular equilibrium with the crustal  $^{232}\text{Th}/^{238}\text{U}$  value of  
1303 3.8. The errors are arbitrarily assumed to be 50%. Samples marked with \*\* were analysed through  
1304 alpha spectrometry. The ( $^{230}\text{Th}/^{234}\text{U}$ ) was corrected using the crustal thorium mean composition.  
1305  $0.85 \pm 0.36$  (Wedephol. 1995), for samples with a  $^{230}\text{Th}/^{232}\text{Th}$  activity ratio lower than 80.

1306

1307 **Table S2.** Concentration or rare earth elements and yttrium for travertine samples of the study area  
1308 (in  $\mu\text{g}/\text{kg}$ ).

1309

Table 1

[Click here to download Table: Semproniano\\_Table1\\_Berardi et al.docx](#)**Table 1.** Samples, sampling sites, and laboratory analyses.

Sample	Locality	Rock Type	$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-PDB)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$	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	Bedded 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
VII	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**[Click here to download Table: Semproniano\\_Table2\\_Berardi et al.docx](#)

**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  $2\sigma$ ), whereas samples indicated with \*\* were analyzed through  $\alpha$  spectrometry at the Laboratorio di Geochimica Ambientale e Isotopica of Roma Tre University, Italy (errors quoted as  $1\sigma$ ).

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

**Table 3**[Click here to download Table: Semproniano\\_Table3\\_Berardi et al.docx](#)

**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  $\delta^{18}\text{O}$  through the equation of Kele et al. (2015).  $\delta^{13}\text{C}_{\text{CO}_2}$ \* have been calculated using the empirical equation of Panichi and Tongiorgi. (1976).  $\delta^{13}\text{C}_{\text{CO}_2}$ \*\* have been calculated using the theoretical equation of Bottinga (1968).

Sample	Locality	Rock Type	$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-SMOW)	$T_{\text{calculated}}$ (°C)	$\delta^{13}\text{C}_{\text{CO}_2}$ * (‰ V-PDB)	$\delta^{13}\text{C}_{\text{CO}_2}$ ** (‰ 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**[Click here to download Table: Semproniano\\_Table4\\_Berardi et al.docx](#)**Table 4.** Strontium, Strontium isotopes and Neodymium isotopes measured on selected samples from travertines of the study area.

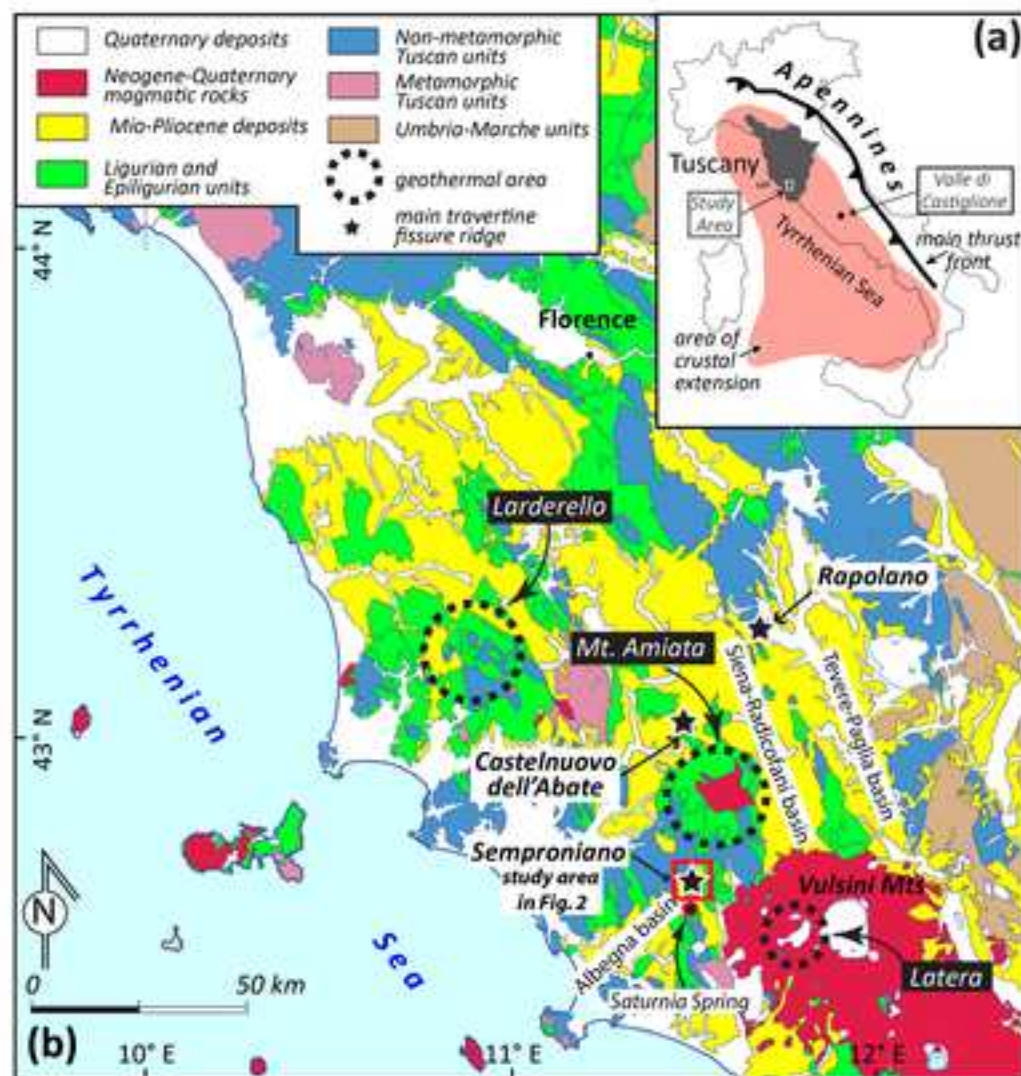
Sample	Locality	Rock Type	Sr (mg/kg)	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\text{se}^*$	$^{143}\text{Nd}/^{144}\text{Nd} \pm 2\text{se}^*$	$\epsilon_{\text{Nd}i}^{**}$
SP12	Semproniano Village	Banded travertine	1189.46	0.708277 $\pm$ 11		
SP14/18	Semproniano Village	Banded travertine	1223.70	0.708395 $\pm$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

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

\*\*  $\epsilon_{\text{Nd}}$  has been calculated at 200Ma

Figure 1

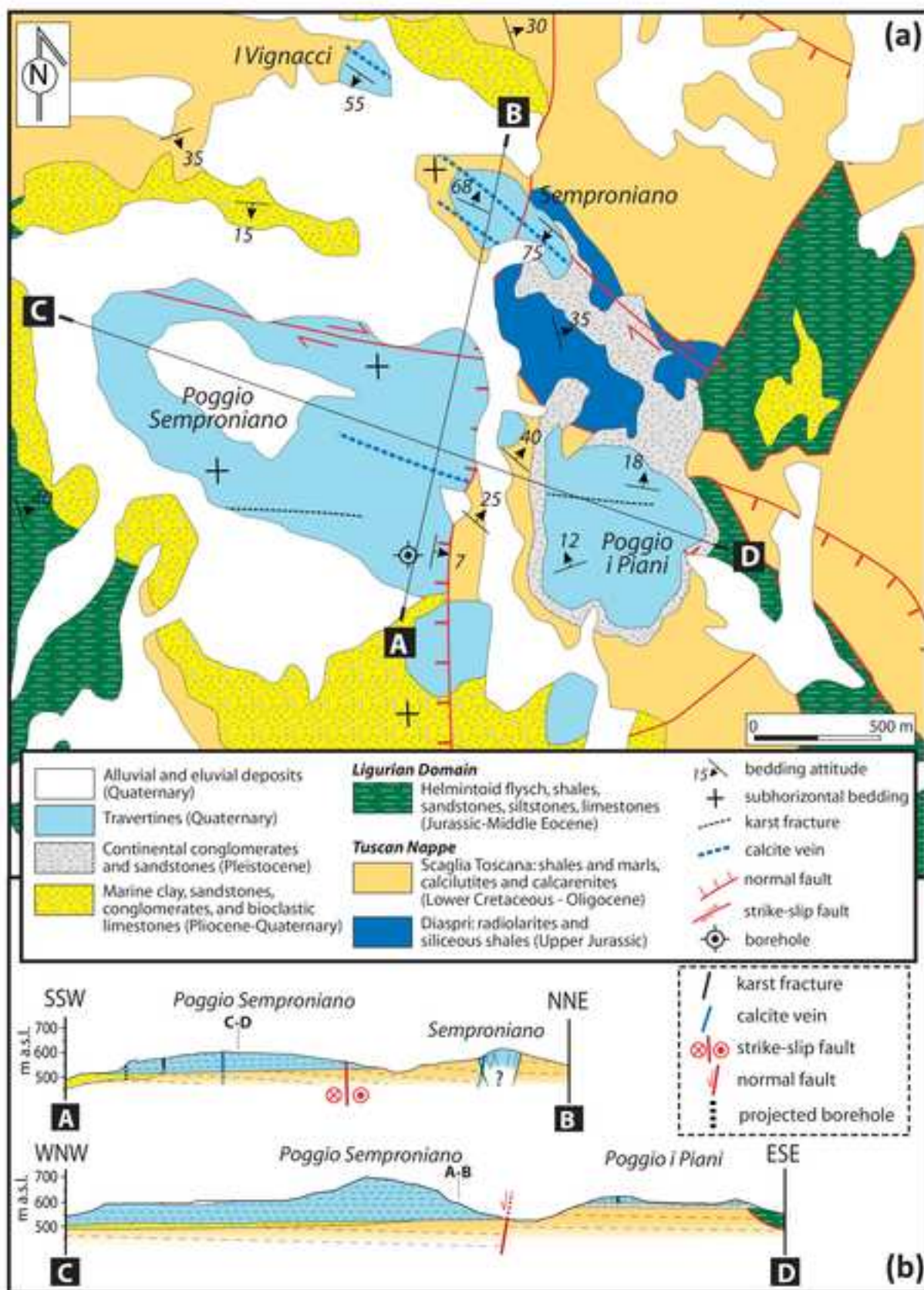
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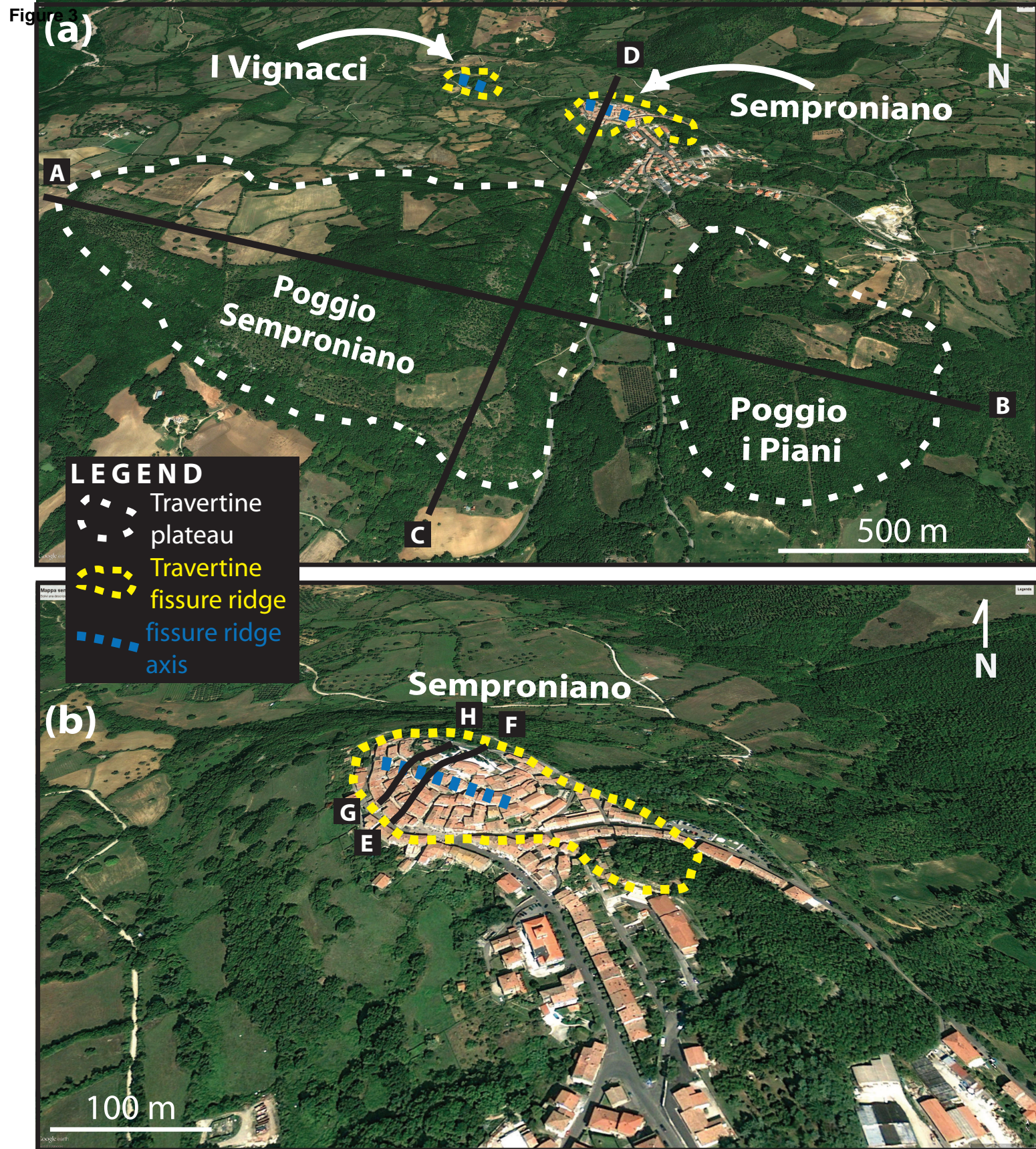
**Figure 1.** (a) Schematic map of Italy showing the Apennines fold-thrust belt and the area affected by crustal extension at the rear (west) of the belt. This latter area includes Tuscany, where the study area (Semproniano, upper Albegna basin, southern Tuscany) is located. (b) Geological map of the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

Figure 2

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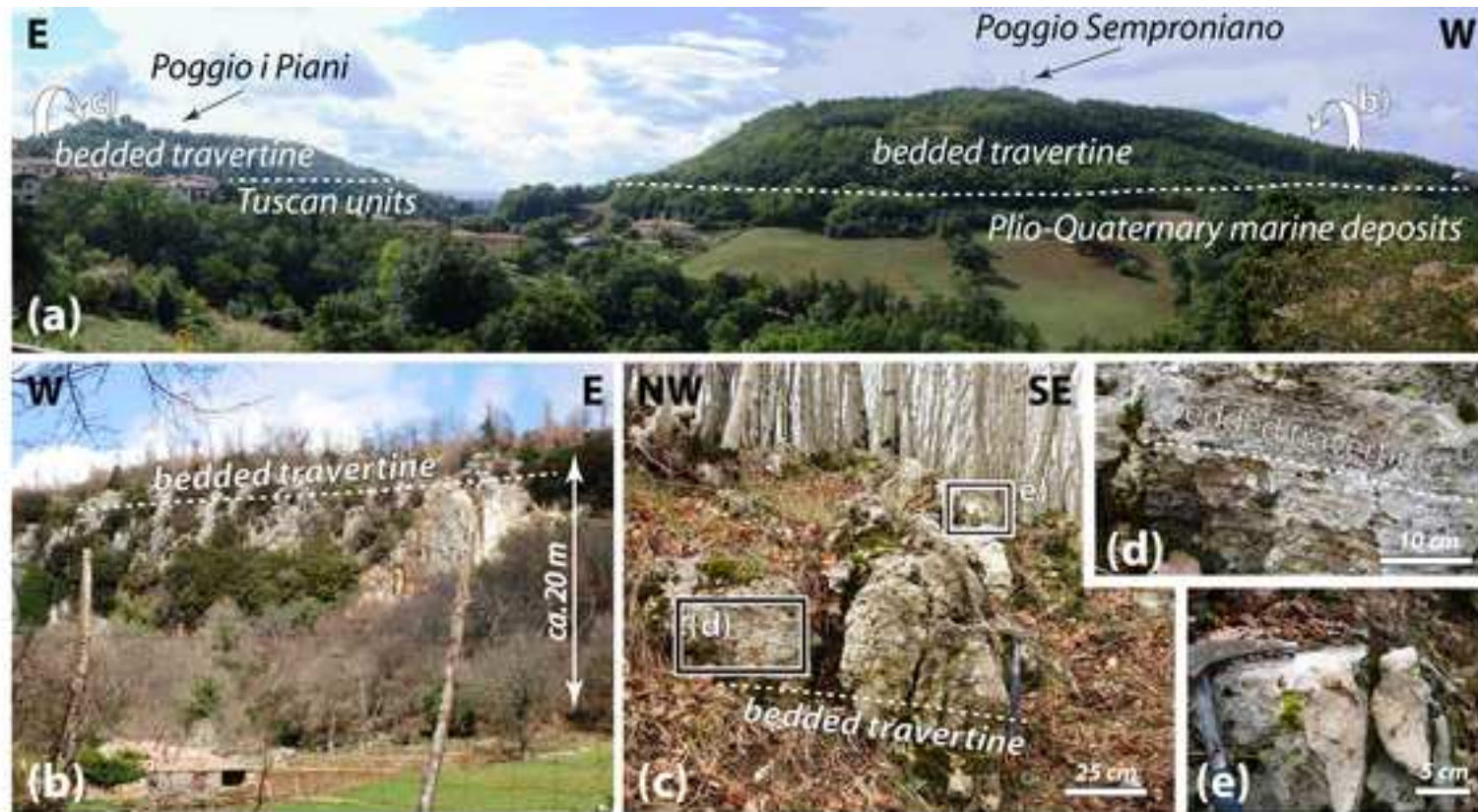


**Figure 2.** (a) Structural geological map of the study area (Semproniano area in the upper Albegna basin) and (b) related geological cross-sections. The map is based on and partly redrawn from the geological map at the 1:10,000 scale available online at [www.regione.toscana.it/-/geologia](http://www.regione.toscana.it/-/geologia).



**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.

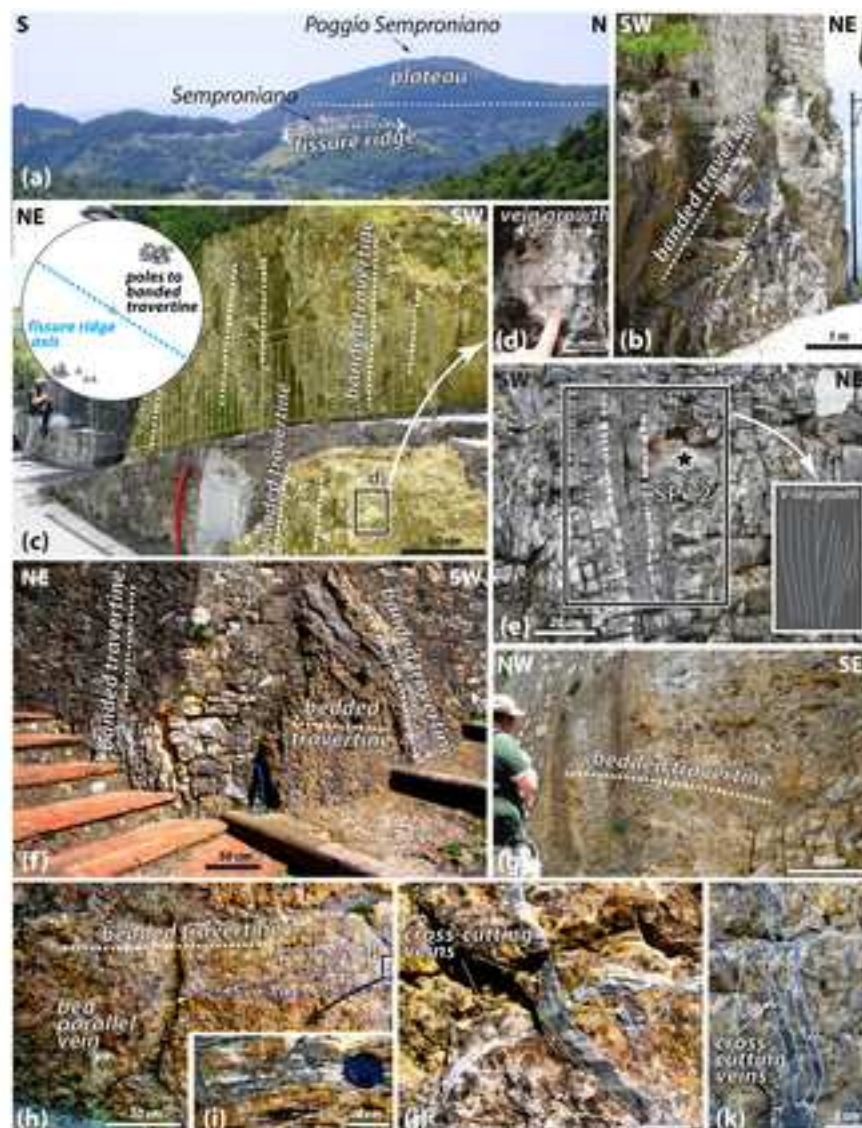
Figure 4  
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**Figure 4.** (a) Southward panoramic view of Poggio i Piani and Poggio Semproniano travertine plateaus. The Poggio i Piani plateau lies on top of the Scaglia Toscana Fmt. (belonging to the non-metamorphic succession of the Tuscan Domain) 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

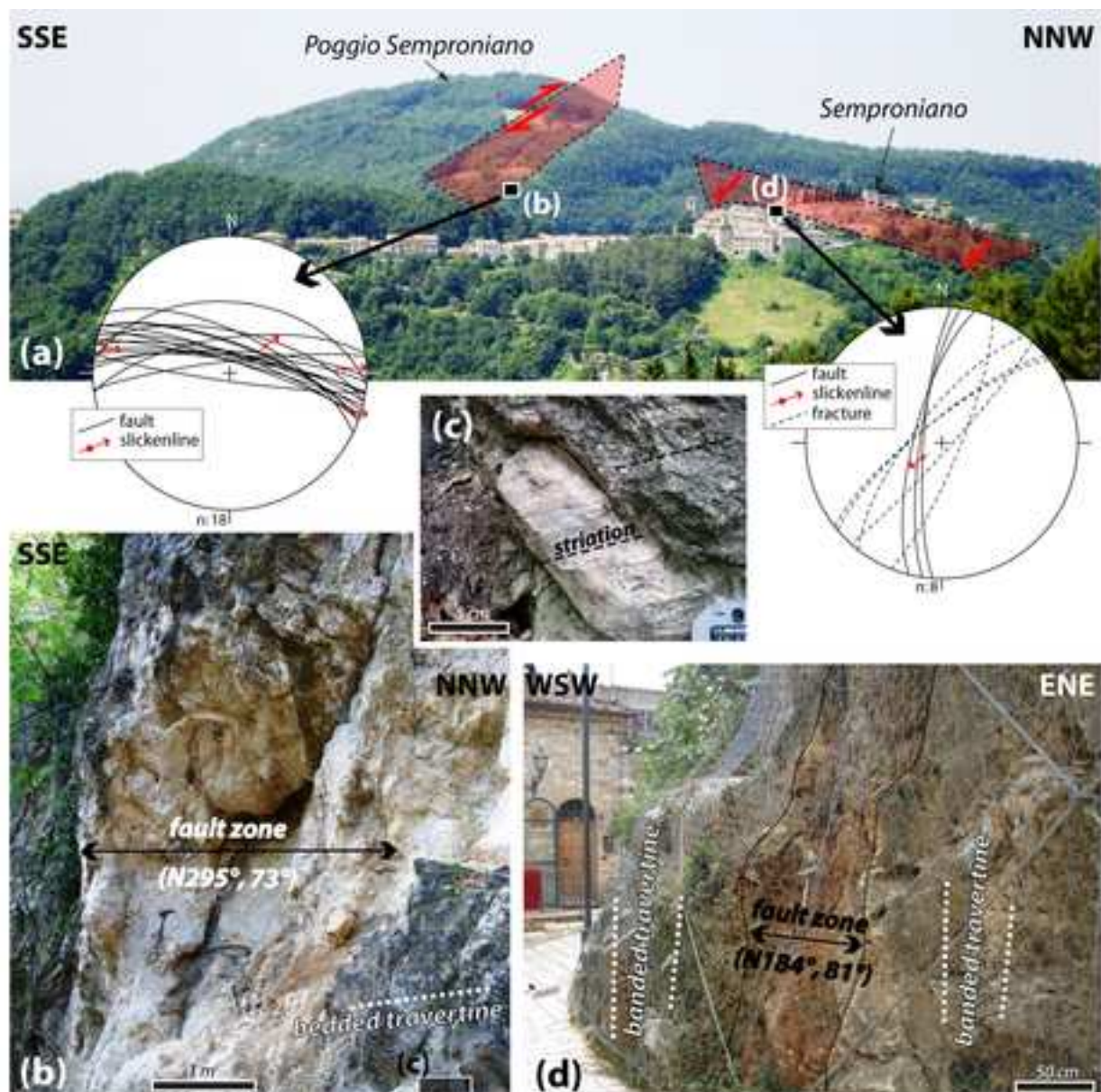
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**Figure 5.** (a) Panoramic view of the Semproniano giant vein and travertine plateau (Poggio Semproniano). (b) Attitude of the sparry bands (banded travertine) forming the Semproniano giant vein (NE flank). This exposure is located below the fortress 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 stereonet: Schmidl 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  $160^{\circ}$  or lesser than  $20^{\circ}$ ; 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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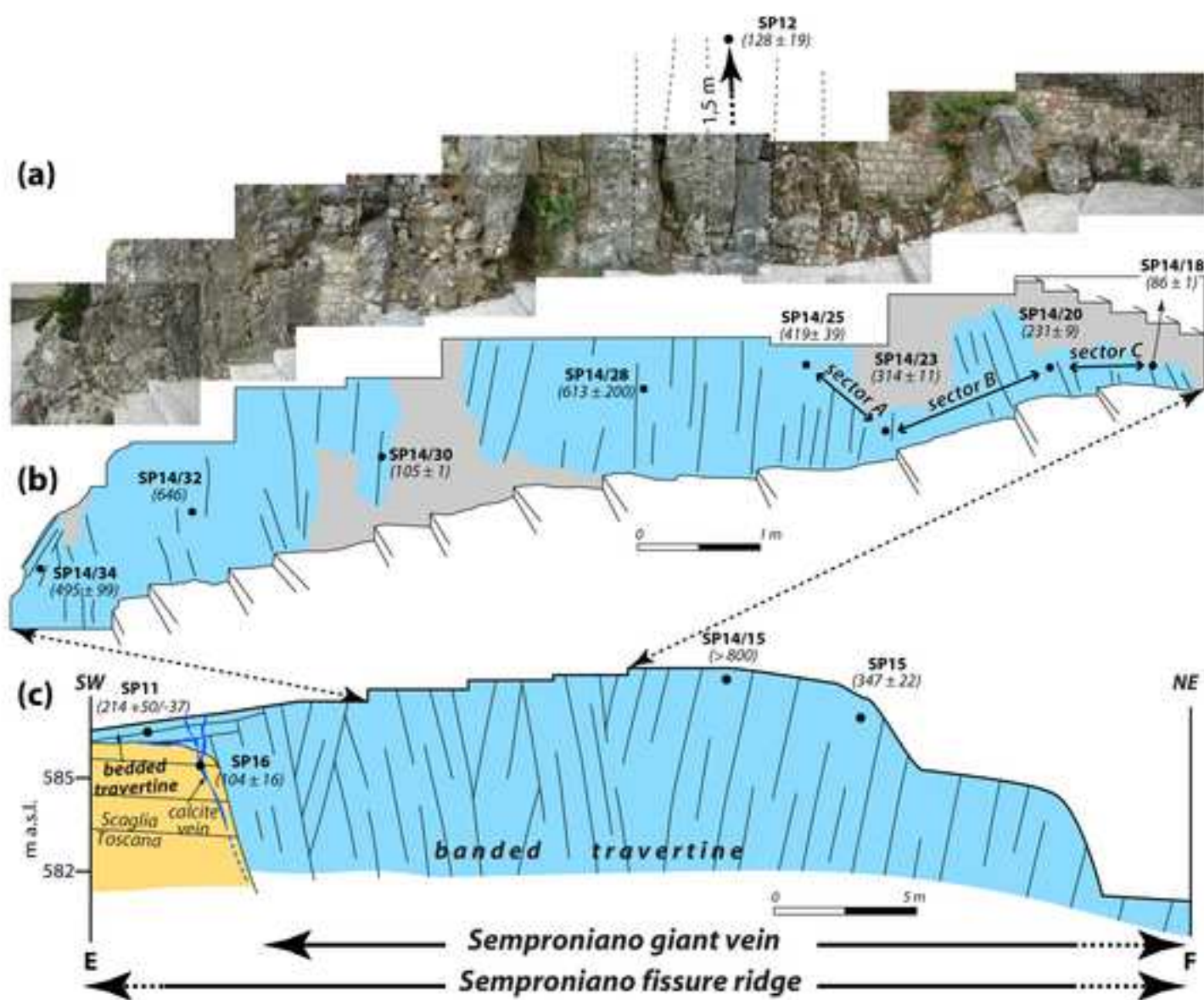
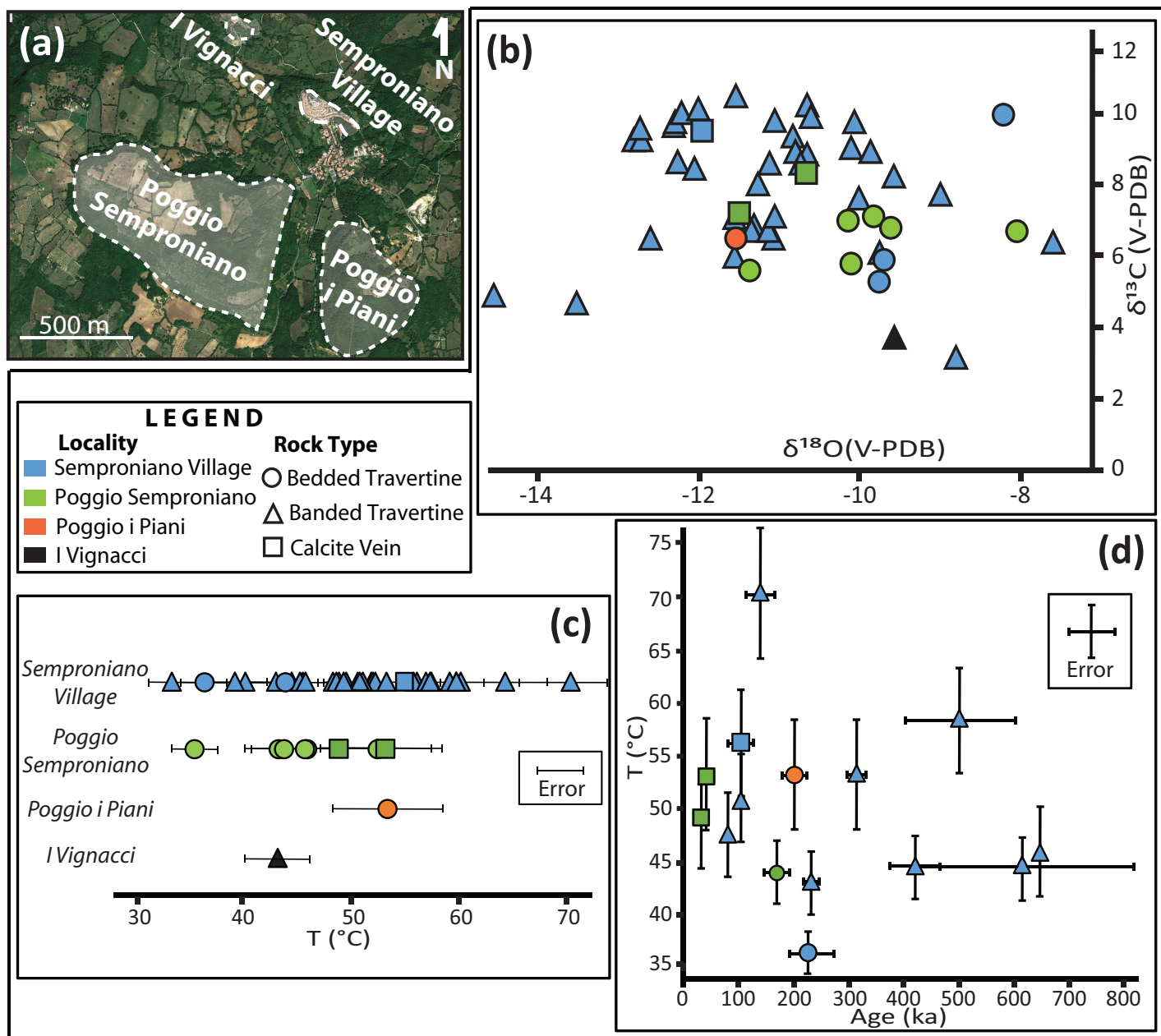


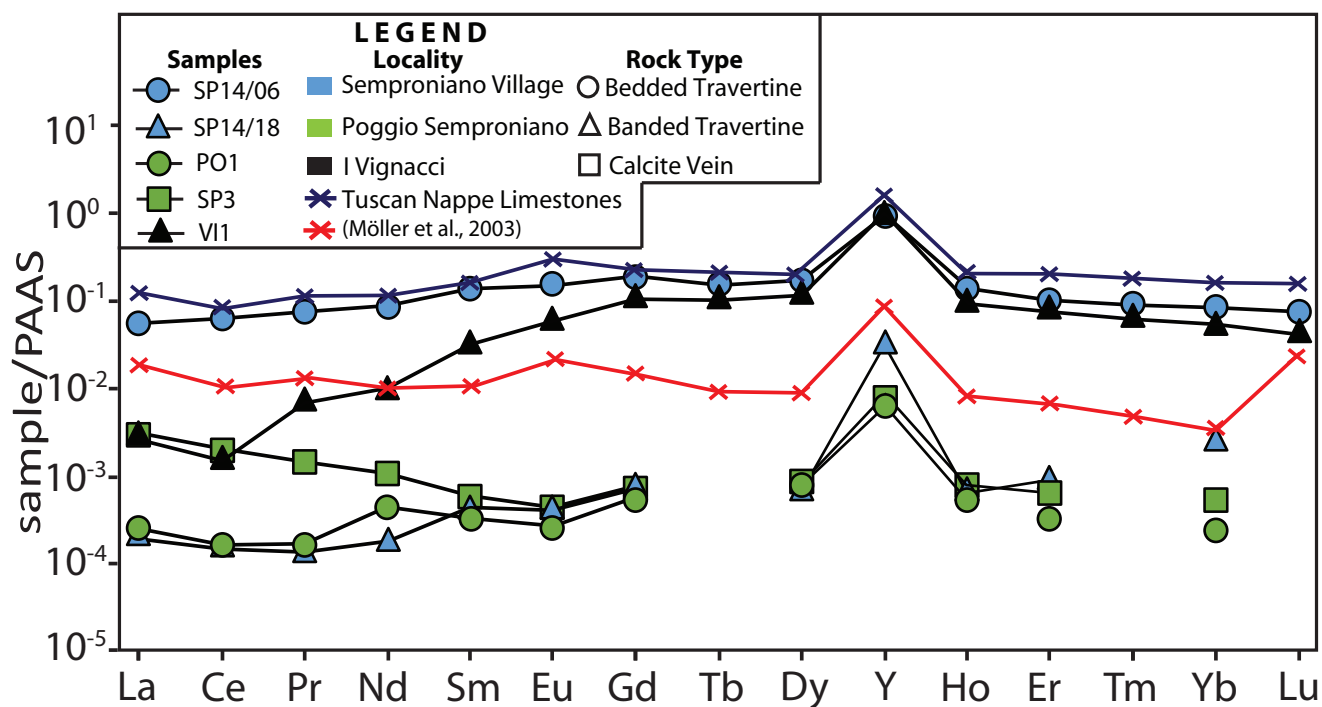
Figure 7. (a) Photomosaic (above) and related line drawing (below) of the Semproniano giant vein as it is exposed in the upper part of the Semproniano village. (b) Conceptual cross-sectional sketch of the Semproniano giant vein that is made of an uninterrupted swarm of sparry bands (banded travertine).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

Figure 8



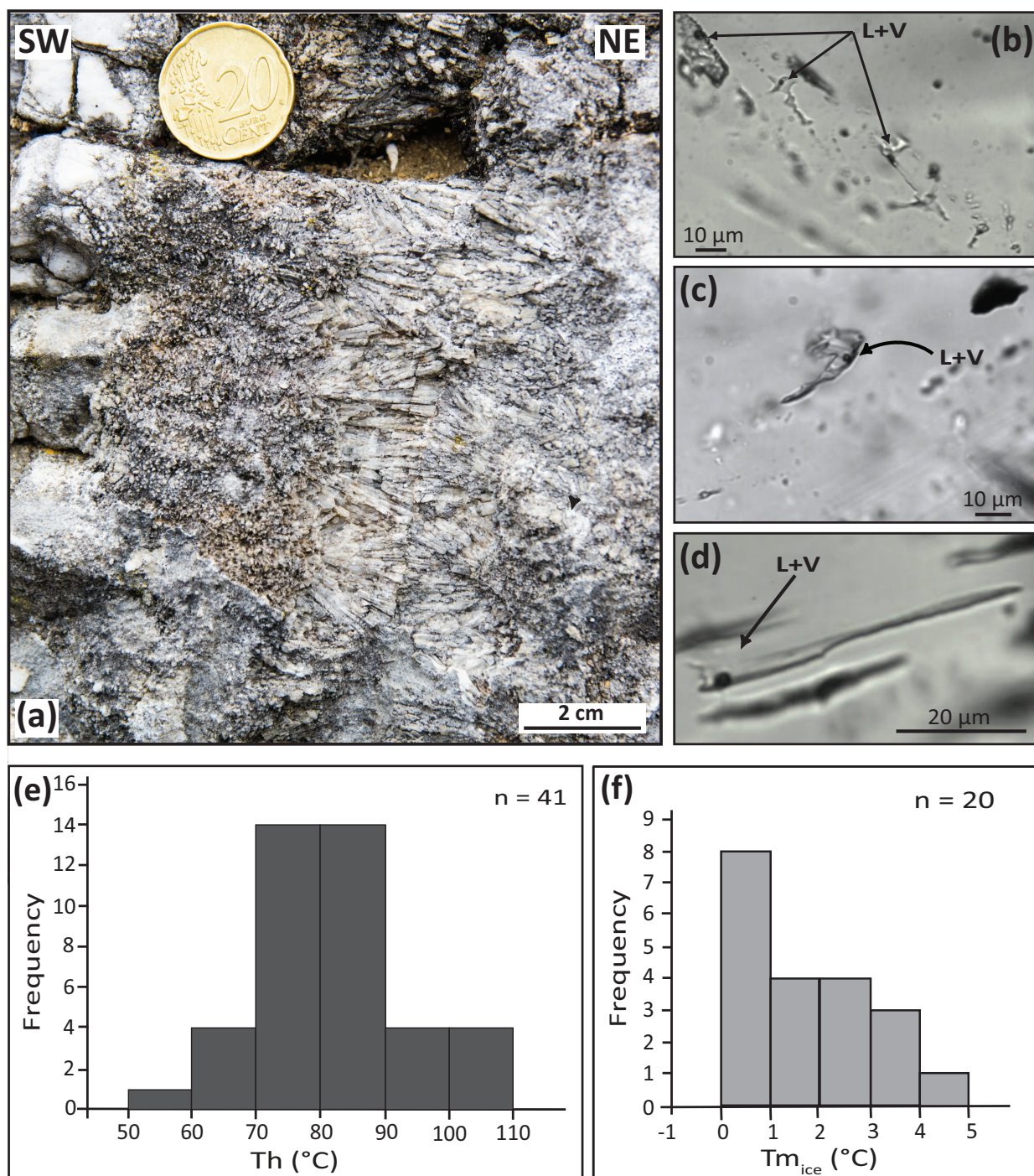
**Figure 8.** (a) Panoramic view (Google Earth image) with localization of the studied travertine deposits (same as Fig. 3a). (b) Combined plot of  $\delta^{13}\text{C}$  (‰ V-PDB) and  $\delta^{18}\text{O}$  (‰ V-PDB) isotope values derived from samples of bedded and banded travertines and calcite veins (Table 3). (c) Plot of calculated temperatures for the parental fluids of the studied travertines and  $\text{CaCO}_3$  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).

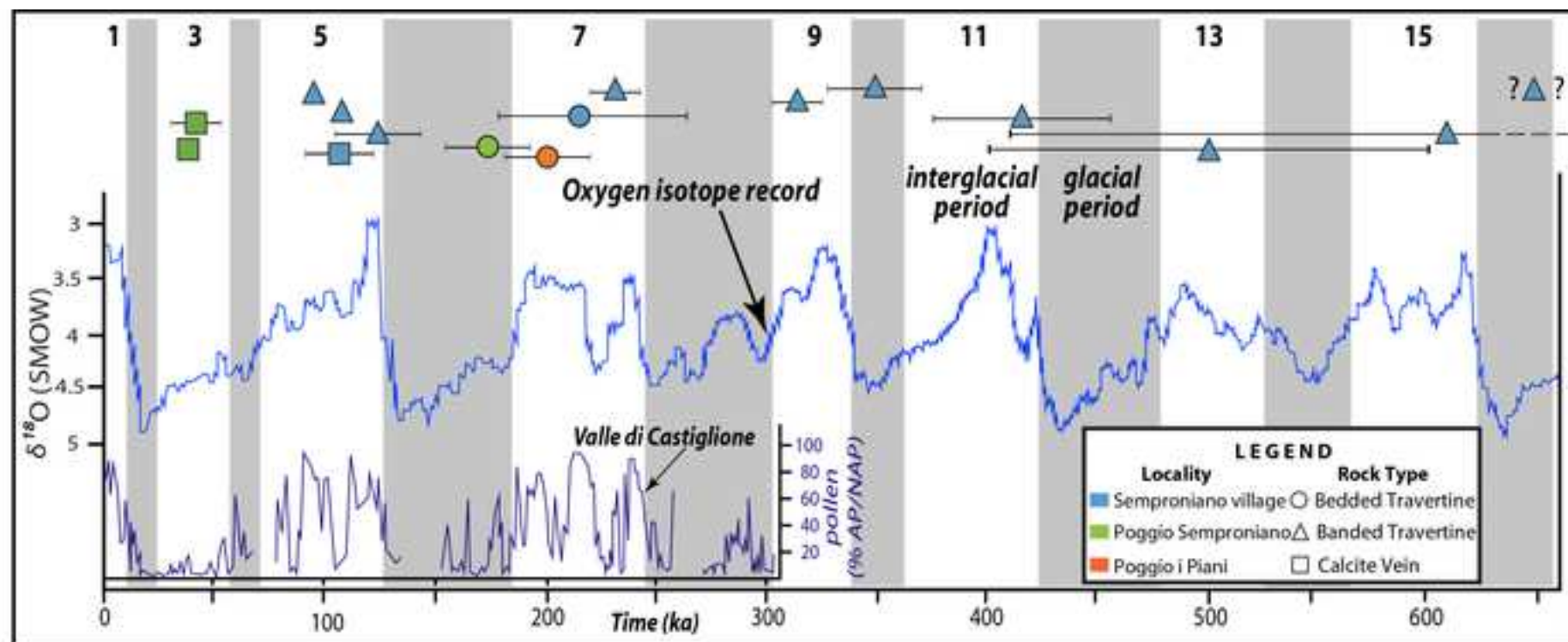
Figure 10



**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<sub>ice</sub> (°C) is the temperature of last melting of ice.

Figure 11

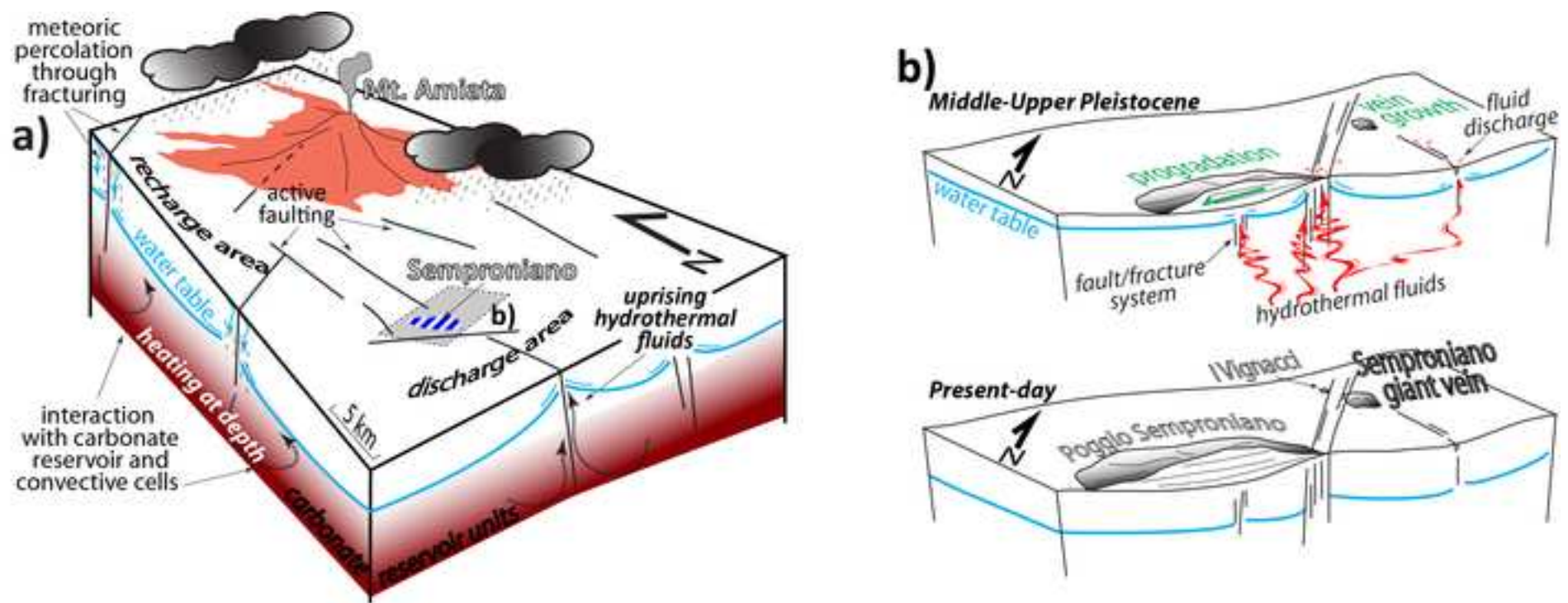
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**Figure 11.** Comparison between U/Th ages of bedded travertine, banded travertine, and calcite veins from the study area and major paleoclimate indicators represented by the deep sea oxygen isotope trend (Zachos et al., 2001) and by the pollen dataset 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 setting in the Mt. Amiata-Semproniano area. Active faulting and related fracturation have primary role in controlling meteoric percolation within the carbonate reservoir at depth, and the uprising 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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