**Fossil travertine system and its palaeofluid provenance, migration and evolution through time:
example from the geothermal area of Acquasanta Terme (Central Italy)**

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Abstract

The geothermal area of Acquasanta Terme has often been studied for its active and fossil travertine deposits to elucidate fluid origin, geodynamic and hydrological setting. Even though present-day thermal springs are usually used to obtain most information, the three travertine terraces bordering the Tronto river contain a plethora of information. A combination of elemental and isotope analyses ($\delta^{18}\text{O}$,

$\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ -ratio), fluid inclusion microthermometry and U-Th dating is used to verify the hydrogeology and its timing. These analyses point out two fluid reservoirs with distinctly different fluids, one with low salinity of 0.7 wt% NaCl eq. and another with 28.5 wt% NaCl eq., which corresponds to the fluid composition of present-day spring fluids. Furthermore, it is demonstrated that geothermal sources were intermittently active in the past 221 ka mainly during uneven-numbered marine isotope stages, which are related to humid, interglacial periods and resulted in three different travertine terraces around 210.5, 126.5, and 36.5 ka. Accordingly, an uplift rate for this area could be estimated at around 1 mm/ka. The fluids were tapped at a depth of approximately 3 km in the tectonized, cataclastic fraction of the Triassic Anidriti di Burano Formation, the Calcare Cavernoso Formation and are originally meteoric based on geochemical evidence of a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ -ratio of 0.707914 ± 0.00019 and a $\delta^{18}\text{O}_{\text{aragonite}}$ value of -11.90 ± 0.34 ‰, which has been depressed by elevated precipitation temperatures between 22.2 and 50 °C. The characterization and dating of fossil travertine deposits gives valuable data providing insights in long-term fluid flow and orogenic uplift rates, adding valuable information to present-day spring fluid characterization.

Keywords: travertine, Apennines, geochemistry, fluid inclusions, isotopes, U/Th

1. Introduction

Continental spring carbonates most commonly precipitate after degassing of fluids comprising dissolved calcium and CO_2 (e.g.: Ford and Pedley, 1996; Pedley, 2009). Their geochemical classification is based on CO_2 origin and the depth at which fluids circulated in the subsurface (Pentecost, 2005; Crossey et al., 2006; Teboul et al., 2016). “Thermogene”, “endogene” or “hypogean” spring carbonates, referred to as travertine (sensu Capezzuoli et al., 2014), are formed due to CO_2 and source fluids having a deep origin, whereas “meteogene”, “epigenic” or “epigean” spring carbonates, referred to as tufa (sensu Capezzuoli et al., 2014), are formed with CO_2 of shallow origin from soil biodegradation, plants or the atmosphere (Pentecost, 2005; Crossey et al., 2006; Teboul et al., 2016). Deducing the origin of CO_2 and palaeofluid

provenance are thus essential for classifying spring carbonates and understanding drivers and processes through time, but also have greater implications with regard to precipitation processes, rock textures, mineralogy, associated biota and palaeohydrology (Minissale, 2004; Pentecost, 2005; Crossey et al., 2006; Teboul et al., 2016; Claes et al., 2019). Geochemical element, stable and radiogenic isotope data are the ultimate tools in deducing fluid characteristics, origin of Ca^{2+} and CO_2 , fluid source rocks and reconstructing the palaeohydrology of ancient spring systems (Minissale et al., 2002; Minissale, 2004; Teboul et al., 2016; Claes et al., 2019). In addition, fluid inclusion studies can provide direct information about the origin, temperature and subsurface interaction of travertine precipitating fluids (Słowakiewicz, 2003; El Desouky et al., 2015; Rimondi et al., 2015; Capezzuoli et al., 2018).

Travertine and tufa are traditional building materials but have ever increasing applications in scientific research (Pedley, 2009). While tufa has potential to be used as a palaeoclimate indicator (Ihlenfeld et al., 2003; Garnett et al., 2004; Fairchild and Treble, 2009), travertines are considered a proxy for natural past CO_2 output in the atmosphere (Kampman et al., 2012; Mancini et al., 2019b). They can also act as indicators for interesting areas for geothermal energy projects (Madonna et al., 2005; Rainone et al., 2013) and water-related landscape formation of continental carbonates can potentially even serve as an analogue for Mars morphologies (e.g.: Pellicer et al., 2014). In addition, spring carbonates on river terraces have been dated to calculate uplift rates and/or river incision rates (e.g.: Ruszkiczay-Rüdiger et al., 2005; Antoine et al., 2007; Burnside et al., 2013). Finally, interest in travertine has significantly increased in the past two decades because they have been considered to make up hydrocarbon reservoirs in the so-called Pre-Salt play offshore Brazil and Angola (Terra et al., 2010; Borsato et al., 2012; Lottaroli et al., 2012). Therefore, reservoir analogues were intensively studied as reported in Claes et al. (2015; 2017a; 2017b), Della Porta et al. (2015), Ronchi and Cruciani (2015), Soete et al. (2015; 2016) and Mancini et al. (2019a). For all these applications, a better understanding of the history of the formation of travertine and tufa is required, in relation to the related subsurface processes. This can be, for example, to constrain geothermal or hydrocarbon reservoir depth and to provide a relative estimate for large scale permeability useful for geothermal, hydrocarbon and even carbon capture and

sequestration research. Furthermore, travertine could help to unravel subsurface processes, the relevant fluid-rock interaction, reservoir configuration and uplift rates.

The main goal of this study is to constrain the processes and their timing that contributed to fossil travertine formation in the eastern section of the Central Apennine mountain chain, as well as to determine the sources and evolution of fluids, CO₂ and Ca²⁺ of travertine in an orogenic area. Therefore, fluid characterization and dating were used to identify fluid flow pathways and important subsurface processes leading to travertine formation. Fluid characterization is straightforward at active (hot) springs but is more challenging in fossil travertine deposits. Therefore, Acquisanta Terme (Central Italy) travertines have been selected because fossil deposits occur on different river terraces along the Tronto river where nearby thermal springs, which have been the topic of several studies (e.g.: Madonna et al., 2005; Menichetti, 2008; Galdenzi et al., 2010; Fusari et al., 2017) are still active, thus allowing comparison of the results with present-day setting. The research goal is reached by analysing fluid composition and proxies like stable isotopes to deduce the provenance of constituent components, coupled with radiometric U-Th dating on fossil travertine sediments and related syndepositional cements, i.e. cements that formed contemporaneous to travertine development (De Boever et al., 2017). In contrast to many fossil travertine studies, fluid composition is determined by microthermometry analysis of fluid inclusions in cements that formed in the fluid conduit of a fissure ridge, also called “banded travertine” (Altunel and Hancock, 1993; De Filippis et al., 2013; Gandin and Capezzuoli, 2014; Capezzuoli et al., 2018) and the results were compared to present-day fluids. The origin of fluids, CO₂ and Ca²⁺ is determined from the same cements by studying the isotopes of oxygen, carbon and strontium, respectively. This research testifies to the presence of deeply circulating fluids, guided by large scale climatic oscillations, indicating the involvement of two fluid reservoirs in forming a fossil fissure ridge in Acquisanta Terme. This approach could also be applied in similar fossil travertine deposits because a striking equivalence to studies on present-day spring fluids demonstrates its efficacy.

2. Geological setting

Acquasanta Terme is located in the eastern part of the Italian Central Apennines orogen (Figure 1A). This fold-and-thrust belt is formed by convergence, collision and subduction between the Adriatic Promontory and the European plate during the late Cretaceous to early Miocene and resulted in a stacked superposition of tectonic units derived from oceanic and continental palaeogeographic domains belonging to the Thetidian Alpine Ocean (Scisciani et al., 2002; Molli, 2008; di Francesco et al., 2010; Calamita et al., 2011; Santantonio and Carminati, 2011; Capozzi et al., 2012; Cardello and Doglioni, 2015). Eastward subduction hinge retreat caused back-arc extension in the western Apennine portion from the middle Miocene (Thyrrenian Domain – Barchi, 2010) and foreland compression in the eastern sector (Adriatic Domain). Acquasanta Terme is located in the latter sector, characterized by significant uplift and active seismicity (Chiaraluce et al., 2004, 2005; Chiarabba et al., 2018) associated with an important compressional feature, the Acquasanta Terme anticline, which was cross-cut by a local transtensional tectonic regime resulting in dextral strike-slip and minor normal faulting during Neogene-Quaternary time (Figure 1B) (Farabollini et al., 2005; Menichetti, 2008; Maggi et al., 2015).

FIGURE 1

The local sedimentary sequence (Koopman, 1983; Madonna et al., 2005; Menichetti, 2008; Galdenzi et al., 2010; Cardello and Doglioni, 2015) (Figure 2) includes Late Triassic carbonates and dolomites, interbedded with anhydrites (Anidriti di Burano Formation) overlain by Lower Jurassic carbonate platform deposits grading towards pelagic well-bedded limestone and hemi-pelagic marl successions by the Oligocene. Final basin deepening is marked by Miocene marly and siliciclastic flysch deposits of the foredeep Laga Basin (Acquasanta Group). Thin continental Quaternary deposits, consisting of colluvium, alluvium and travertine sediment (Figure 1B and C; Galdenzi et al., 2010) cover the succession.

FIGURE 2

Acquasanta Terme travertines are considered to represent Middle Pleistocene deposits (144.7 ka - Minissale et al., 2002) consisting of three terraces on the east bank of the Tronto river (Figure 1C) (Boni

and Colacicchi, 1966; Madonna et al., 2005; Della Porta et al., 2017). These terrace deposits, prograding towards the river valley, reflect a shift in hydraulic head between travertine formation phases, related to local uplift (Boni and Colacicchi, 1966; Pentecost, 2005), with the oldest travertine terrace (1st order Terrace – Figure 1C) located in the highest position at altitudes ranging between 600 and 450 m a.s.l.. The middle and younger ones (respectively 2nd and 3rd order Terraces – Figure 1C) are located between 500-350 and 400-300 m a.s.l. respectively and mainly formed by coalescence of different travertine aprons consisting of vertically/laterally stacked, different aggradational-progradational units reflecting multi-phase travertine deposition on the local fluvial-alluvial clastic succession (Della Porta et al., 2017). Thermal waters are presently emerging from sources along the eastern river bank (Figure 1C) that only result in limited travertine deposition (Madonna et al., 2005; Galdenzi et al., 2010). Studies on these thermal waters suggest that mixed fluids are derived from deep processes that dissolved Triassic anhydrite and shallow meteoric fluids (Minissale et al., 2002; Menichetti, 2008; Galdenzi et al., 2010; Fusari et al., 2017). The heat source of thermal fluids is not yet well constrained. Madonna et al. (2005) proposed a magmatic heat source, whereas Menichetti (2008) considered it a consequence of a normal geothermal gradient. The presence of travertine located in the eastern Central Apennines is not restricted only to Acquasanta Terme area because several travertine bodies occur in a radius of 20 km, including the deposits of Colle San Marco (Ascoli Piceno), Triponzo, Civitella del Tronto, among others (Boni and Colacicchi, 1966; Farabollini et al., 2005; Della Porta et al., 2017).

3. Methodology

3.1. Field work and sampling

For the characterization of each terrace, representative key sites were chosen. Field work was primarily performed in the San Pietro Quarry (1st order Terrace). The samples taken from this quarry were used for all analyses reported in this paper, apart from dating, for which additional samples were collected from the external part of the Tancredi Quarry (2nd order Terrace) and in the Cardi Quarry (3rd order Terrace) (Figure 1C). These last two quarries were characterized in detail by Della Porta et al. (2017),

while the San Pietro quarry is now studied for its sedimentary complexity and thick veins crosscutting the sediments. Lithotypes are described macroscopically on quarry walls and lithotype maps are created to unravel their lateral relationships and to obtain insights into the depositional architecture of the deposit. The lithotype maps were subsequently digitized and simplified versions were constructed included in a three-dimensional quarry representation using SketchUp™ (Trimble, California, U.S.A.). Furthermore, an explorative photogrammetric study was performed in the San Pietro Quarry to have a three-dimensional representation. The point cloud is generated using Agisoft PhotoScan software (Agisoft LLC, St. Petersburg, Russia).

Sampling was performed by drilling core plugs perpendicular to quarry walls. Thus, these core plugs are horizontally oriented to the deposits and mainly have dimensions of 2.54 cm in diameter and are 4 to 10 cm long. Some core plugs are 10 cm in diameter and approximately 30 cm long. Two veins are sampled, to provide material for stable isotope and fluid inclusion analysis.

3.2. Petrography

Lithotypes have been described macroscopically and microscopically based on the nomenclature of Dunham (1962), Guo and Riding (1998), Claes et al. (2015, 2017a) and Croci et al. (2016). For classical microscopy, a Leica DM LM microscope (Leica Microsystems, Wetzlar, Germany) was used and was equipped with a Deltapix DP200I camera. Cathodoluminescence was performed with a modified Technosyn Model 8200 MARK II (Nikon Corporation, Tokyo, Japan) with a 5 mm wide electron beam and was operated at a voltage between 6 and 8 kV at a current between 350 and 500 mA.

3.3. Geochemistry (stable isotopes and trace elements) and mineralogy

Stable isotopes of oxygen ($\delta^{18}\text{O}$), carbon ($\delta^{13}\text{C}$) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and major and trace elements Ca, Al, Fe, K, Mg, Na, P, Sr, S and Ba were analysed to characterize the origin of mineralizing fluids. This selection of elements was based on Teboul et al. (2016) and Claes et al. (2019). Powders for stable isotope analyses were extracted using a dental drill with a diameter of approximately 1 mm, which was cleaned using distilled and ultrapure water. Isotopic values were measured from carbonate samples and reported in standard $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ notation, with respect to V-PDB standards. Strontium isotope values

are presented in the fractional notation ($^{87}\text{Sr}/^{86}\text{Sr}$), while trace element concentrations are reported in mg/kg. Samples for major and trace element analysis were mortar-milled, while the mortar was cleaned using distilled water after clearing out potential residue by grinding pure quartz sand.

Stable oxygen and carbon isotope ratios were simultaneously measured for twenty-eight samples at the Friederich-Alexander-Universität (Erlangen-Nürnberg, Germany). Carbonate powders were reacted with 100% phosphoric acid at 70°C using a Gasbench II connected to a ThermoFinnigan Delta-V Plus mass spectrometer (Thermo Scientific Inc.). The laboratory standards ERL-5 and Sol-1 were used and experimentally determined mean values were -49.20 ‰ $\delta^{13}\text{C}$ and -16.83 ‰ $\delta^{18}\text{O}$ for ERL-5 and 0.13 ‰ $\delta^{13}\text{C}$ and -5.78 ‰ $\delta^{18}\text{O}$ for Sol-1 and standard deviations were 0.6 ‰ $\delta^{13}\text{C}$ and 0.2 ‰ $\delta^{18}\text{O}$ for ERL-5 and 0.5 ‰ $\delta^{13}\text{C}$ and 0.04 ‰ $\delta^{18}\text{O}$ for Sol-1. Fractionation factors between carbonate powder and acids are different for aragonite and calcite (Rosenbaum and Sheppard, 1986; Kim et al., 2007). Therefore, complementary X-ray Powder Diffraction (XRD) analyses were performed with a Philips PW 1830 diffractometer (Philips Analytical, Almelo, Netherlands) with a copper anode giving 1.544 Å $K\alpha$ -radiation. Qualitative results were analysed with EVA-software (Bruker, Massachusetts, U.S.A.), while a Rietveld analysis with the Topas software package (Bruker, Massachusetts, U.S.A.) was performed for quantifying minerals. Structural mineral information was retrieved from the FindIt database.

The strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) was measured for seven samples at the Scottish Universities Environmental Research Centre. The powdered carbonate samples were digested in 2.5M HCl after being leached in 1M NH_4Ac . The Sr fraction was separated from the matrix by elution of 2.5M HCl on Bio-Rad AG50WX8 200-400 mesh cation exchange resin. Prior to mass spectrometry analysis with a VG Sector 54-30 multi-collector MS, the sample is loaded on Ta-filaments with 1M H_3PO_4 . A ^{88}Sr intensity of 1V ($1 \times 10^{-10}\text{A}$) $\pm$ 10 % was maintained throughout the measurement. Application of Russel's law and the invariant $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 corrects the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for mass fractionation. NIST SRM987 gave 0.710258 $\pm$ 13 (2 SD, N=15) during the period of this study. Of the seven samples studied, one is from a major aragonite vein and the other six are from bedded travertine spread throughout the San Pietro quarry.

Trace element analysis was performed on a set of 17 powdered samples, dissolved by four acid digestion to ensure dissolution of all mineral phases (Claes et al., 2019). These four acids were 65 % sub-boiled HNO₃, 70 % HClO₄, 48 % sub-boiled HF and 2.5 M HCl. Digested samples were analysed with a VARIAN ICP-OES 700 series spectrometer (Agilent technologies, Santa Clara, CA, United States). A principal component analysis with three principal components has been performed on the results to visualize variation between samples.

3.4. Fluid inclusion microthermometry

Double polished thin sections, i.e. “wafers”, with a thickness of 120 µm were created of six samples taken from crystalline travertine veins. A detailed description of the wafer preparation technique is given by Muchez et al. (1994). Fluid inclusion studies on travertines are challenging as they often consist of fine crystalline fabrics. These micritic to microsparitic textures are not suitable for fluid inclusion investigation (El Desouky et al., 2015). In addition, fluid inclusions should be sufficiently large (>2µm) and re-equilibration after precipitation (stretching, leaking-refilling, necking down and decrepitation) is often observed within carbonates (Roedder, 1984; Shepherd et al., 1985; Goldstein and Reynolds, 1994). It is consequently necessary to focus on coarse crystalline fabrics, to critically evaluate each inclusion individually and data should be integrated in a broader sedimentological-geochemical study. Only three wafers were suitable for microthermometry as not all cemented zones had sufficiently large crystals. Wafer petrography was done with an Olympus BX60 microscope (Olympus Corporation, Tokyo, Japan), after cooling samples at -18 °C for two weeks. The microthermometry analysis was performed on wafer chips measuring approximately 5 x 5 mm in a Linkham MDS 600 cooling/heating stage (Linkham Scientific Instruments, Tadworth, United Kingdom) mounted on an Olympus BX51 microscope (Olympus Corporation, Tokyo, Japan). Calibration of the cooling/heating stage for temperatures between -56.6 °C and 0 °C was performed with four synthetic inclusions. The first step in the analysis was heating to 160 °C to check for homogenization temperature. This step is done prior to freezing to avoid artificial stretching, which is typical for soft carbonate crystals (Goldstein & Reynolds, 1994). Subsequently, samples were cooled to -120°C attempting to stretch mono-phase inclusions,

allowing measurement of stable phase transitions, which is impossible in mono-phase inclusions. Finally, temperatures were gradually increased to record first and final melting temperatures.

3.5. Radiometric dating

Six travertine samples were collected for U-Th dating in fresh quarry cuts of the Acquasanta Terme area. Two were sampled from veins of the lowest (3rd terrace - S1) and highest terrace (1st terrace - S2) while four different samples are derived from bedded travertines of the three different terraces (1st terrace - S3; 2nd terrace - S4, S5; 3rd terrace - S6; Figure 1). In this way, samples are homogeneously distributed throughout the different Acquasanta Terme travertine bodies and thus can be considered as representative for the evolution of the whole travertine system.

Veins (Banded travertine of Altunel and Hancock, 1993; Calcite veins of Capezzuoli et al., 2018), similarly to crystalline crusts (Brogi et al., 2010), are the most suitable material for U-Th age determination due to their highly crystalline and low porous fabric, resulting in the absence of neoformational calcite or aragonite which could influence measurement reliability. Therefore, the more crystalline samples have been selected for bedded travertine and the two selected vein samples are taken from one single crystal band of their respective layered vein samples. Afterwards, samples were inspected with the optical microscope to avoid samples with secondary cements

U-Th dating was conducted on six selected samples at the High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University (Shen et al., 2003, 2012). Seven subsamples of calcite veins, 0.5 g each, were selected, gently crushed, ultrasonicated, and then dried at 50 °C on a class-100 bench in a class 10,000 clean room (Shen et al., 2008). The cleanest fragments, 0.04-0.17 g each, were picked for U-Th chemistry (Shen et al., 2003). U-Th isotopic compositions and contents were determined by single secondary-electron-multiplier protocols on a Thermo-Fisher NEPTUNE multi-collection inductively coupled plasma mass spectrometer (MC-ICP-MS) (Shen et al., 2012). Offline data reduction methods followed Shen et al. (2002) and Hiess et al. (2012). Half-lives of U-Th nuclides used for ²³⁰Th age calculation are given in Cheng et al. (2013) and Jaffey et al (1971). Isotopic and age errors given are two standard deviations of the mean and two standard deviations, respectively, unless otherwise noted.

4. Results

4.1. Petrography

Nine lithotypes have been mapped throughout the studied quarries and are represented in Table 1, with corresponding photographs shown in Figure 3. The most common lithotypes are *vacuolar boundstone*, *dendrite crust*, *grey mudstone* and *peloidal packstone*. Less common lithotypes are *aragonite vein* and *laminite-phytocrust* travertine. Finally, minor lithotypes include macroscopically recognizable *arborescent shrub*, *crystalline crust* and the infill of a *fossil cave*.

TABLE 1

FIGURE 3

4.2. Travertine body description

The travertine deposits of the San Pietro Quarry (200 by 100 m, a height of 30 m at the time of description in September 2015) were mapped and an overview of the entire quarry is displayed in Figure 4. The observed lithotypes have been subdivided in packages, based on deposit angles. These packages are shown in Figure 4D. The first package has deposits sloping with dips up to 45° and dominantly contain *dendrite crusts* and *peloidal packstone*. The second package partially follows these dips, but also laps onto the first package, as clarified in Figure 4. Layers in this second package slope smoothly, sometimes interfingering (Figure 5A) but are mostly subhorizontal and chiefly consist of *vacuolar boundstones* with regular intervals of *peloidal packstone*. The third package occurs lateral to the second package but consists of steeply sloping to subvertical deposits, mainly made up by *crystalline crust*. The fourth package displays an arc-shaped morphology in which the *aragonitic vein* is central in the arc (Figure 5B). Lithotypes vary from *vacuolar boundstones* nearby the vein, with smooth slopes to *dendrite crusts* and *peloidal packstones* at increasingly steeper slopes (Figure 5B). The final, fifth package laps onto the fourth package and both packages are separated by thick *grey mudstone* deposits. This fifth package consists of flat deposits, which mainly consist of *laminite-phytocrustic travertine*.

FIGURE 4

FIGURE 5

4.3. Mineralogy

The XRD patterns of vein or white cement samples indicate at least 99 % aragonite as opposed to samples from bedded travertine which show a mineralogy of at least 97 % calcite, with minor amounts of quartz.

4.4. Major and trace elements

Major and trace element results are organised in three groups, according to petrographical description: (i) bedded travertine and speleothems, which encompasses *dendrite crusts*, *peloidal packstone*, *crystalline crust*, *vacuolar boundstone* as well as *fossil cave infill*; (ii) *grey mudstone*, which is also belonging to bedded travertine, but was differentiated in this section because of clearly distinct composition and (iii) *aragonite vein* or aragonite crystals. The mean values of elements with concentrations above the detection limit are summarized in Table 2 and Figure 6 shows a plot with the first two components of a Principal Component Analysis. The three analysed principal components explain 60.25 %, 22.05 % and 13.04 % of all variance, explaining 95.34 % of all variance. Table 2 and Figure 6 show that the second group, *grey mudstone*, is marked by highest Al, Ba, Fe, K, Mg and Na concentrations and the third group has high Sr and lower Mg content. The overall Sr, Mg and S content is high in all lithotypes. Among the studied elements, Ca, Sr, S, Ba, Na and Mg are carbonate related elements which are derived from the fluid source rocks, whereas Al, Fe, K and P are mainly related to siliciclastic phases like clay minerals (Claes et al., 2019).

FIGURE 6

TABLE 2

4.5. Stable isotopes

4.5.1. Oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotopes

The stable isotope results are summarized in Table 3 and illustrated in Figure 6. Aragonite crystals (vein and cement) have similar oxygen isotopic values varying between -12.35 and -11.34 ‰ averaging at -11.90 ± 0.36 ‰ (n=8), and carbon isotopes of these groups differ only slightly with averages of 6.80 ± 0.38 ‰ (n=3) for cements and 7.79 ± 0.20 ‰ (n=5) for veins, giving a total average for aragonite crystals of 7.42 ± 0.57 ‰ (n=8), while varying between 6.42 and 7.95 ‰. In contrast to aragonite crystals, bedded porous travertine has less depleted oxygen, varying between -12.27 and -6.29 ‰, with an average of -10.68 ± 1.22 ‰ (n=25), and carbon isotopes varying between 7.75 and 14.58 ‰, with an average of 8.96 ± 1.72 ‰ (n=25). Further grouping of all values for different lithotypes of bedded travertine is provided in Table 3, in which it is clear that most variance on the presented results relates to the *fossil cave infill*. For example, two measurements have clearly deviant carbon isotope values of +13.44 and +14.58 ‰ and come from the *fossil cave infill*. Finally, *grey mudstone*, which is considered separately from the bedded travertine has a $\delta^{18}\text{O}$ varying between -11.68 and -8.93 ‰, with an average of -10.58 ± 1.16 ‰ (n=4) and a $\delta^{13}\text{C}$ varying between 2.68 and 9.15 ‰, averaging at 6.66 ± 2.79 ‰ (n=4).

TABLE 3

FIGURE 7

4.5.2. Strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$)

One sample was measured in the *aragonite vein* and has a $^{87}\text{Sr}/^{86}\text{Sr}$ -value of 0.70790, while values from six samples from bedded travertine vary between 0.70790 and 0.70795. The average $^{87}\text{Sr}/^{86}\text{Sr}$ -value is 0.707914 ± 0.00019 further testifying that only very small variation is present, even though samples were collected throughout the travertine body, including the aragonite vein in Figure 5B. In Figure 7, the results are plotted in relation to local marine carbonates and the strontium stratigraphy curve of McArthur (2010) and McArthur et al. (2012) and data is presented as supplementary material.

FIGURE 8

4.6. Radiometric dating

The resulting data are reported in Table 4. Ages are clustered in a range between 221 ± 6 ka (sample S2)

and 28 ± 8 ka (sample S1), corresponding to the highest (1st order terrace in Figure 1) and lowest (3rd order terrace in Figure 1) travertine terrace in topography, respectively. Two samples of each terrace have been dated at 221 ± 6 ka and 200 ± 16 ka for the upper terrace, 130 ± 8 ka and 123 ± 18 ka for the middle terrace and 45 ± 16 ka and 29 ± 9 ka for the lowest terrace.

TABLE 4

4.7. Fluid inclusions

4.7.1. Fluid inclusion petrography

Three samples, retrieved from palisade crystals (sensu Rimondi et al., 2015; Capezzuoli et al., 2018) of *aragonite veins*, appeared most suitable for fluid inclusion analysis as these were the only ones containing sufficiently large two-phase inclusions, even after attempting stretching inclusions. Samples from *crystalline crust* were not suitable for a microthermometry study.

Fluid inclusions found in vein crystals have variable sizes, shapes and vapour content. They are subdivided into four morphological classes, which have subtypes *a*, without vapour and *b*, with vapour. The majority (80 %) of all inclusions has a needle-like appearance with length-to-width ratio exceeding 10 and are often less than 2 μm wide, occurring in between crystal faces (Type I – Figure 8A). Most of these needle-like inclusions are monophasic full liquid inclusions and the two-phase present contain approximately 20 Vol% of vapour. Triangular and rhombic inclusions (type II – Figure 8B, C, E and F) compose about 5 to 10 % of all inclusions and vapour content mainly varies between 0 and 50 Vol%, even ranging up to full vapour inclusions (Figure 8H). These inclusions have proven most useful for microthermometry analysis. Finally, inclusions without specific shape (type III – Figure 8D and E) and lenticular-shaped inclusions (type IV – Figure 8G) make up the rest of the inclusions. These inclusions are characterized by a tail at one (type III) or two extremities (type IV) of the inclusions. This tail follows crystal boundaries.

FIGURE 9

4.7.2. Microthermometry data

The two-phase fluid inclusions of subtypes Ib, IIb, IIIb and IVb were microthermometrically analysed. Subtypes Ia, IIa, IIIa and IVa inclusions could not be analysed as a vapour bubble was initially absent, neither could these inclusions be artificially stretched. Only four of all analysed inclusions ($n = 57$) homogenized at 61, 65, 127 and 135 °C. Vapour bubbles of other inclusions did not shrink during heating, neither did they homogenize.

Two fluid types are recognized and neither of these fluids are restricted to one specific inclusion type, neither can any of these fluids be related to specific crystal bands. One fluid shows first observable melting (T_{fm}) only at of -1.9 ± 1.0 °C ($n = 39$) and final melting of ice ($T_{m, ice}$) at -0.4 ± 0.3 °C ($n = 48$). Metastable freezing of these inclusions occurs between -38.6 and -47 °C. The other fluid has an average T_{fm} of -32.9 ± 6.1 °C ($n = 8$) and $T_{m, ice}$ of -29.2 ± 0.3 °C ($n = 9$).

FIGURE 10

5. Discussion

5.1. Interpretation of the San Pietro travertine depositional system

Several depositional units can be determined based on the three-dimensional mapping of lithotypes in the San Pietro travertine body (Figures 3, 4 and 5). The first, oldest, unit displays sloping layers, mainly consisting of *dendrite crusts* and *vacuolar boundstones*. The second unit consists of smoothly sloping to subhorizontal deposits, onlapping unit 1. Within this second unit, layers interfinger (Figure 5A), reflecting migrating flow paths. Next to the second unit, the third unit consist of steeply sloping, subvertical deposits, which appear to be waterfalls rimming the flat pools of the second unit. On top of these units, the fourth unit defines an arc shaped structure that is cross-cut by two veins. Upon tracking the deposits adjacent to these veins laterally, it can be demonstrated that these veins represent one feeder conduit of a fissure ridge (sensu De Filippis et al., 2012; 2013a), rather than two separate point-sources. The *grey mudstone* horizons that can be followed throughout these deposits contain karstic dissolution features and micritization of previously existing features, thus suggesting that these deposits represent periods of reworking without sedimentation and thus most likely the fissure ridge, or at least this sector of the ridge, was not permanently active. This interpretation is in line with similar hillwash breccia, as

described by Pedley (2009) and fine-grained lithoclast travertine described by Gradziński et al. (2014) which were linked to activity or sedimentation breaks. The deposits in the arc vary from *vacuolar boundstone* to *dendrite crusts* to *peloidal packstone* with increasing distance from the central vein with increasingly steeper slopes. This lithotype variation could reflect a shift to faster fluid flow and/or less fluid availability. In the northernmost part of the quarry, small decameter-scale terraces developed in the fissure ridge deposits. The final, fifth unit laps on the fissure ridge deposits and consists dominantly of *laminite-phytoclast travertine* suggesting deposition in more distal marsh environments (Gandin and Capezzuoli, 2014). The increased abundance of phytoclasts suggests lower water temperature, testifying to longer fluid paths or increased mixing with rain water, thus suggesting a shift in fluid emergence location.

The resulting depositional system is typical of a slope travertine evolving from a proximal (fissure ridge) to a marginal system (fluvial to marsh) which is first observed to be prograding during the first three units, culminating in large waterfalls adjacent to the river. From the fourth unit onwards, deposits were deposited further from the river in a clear fissure ridge and finally marshy deposits accumulated in the fifth unit, suggesting retrograding of the travertine system. Also in the other, 2nd and 3rd order terraces, represented by the Tancredi and Cardi quarries respectively, evolution of comparable slope travertine depositional systems, especially the first prograding phases, were described (Della Porta et al., 2017) implying the repetition of comparable depositional systems at different ages.

5.2. Age and depositional evolution of the Acquasanta Terme travertine system

The age of the Acquasanta Terme travertine deposits has been differently assigned by previous authors. Boni and Colacicchi (1966) ascribe them to a Quaternary age, Farabollini et al. (2005) to the Late Pleistocene on the basis of stratigraphic considerations and Minissale et al. (2002) provided a single age at 144.7 ka (Middle Pleistocene) without indication of which terrace was sampled. Therefore, in this study, new radiometric dating was performed for each terrace, assigning ages between 199.7±16.3 ka and 221.4±5.8 ka for the upper terrace, between 123.2±17.6 ka and 129.9±8.2 ka for the middle terrace

and between 28.6 ± 8.5 ka and 44.7 ± 16.5 ka for the youngest, lowest terrace. In fact, these ages correspond to the odd-numbered Marine Isotope Stages (MIS) of Martinson et al. (1987) and Lisiecki and Raymo (2005) (Figure 9). In detail, deposition of the upper, 1st order terrace is coeval with MIS 7, while the middle, 2nd order terrace, corresponds to the onset of MIS 5. Both events represent important interglacial stages in the Mediterranean area and record important pollen flourishing, correlated to major vegetational events and humid conditions (Tzedakis et al., 2001). The lowest 3rd order terrace, formed during MIS 3 which is not considered a typical interglacial with uniform warm and wet conditions (Fitzsimmons et al., 2012), but is characterized by widespread continental carbonate deposition, at least in Italy (e.g. Rocchetta al Volturno – Brancaccio et al., 1986; Aniene River – Carrara et al., 2006; Tivoli - Faccenna et al., 2008; Valdelsa - Capezzuoli et al., 2010; Rapolano Terme - Brogi et al., 2012).

FIGURE 11

The new radiometric dating furthermore implies a complex relationship between local tectonic uplift, fluvial morphodynamics and climate. In brief, similar to other Italian travertine areas (Soligo et al., 2002; Faccenna et al., 2008; Brogi et al., 2010, 2012), fluids emerging in the Acquasanta Terme area were dominantly related to humid periods when it was possible to recharge the deep reservoir, with consequent travertine deposition during the odd-numbered Marine Isotope Stages. During the even-numbered stages, fluvial erosion led by regional uplift prevailed. Based on the ages and heights of the three travertine terraces, the average long-term uplift rate of the area can be deduced. In fact, the data in Table 5 suggest a difference in height between the first order Terrace and the Tronto River of about 225-230 m (in the different SW/NE areas) that, coupled with the 200-221 ka difference in age, imply a long-term uplift rate of about 1 mm/y. This value is in agreement with bibliographic data (0.5-1 mm/y - D'Agostino et al., 2001) for the Central Apennines. Short term values calculated between each terrace order show a similar rate in Table 5. This uplift rate assumes that travertine deposition took place at the same level as the Tronto River, which is a viable assumption because travertine is directly overlying fluvial sediments (Boni and Colacicchi, 1966). However, during deposition the point of fluid emergence might shift upwards because of conduit cementation, although this shift would not majorly impact the calculated uplift rates.

TABLE 5

Within the internal evolution of each terrace, as shown by studies in the Cardi and Tancredi quarries (3rd and 2nd order terrace – Della Porta et al., 2017) and San Pietro quarry (1st order terrace), travertine deposition was discontinuous. This is supported by the widespread presence of palaeokarst horizons, like *grey mudstone*, angular unconformities, palaeosoils and colluvial deposits (Pedley, 2009; Gradziński et al., 2014). The processes that relate to temporal sedimentation stops are controlled by local factors like water diversion and ephemeral subaerial processes and could indicate local, temporal variation in water flow unrelated to large scale processes like climatic variation and tectonic uplift which are responsible for the deposition of the different terraces.

5.3. Origin of CO₂ and Ca²⁺

The main rock constituents to create continental spring carbonates are dissolved CO₂ and Ca²⁺, the origin of both can be determined from geochemical signatures of fossil deposits (Claes et al., 2015, 2019; El Desouky et al., 2015). In order to reduce the impact of surficial processes like degassing and evaporation on fractionation, only cements in the central vein of the fissure ridge are used as they are expected to provide the most pristine signature of the studied fossil travertine deposit.

CO₂ provenance could be determined by applying the empirical Panichi and Tongiorgi (1975) equation for obtaining $\delta^{13}\text{C}_{\text{CO}_2}$ from measured $\delta^{13}\text{C}_{\text{CaCO}_3}$ (Claes et al., 2015; El Desouky et al., 2015). The calculated average $\delta^{13}\text{C}_{\text{CO}_2}$ is -1.15 ‰. This slightly negative value rules out CO₂ related to soil or hydrocarbons as both would produce values of -25 ‰ and lower. Neither could it have a meteoric origin which would give $\delta^{13}\text{C}_{\text{CO}_2}$ of -7 ‰. Thus, the CO₂ is most likely derived from deeper processes like magmatic degassing or thermal decarbonation of carbonates. The former is not likely because it would produce more depressed $\delta^{13}\text{C}_{\text{CO}_2}$ values between -4 and -8 ‰ (Sano and Marty, 1995; Rose and Davisson, 1996; Minissale et al., 2002; Hoefs, 2009) and no igneous processes have been described in the Acquasanta Terme area, apart from Madonna et al. (2005). Furthermore, Minissale et al. (2002) and Fusari et al. (2017) studied present-day springs and provided arguments, e.g. low ³He/⁴He ratios, to confirm the absence of magmatic degassing. Thermal decarbonation, however, is able to produce

468 substantial amounts of CO₂ (Kerrick and Caldeira, 1993) with inferred high $\delta^{13}\text{C}_{\text{CO}_2}$ value if the process
 469 occurred at 110 °C (Bottinga, 1968; Minissale et al., 2002; Minissale, 2004). This temperature suggests
 470 decarbonation at a depth of approximately 3 to 3.5 km when assuming a geothermal gradient between
 471 25 and 30 °C/km, which is a realistic value in the absence of igneous activity. This depth corresponds
 472 to the Triassic Anidriti di Burano Formation in the study area (see Figure 2). It has to be noted that
 473 dissolution of carbonates and water-rock interaction could have buffered the $\delta^{13}\text{C}$ values and thus
 474 overprinted the original signature, although a more positive value would be expected (Claes et al., 2015).

475 The second rock constituent is Ca²⁺, which could be derived from carbonate dissolution or other water-
 476 rock interaction processes, like albitization of calcic plagioclase, dolomitization or cation exchange with
 477 clay minerals (Connolly et al., 1990; Goldstein and Reynolds, 1994; Heijlen et al., 2001). The Ca²⁺
 478 origin can be found through ⁸⁷Sr/⁸⁶Sr signatures because Sr²⁺ preferentially substitutes Ca²⁺ in the
 479 calcite/aragonite crystal lattice and in general, no fractionation of the isotope ratio is present (Minissale
 480 et al., 2002; Minissale, 2004; El Desouky et al., 2015). The strontium isotope ratio of travertine from
 481 San Pietro Quarry is remarkably constant at 0.707914 ± 0.00019 , which implies a uniform Ca²⁺ source.
 482 Such a uniform source can be found from interaction with deep carbonates and would refute cation
 483 exchange with clay minerals which would give a more variable signature (Barbieri et al., 1979; Claes et
 484 al., 2015; El Desouky et al., 2015). Thus, the most likely Ca²⁺ source is carbonate dissolution and
 485 because marine carbonates are present throughout the entire lithostratigraphic column (Figure 2),
 486 strontium isotope stratigraphy curves can be used to determine the approximate age of dissolved
 487 carbonates (McArthur, 2010; McArthur et al., 2012; El Desouky et al., 2015). Such a curve is shown in
 488 Figure 7 where three intersections between seawater ⁸⁷Sr/⁸⁶Sr and the measured strontium isotope ratio
 489 can be seen. Two of these intersections are Triassic and one Oligocene in age. In the study area the
 490 Oligocene rocks are marly deposits and due to the fact that clay mineral influence has already been
 491 dismissed, these rocks most likely did not contribute Ca²⁺ to the fluids. Therefore, the Late Triassic
 492 rocks are the most likely candidates. This corresponds to the Anidriti di Burano Formation, which indeed
 493 has a similar ⁸⁷Sr/⁸⁶Sr ratio (Figure 2; Dinelli et al., 1999) and furthermore, the depth of this formation

matches the calculated depth of CO₂ provenance. Note that rocks older than Triassic are not included as they are dominantly siliciclastic in the study area (Tozer et al., 2006; Fusari et al., 2013, 2017).

Furthermore, comparing the strontium and barium content of *aragonite veins*, which are 7786 ± 177 mg/kg and 30 ± 6 mg/kg respectively and stable isotopes to data (Teboul et al., 2016) indicates that the fluids have a hypogean origin (Figure 7) and were in contact with late Triassic/lower Jurassic limestones, dolostones or evaporites. Also the high sulphur content of 1023 ± 367 mg/kg and even higher values of 3095 ± 1988 mg/kg for bedded travertine adds to the likelihood that evaporites were directly involved in the process. Additionally, the same strontium isotope ratio is reported by Fusari et al. (2017) for the present day fluids emerging at Acquasanta Terme.

The interpretations of CO₂ and Ca²⁺ provenance are based on the assumption that none of the geochemical signals has been altered or reset due to water-rock interaction (Andrews et al., 1993; 1997). Uniformity of isotope measurements supports the hypothesis that such resetting has not taken place.

5.4. Fluid origin, composition and spring temperature estimates.

Average stable oxygen isotopes of *aragonite vein* crystals ($\delta^{18}\text{O}_{\text{vein}}$) vary around -11.90 ‰ V-PDB, suggesting fluids were originally meteoric (Verhaert et al., 2004; Kele et al., 2011; Claes et al., 2015). Present day $\delta^{18}\text{O}_{\text{rain}}$ at the latitude of the study area varies between -6.4 and -5.4 ‰ V-SMOW (Swart et al., 1993), demonstrating further fractionation related to spring temperature. Lacking local data on the spring water oxygen isotopes during the Quaternary and assuming, for simplicity, that spring water oxygen isotopes remained constant over at least 221 ka, this temperature can be calculated, based on a present-day spring water $\delta^{18}\text{O}$ -isotope values, varying between -9.36 ‰ and -10.10 ‰ SMOW depending on seasonal variability (Minissale et al., 2002; Fusari et al., 2013; 2017). Resulting calculated temperatures are between 23.9 and 27.5 °C when assuming equilibrium fractionation (O'Neil et al., 1969; Friedman and O'Neil, 1977), 22.2 to 25.9 °C based on Kim and O'Neil (1997), varying between 28.9 and 32.8 °C based on Demény et al. (2010) or between 36.6 and 40.0 °C based on Kele et al. (2015) when assuming disequilibrium precipitation. The latter two equations are most representative for

travertine as they are based on empirical relationships determined from actual active travertine systems, although samples used for calculations come from a vein which supposedly did not form under subaerial conditions. However, disequilibrium precipitation could not be disregarded as the vein was probably surface proximal. Apart from temperature calculations, fluid inclusion homogenization temperatures (T_H) could also be used to estimate precipitation temperatures. However, most inclusions did not homogenize ($n = 53$) and those that did ($n = 4$), homogenized at variable temperatures. Furthermore, variable vapour contents of all studied inclusions and the inability to obtain homogenization temperatures suggest heterogeneous trapping, post-depositional leakage through crystal boundaries or leakage during measurement (Roedder, 1984; Goldstein and Reynolds, 1994; Muchez and Slobodnik, 1996; El Desouky et al., 2015). The former process could be caused by vadose trapping (Goldstein et al., 1990; Goldstein and Reynolds, 1994), fluid boiling (El Desouky et al., 2015) or degassing of CO_2 , three processes often associated with continental carbonates.. A temperature estimate could however be given by the majority of fluid inclusions being mono-phase even after cooling at $-18\text{ }^{\circ}C$ for two weeks, suggesting trapping below $50\text{ }^{\circ}C$ (Goldstein and Reynolds, 1994; Muchez and Slobodnik, 1996).

In conclusion, oxygen isotope calculations and fluid inclusion data suggest precipitation temperatures between 28.9 and $50\text{ }^{\circ}C$. This is in accordance with present-day spring waters having temperatures between 32 and $44^{\circ}C$ according to Galdenzi et al. (2010) and approximately $30\text{ }^{\circ}C$ according to Fusari et al. (2017).

Two fluid types are described through microthermometry analyses on fluid inclusions in palisade crystals of *aragonite veins* in the San Pietro Quarry, however neither fluid could be constrained to specific crystal bands. One fluid has final melting temperatures around $-0.4\text{ }^{\circ}C$, indicating a very low saline water with a calculated average salinity of $0.7 \pm 0.5\text{ wt\% NaCl}$ equivalent and salinity varying between 0 and $2.7\text{ wt\% NaCl}$ (based on Bodnar, 1993).

The second fluid has a much higher salinity as evidenced from T_{fm} down to $-48.7\text{ }^{\circ}C$ and final melts around $-29.2\text{ }^{\circ}C$. Base on the low T_{fm} values, the fluid most likely contains divalent cations, such as Ca^{2+} or Mg^{2+} in addition to monovalent cations (Davis et al., 1990; Steele-MacInnis et al., 2011). Since no

hydrohalite melting temperature is found salinity can only be given in equivalent percentage of NaCl. Applying the equations of Bodnar (1993) results in an average salinity of 28.2 wt% NaCl equivalent. These two salinity-type fluids were also recognized in present-day spring-water analyses at Acquasanta Terme (Madonna et al., 2005; Galdenzi et al., 2010; Fusari et al., 2017). However, these studies note that the two fluids occur at different sources, whereas in our study both fluids occur within the same fossil spring (Aragonite vein).

5.5. Fluid circulation implications

The assembly of trace element, stable oxygen, carbon and strontium isotope data suggests that spring fluids migrated through the Triassic Anidriti di Burano Formation at depth (Figure 2). However, two fluid types with significantly different salinities are identified within the same vein. One fluid has low salinity (0 - 2.7 wt% NaCl equivalent), whereas the other fluid has high salinity and there is no evidence of fluids mixing. Because both fluids were encountered within the same vein, which is a conduit for mineralising fluids, two fluid reservoirs present at depth are implied. The high salinity fluid was likely in contact with evaporite layers of the Anidriti di Burano Formation explaining the high salinity due to evaporite dissolution (Koopman, 1983). Similar processes are seen in other geothermal systems, e.g. Tuscany in Italy (Ruggieri et al., 1999; Gasparrini et al., 2013; Brogi et al., 2016), Denizli in Turkey (El Desouky et al., 2015) or other settings like the Wytch Farm oilfield in the UK (Worden et al., 2006). Notably, in the Italian and Turkish geothermal systems, the high salinity fluid was also related to dissolution of Triassic evaporite deposits.

The low salinity fluid also appears to pass through the Anidriti di Burano Formation, based on the uniformity of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and interpretations of CO_2 provenance, but the dissolution of evaporites was very limited. The exact reservoir configuration and fluid paths could not be determined based on the available data but two reservoirs appear to be present throughout the Anidriti di Burano Formation (Figure 10). One reservoir would be hosted in carbonates devoid of evaporites, which could correspond to the main cataclastic carbonate structural level (Calcare Cavernoso Fm Auctorum; Brogi et al., 2016)

derived from the tectonization of the Anidriti di Burano Formation and from which evaporites dissolved in the past (Lugli, 2001). This structural level, known also as the “first” reservoir in the geothermal areas of the Apennine western side (Brogi et al., 2016), represent the bulk of the epithermal mineralization of southern Tuscany-Latium and is also characterized by low-salinity aqueous liquids, sometimes containing small amounts of CO₂.

The second reservoir should have been directly in contact with evaporites and sufficient residence time would have occurred to allow fluid-rock interaction in order to create this distinctly different fluid. In Tuscany, such reservoir contains fluids with variable salinities and containing dissolved Ca²⁺ and Mg²⁺ in addition to Na⁺, and is believed to be derived from the interaction of meteoric water with the Mesozoic evaporite-carbonate sequence and/or to represent connate waters mobilized during geothermal activity and/or the result of fluid boiling and mixing processes (Ruggieri et al., 1999; Brogi et al., 2016). These reservoirs would open up to the surface and are able to deposit travertine when sufficient pressure build up took place. This appears to be the case during warmer and wetter climatologic periods, as indicated by the dating of the different terraces and was similarly reported in other situations (Ruszkiczay-Rüdiger et al., 2005; Antoine et al., 2007; Burnside et al., 2013).

In this view, fluid circulation is interpreted to be dominated by an interplay of climatic, gravitational and tectonic factors. Spring fluids had a meteoric origin and because the ages of major travertine deposition suggest that spring activity is related to more humid periods, a strong climatic control is inferred. Fluid circulation itself is dominated by a hydraulic head caused by meteoric fluids infiltrating at nearby mountain ranges, like the Sibillini mountains to the East (Menichetti, 2008) or Laga mountains to the South (Fusari et al., 2017) of the study area. Furthermore, fluid circulation is expected to rapidly respond to changes in meteoric water infiltration rates because fluid flow is dominated through the cataclastic and karstified Calcare Cavernoso Fm.

From a geometrical point of view, the two reservoirs (Anidriti di Burano Fm and Calcare Cavernoso Fm) could be located at the same structural level, with the Calcare Cavernoso Fm forming the upper, tectonized portion of Anidriti di Burano Fm (Case 1 in Fig.10A), or at different structural levels determined by thrust and fold architecture (Case 2 in Fig. 10B). In both cases, fluid circulation was then

facilitated by fault presence caused by thrust faulting during compressional deformation and subsequent normal and transverse faulting able to connect different structural levels. Unfortunately, this study cannot provide additional arguments for the fluid migration pattern and exact source region. Apart from a gradient driven by hydraulic head, tectonic control could influence fluid discharge, as seen after the Central Italy earthquake swarms in 2016-2017 (Barberio et al., 2017; Petitta et al., 2018; Rosen et al., 2018).

FIGURE 12

6. Conclusions

This paper aimed to unravel, describe and time fluid flow in the Acquasanta Terme area for the past 200 ka, while describing the sedimentological build-up of the travertine terraces at Acquasanta Terme, with special attention to the uppermost terrace because this terrace was not previously described. These objectives were achieved by detailed macroscopic and microscopic analyses, geochemical characterisation of fossil carbonates, fluid inclusion analysis and U-Th dating of three different travertine generations.

1. The travertine depositional system of the upper terrace evidenced at San Pietro Quarry is typical of a slope system grading from a proximal feeding system into flat marginal deposits bordered by waterfall travertine through smoothly sloping deposits and eventually a more distal system. Similar depositional systems are also present in the lower and younger terraces.
2. At Acquasanta Terme, CO₂ is derived from thermal decarbonation of carbonates at a depth of at least 3 km and Ca²⁺ is obtained from dissolution of Triassic Anidriti di Burano Fm, which also occur at a depth of approximately 3 km in the study area. Furthermore, the high sulphur content of the travertine and the identical Sr-isotope signature further supports dissolution of Burano evaporites.

3. Two fluids, one with a mean salinity of 0.66 ± 0.47 wt% NaCl equivalent and the other with 28.2 wt% NaCl equivalent, probably containing divalent cations, have been recognized. There is no evidence for mixing between these fluids though both appear to emerge at the same spring.
4. Inferred meteoric fluids migrated through Anidriti di Burano Fm carbonates and evaporites. One fluid was in contact with anhydrites and had a sufficiently long residence time to dissolve them, whereas the other did not dissolve evaporites and is probably related with tectonized, cataclastic version of the same formation (Calcare Cavernoso Fm).
5. Deep reservoir recharge especially occurred during more humid periods. Fluids probably migrated and emerged in the Acquasanta Terme area along transcurrent faults. This process has been active for at least the last 221 ± 5 ka and travertine deposition occurred during odd-numbered MIS stages (7-5-3), corresponding to suitable palaeoclimatic conditions, while fluvial erosion dominated during even-numbered stages. Tectonic uplift of the Apennine orogen is recorded by three different terrace orders, and an uplift rate of approximately 1 mm per year is inferred.

This study provides a unique situation in which data derived from fossil travertine can be compared to information from present-day springs and notes a remarkable equivalence, proving the strength of a combined fluid inclusion and geochemical approach.

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9. Figure captions

Figure 1: Geological setting and localization of the studied area (redrawn from Della Porta et al., 2017); A. Geographical setting. B. Geology of the area between Ascoli Piceno and Acquasanta Terme with the main Pleistocene travertine deposits of the Tronto river Valley; C. Detail of the Acquasanta Terme anticline with the Travertine terraces, location of the investigated travertine quarries (San Pietro Quarry Tancredi Quarry; Cardi Quarry), samples (S1-S6) for radiometric analyses and main faults (redrafted after Madonna et al., 2005; Menichetti, 2008; Galdenzi et al., 2010; Maggi et al., 2015).

Figure 2: Stratigraphy at Acquasanta Terme, in the core of the anticline, based on the stratigraphy from nearby mountain ranges (Koopman, 1983; Menichetti, 2008; Cardello and Doglioni, 2015). This succession is approximately 3 to 3.5 km thick.

Figure 3: Petrography. If based on thin-section petrography, then “T” is transmitted light and “P” is polarising light, with porosity in yellow and dark green, respectively. A. *vacuolar boundstones* (quarry wall). B. Microterraces as upper surface of dendrite crusts (rock specimen). C. Dendrites of *dendrite crusts* (T). D. *Grey mudstone*, arrows indicate phytoclastic fossils and vugs in upright position (quarry wall). E. *Grey mudstone* with vugs in yellow and more whitish calcite cements (T). F. *Peloidal packstone* (T). G. *Aragonite vein* showing three different crystal habits (P). H. *Laminite-phytoclast travertine*, containing transported phytoclast fragments with thin curving layers in between fragments (quarry wall). I. *Laminite-phytoclast travertine*, showing laminites (T). Laminites consist of dark micrite and are surrounded by calcite crystals (white). J. Shrubs in pools of terraced deposits (quarry wall). K. White aragonite cements with needle-like habitus in *vacuolar boundstone* (P). L. *Fossil cave infill* (quarry wall). M. *Crystalline crust* (quarry wall).

Figure 4: Three-dimensional overview of the San Pietro quarry, three coloured dots (green, yellow and red) are added as marker points. Three excavators in the SketchUp model for scale. A to C. Linedrawings simplified to a SketchUp model at three different angles. D. Five different sedimentological packages overlain on a 3D photogrammetrical quarry reconstruction.

Figure 5: Lithotype distribution. A. Interfingering of smoothly sloping deposits of the second depositional package (see Figure 4), mainly consisting of *vacuolar boundstone*. B. More steeply sloping deposits in the top of the quarry (near green marker point in Figure 4) in which a vein crosscuts an arc shaped topology. These deposits make up the fourth depositional phase (Figure 4).

Figure 6: Plot showing two first principal components of a principal component analysis with three principal components of major and trace element data, with explained variance indicated per component. This plot shows which elements introduce most variance between samples. The colours indicate the lithotype group to which the samples belong.

Figure 7: Results of stable isotopes overlain on clusters of Teboul et al. (2016). Blue dots represent the *aragonite veins*, grey dots represent the aragonitic cements, yellow dots represent porous, bedded travertine and orange dots represent *grey mudstone*. All dots, apart from two dots plot within the hypogean travertine area of Teboul et al. (2016), with CO₂ derived from carbonates or an igneous source.

Figure 8: Strontium isotopes plotted on strontium stratigraphy curve (McArthur, 2010; McArthur et al., 2012), with indication of local subsurface and outcropping carbonates at Acquasanta Terme. Results of strontium isotopes of analysed travertines are indicated in red. The stratigraphy at Acquasanta Terme contains carbonates from Triassic up to Neogene age. Part of this sequence is outcropping. The arrows indicate possible candidates of dissolved rocks in the subsurface.

Figure 9: Fluid inclusion types. A. Long type Ia inclusion, dimensions: 2 x 130 µm. B. Type IIb inclusions with 10 Vol% vapour and a type IVb inclusion. C. Large type IIa and IIb inclusions with dimensions 15 x 30 µm. D. Inclusion types Ia, IIIa and IIIb. E. Type IIb and IIIa inclusions. F. Type IIb inclusion with approximately 70 Vol% vapour. G. Ia and IVb inclusion, the latter with a deformed lenticular shape. H. Empty inclusions with dark appearance.

1096 Figure 10: Histogram indicating final melt temperatures of fluid inclusion microthermometry measurements. Note
1097 that the histogram is discontinuous in the middle, because no analyses fell within that range.

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1099 Figure 11: Comparison between available paleoclimate and travertine data of Acquasanta Terme area. Travertine
1100 data (samples S1-6) are reported with their standard deviation. The grey dark area identifies the three depositional
1101 stages (1°-2°-3°Terrace) corresponding to the odd-numbered MIS (7-5-3), respectively. Shaded area characterises
1102 standard deviations on age dating; Black line is the SPECMAP marine paleoclimatic $\delta^{18}\text{O}$ record during late
1103 Pleistocene time (Martinson et al., 1987)

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1105 Figure 12: Two potential interpretations of fluid flow overlain on profile presented by Menichetti (2008). A. Case
1106 1: Two reservoirs at different structural levels in the Anidriti di Burano Fm, of which the Calcare Caveroso Fm
1107 forms the upper part. Both reservoirs are separated by an aquiclude. B. Case 2: Two reservoirs, each in the
1108 cataclized Calcare Cavernoso Fm of the Anidriti di Burano Fm, at different structural levels. C. Close-up sketch
1109 of the close to surface geological situation, where fluids are seen to be migrating through transform faults, which
1110 best fit with the current structural situation.

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1112 **10. Table captions**

1113 Table 1: Lithotype descriptions

1114 Table 2: Major and minor element analysis, with samples separated in different groups. Only elements that
1115 surpassed the detection limit are indicated.

1116 Table 3: Stable oxygen and carbon isotope results with the respective standard variation and number of samples
1117 analysed.

1118 Table 4: U–Th geochronological analyses from Acquasanta Terme. For localization of samples S1-6, see Figure
1119 1. Colour coding of samples uses colours of Figure 1.

1120 Table 5: Calculated uplift rates.

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1125 Figure 1

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Legend

Evaporites

Limestone

Dolomite

Marly limestone

Marl

Siliciclastic deposits

Brecciated and dissolved limestone

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1136 **Figure 6**

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1141 **Figure 8**

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1147 **Figure 10**

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1150 **Figure 11**

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1157 Table 1

	Lithotype	Description	Figure
BEDDED TRAVERTINE	Vacuolar boundstone	Thin layers of creamy coloured travertine with vacuolar, lens shaped, interlayer porosity and regular intercalations of more micrite-rich zones. The thin layers consist of microspar, with dark crystal cores and pores that are often partly filled with calcite cements. The zones with more micrite are less porous and the micrite morphology microscopically consists of dark peloids arranged as small dendritic shrubs. On steeply ($> 30^\circ$) dipping deposits, this lithotype dominantly contains vacuolar pores with length exceeding 3 cm and a height of 1 cm maximum. In flat deposits, these strata are more commonly interlayered with thin layers containing pisoids, which microscopically correspond to radial shrubs, in which small black dendrites grow outward from a small, often invisible core. The vacuolar pores are smaller (< 1 cm), compared to sloping deposits.	Figure 3A
	Dendrite crust	Crusts with macroscopically recognizable dendrites, with length-to-width ratios exceeding 10:1. The dendrites readily reach lengths up to 10 cm and microscopically consist of dense dark micritic peloids surrounded by a consolidating cement. The area in between dendrites is porous. The ends of the dendrites form microterraces about 2 cm across. This lithotype mainly occurs on deposits with slopes exceeding 30° and often reaching 60° .	Figure 3B & C
	Grey mudstone	Horizons that can span over long distances that are differentiated from all other lithotypes by their grey colour, in contrast to the creamy white colour of other lithotypes. Their thickness varies from a couple of centimetres to 1 meter and they can overly any other lithotype. Monomict breccia fragments regularly float in the grey matrix and are mainly composed of creamy white porous travertine fragments. The deposits are generally micritic with irregular vugs which are often filled with calcite cements (dogtooth, bladed and equant in outline). These cements show variable luminescence, with Non-Bright-Dull (NBD) sequences and micritized structures. A limited amount of detrital minerals is present, including quartz and biotite. Reed moulds occur in growth position.	Figure 3D & E
	Peloidal packstone	Lithotype dominated by dark brown to black peloids, which are sometimes organized as dendritic shrubs in small clusters of approximately 10 peloids. In between peloids, a microsparitic to sparitic cement is present. Macroscopically, the deposits appear micritic and no distinct features can be distinguished. Pores are usually only visible under the microscope. These deposits are dominantly found in steeply sloping deposits with angles larger than 45° .	Figure 3F
	Laminite-phytoclast travertine	Lithotype mainly consisting of thin (~ 1 mm) layers which are regularly straight for a couple of centimetres, resembling paper-thin rafts. A major contrast to classical rafts is that the layers often curve when overlying some prior topography or when occurring adjacent to macrophyte moulds. The layers resemble puff pastry. Reed moulds occur in between these laminites and can be up to 5 cm in width. They are preserved in growth position and as transported fragments and they may correspond to full plants, roots included. Microscopically, the individual sheets consist of a thin micritic film, lined by crystals. From this micritic film, peloids and very small dendritic shrubs protrude downwards. This lithotype only occurs in flat deposits.	Figure 3H & I
	Crystalline crust	This lithotype is largely similar to dendrite crusts but more crystalline zones are interlayered with more porous zones. Microscopically, crystal rays have a banded to fan-like appearance. The crystalline crusts are mainly recognized in steeply dipping deposits (sub-vertical) and continuous layers can be followed over several meters.	Figure 3M
	Shrubs	Shrubs are present in pools of small fossil terraces. These terraces are seldomly developed in the exposed deposits. Arborescent shrubs, with dimensions exceeding 5 cm in height and length-to-width ratios of approximately 3:1 are most common.	Figure 3J
BANDED TRAVERTINE	Aragonite vein	Vertically continuous veins that crosscut porous bedded deposits. These veins have clear crystals with colours varying between translucent, white and brown. The crystals have variable habitus. The brown translucent zones generally contain large thick crystals with lengths up to 5 mm. The white zones contain thin needles. Crystal growth zones are often interrupted by dark micritic patches on microscopic scales. Furthermore, aragonite cements are rarely found in vacuolar boundstones and are clearly visible by their bright white colour. These crystals appear as needle botroids in thin sections, similar to the white zones in aragonite veins. XRD analysis attests that these crystals are 99% aragonite, whereas the surrounding travertine is 99% calcite.	Figure 3G and 3K

SPELEOTHE M	Fossil cave infill	A peculiar structure is present in the San Pietro travertine. It consists of a triangular shaped feature of which the borders resemble the gray micritic travertine. The dimensions of this structure are 5.5 by 5 m by (at least) 2 m. The travertine within this structure is discontinuous from the travertine outside of it. The rocks are typically porous and microscopically crystal or micritic bands and fans dominate.	Figure 3L
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1160 **Table 2**

	Mean elemental composition (mg/kg)										Number of samples (N)
	Carbonate related						Siliciclastic related				
Lithotype	Ca (%)	Sr	S	Ba	Na	Mg	Al	Fe	K	P	
Detection limit	1	15	50	2	80	10	15	5	15	15	
Bedded travertine	38.3 ± 0.5	1335 ± 583	3095 ± 2095	16 ± 9	322 ± 263	2657 ± 732	111 ± 70	18 ± 10	96 ± 80	26 ± 13	10
Grey mudstone	37.0 ± 1.1	1832 ± 518	6487 ± 3166	98 ± 122	1097 ± 335	4468 ± 1166	2906 ± 3129	932 ± 1342	922 ± 992	89 ± 35	4
Aragonite crystals (veins and cements)	38.1 ± 0.1	7786 ± 216	1023 ± 449	30 ± 7	555 ± 184	53 ± 22	646 ± 104	9 ± 3	73 ± 5	84 ± 46	3

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1163 **Table 3**

	$\delta^{18}\text{O}$ (‰ V-PDB)		$\delta^{13}\text{C}$ (‰ V-PDB)		n
	average	σ	average	σ	
Aragonite crystals	-11.90	0.36	7.42	0.57	8
<i>Veins (banded)</i>	-11.90	0.32	7.79	0.20	5
<i>White cement rims</i>	-11.92	0.50	6.80	0.38	3
Bedded travertine	-10.68	1.22	8.96	1.72	25
<i>Dendrite crust</i>	-10.74	0.84	8.31	0.53	8
<i>Vacuolar boundstone</i>	-11.28	0.66	8.03	0.18	6
<i>Crystalline crust</i>	-10.23	0.68	10.85	0.23	2
<i>Laminite-phytoclast</i>	-11.32	0.43	8.32	0.20	3
<i>Arborescent shrub</i>	-10.94	/	8.25	/	1
<i>Fossil cave infill</i>	-9.62	2.14	10.87	2.90	5
Grey micritic travertine	-10.58	1.16	6.66	2.79	4

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Sample ID	Weight g	²³⁸ U ppb ^a	²³² Th ppt	δ ²³⁴ U measured ^a	[²³⁰ Th/ ²³⁸ U] activity ^c	²³⁰ Th/ ²³² Th atomic (x 10 ⁻⁶)	Age (yr ago) uncorrected	Age (yr ago) corrected ^{c,d}	δ ²³⁴ U initial corrected ^b
S1	0.07759	4.5937 ± 0.0084	3777 ± 10	470.2 ± 8.9	0.497 ± 0.020	9.97 ± 0.41	43,960 ± 2183	28,630 ± 8537	510 ± 15
S2	0.07653	16.379 ± 0.026	420.0 ± 6.1	314.6 ± 4.4	1.213 ± 0.010	780 ± 13	221,813 ± 5848	221,385 ± 5830	588 ± 13
S3	0.0871	13.108 ± 0.042	8467 ± 32	80.1 ± 4.9	0.948 ± 0.022	24.20 ± 0.58	215,768 ± 15960	199,705 ± 16331	141 ± 11
S4	0.0921	6.090 ± 0.015	3320 ± 10	236.2 ± 7.7	0.928 ± 0.020	28.06 ± 0.62	141,182 ± 6280	129,905 ± 8246	341 ± 14
S5	0.0645	15.837 ± 0.043	18264 ± 84	166.2 ± 5.4	0.898 ± 0.026	12.83 ± 0.37	151,014 ± 9186	123,244 ± 17649	235 ± 14
S6	0.0895	8.545 ± 0.022	9868 ± 42	205.4 ± 6.5	0.595 ± 0.024	8.50 ± 0.35	72,545 ± 4185	44,671 ± 16500	233 ± 13

Analytical errors are 2σ of the mean.

^a [²³⁸U] = [²³⁵U] x 137.818 (±0.65‰) (Hiess et al., 2012); δ²³⁴U = ([²³⁴U/²³⁸U]_{activity} - 1) x 1000.

^b δ²³⁴U_{initial} corrected was calculated based on ²³⁰Th age (*T*), i.e., δ²³⁴U_{initial} = δ²³⁴U_{measured} X e^{-λ₂₃₄·*T*}, and *T* is corrected age.

^c [²³⁰Th/²³⁸U]_{activity} = 1 - e^{-λ₂₃₀·*T*} + (δ²³⁴U_{measured}/1000)[λ₂₃₀/(λ₂₃₀ - λ₂₃₄)](1 - e^{-(λ₂₃₀ - λ₂₃₄)·*T*)}, where *T* is the age.

Decay constants are 9.1705 x 10⁻⁶ yr⁻¹ for ²³⁰Th, 2.8221 x 10⁻⁶ yr⁻¹ for ²³⁴U (Cheng et al., 2013), and 1.55125 x 10⁻¹⁰ yr⁻¹ for ²³⁸U (Jaffey et al., 1971).

^d Age corrections, relative to chemistry date on March 2th, 2017, were calculated using an estimated atomic ²³⁰Th/²³²Th ratio of 4 (± 2) x 10⁻⁶.

Those are the values for a material at secular equilibrium, with the crustal ²³²Th/²³⁸U value of 3.8. The errors are arbitrarily assumed to be 50%.

1168 **Table 5**

		Zone SW	Zone NE	Ages (ky)	MIS	Long-term uplift rate	Short-term uplift rate	
First order Terrace	Top	600 m	530 m	221±5	7	≈1mm/y	≈1mm/y	
	Base	450/480	430	200±16				
Second order Terrace	Top	470/500	410/415	123±18	5		≈1mm/y	≈0.5mm/y
	Base	380/400	350	130±8				
Third order Terrace	Top	410	360	44±16	3			≈1mm/y
	Base	390	330	28±8				
Tronto River		375	300					

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