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Geochemical Evolution in Historical Time of Thermal Mineral Springs at Campetti Southwest (Veii, Central Italy) through Geoarcheological Investigation

Stefano Viaroli [1,*], Tiziano Latini [2,3], Emilio Cuoco [4], Angela Mormone [4], Monica Piochi [4] and Matteo Maggi [5]

1 Department of Earth Sciences, University of Pisa, 56126 Pisa, Italy
2 Departement of Antiquities, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy; tiziano.latini@uniroma1.it
3 MiC—Ministry of Culture, Via del Collegio Romano 27, 00186 Rome, Italy
4 Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Via Diocleziano 328, 80124 Naples, Italy; emilio.cuoco@ingv.it (E.C.); angela.mormone@ingv.it (A.M.); monica.piochi@ingv.it (M.P.)
5 Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA), 00144 Roma, Italy; matteo.maggi@isprambiente.it
* Correspondence: stefano.viaroli@unipi.it

Abstract: A multidisciplinary study, involving hydrogeological, geochemical, and mineralogical analyses, was conducted to define the evolution of thermal mineral springs in the Sabatini Volcanic District (SVD) (Central Italy) in a historic period. The outcomes were integrated with the archeological findings to improve the knowledge of the evolution of Veii, a settlement established since the Iron Age and later expanded by Etruscans and Romans. During the archeological excavations, water-related buildings were identified, especially at the Campetti Southwest site in the Veii settlement. Votive inscriptions also suggest the presence of buildings linked to sacred waters, even if a clear definition of the source and type of water is missing. In the SVD, some low-flow thermal mineral springs are present as a result of the mixing of thermal and CO_2-rich groundwater from the deep carbonate aquifer and the cold, shallow volcanic aquifer. Mineralogical and chemical analyses characterized the travertine and Fe-hydroxide deposits on Roman tanks and walls in Campetti Southwest and in a nearby ancient Roman bath along the Valchetta River. These deposits showed different relative concentrations of sedimentary and volcanic-related elements, testifying a geochemical evolution of the groundwater mixing and the presence of a paleothermal mineral spring in Campetti Southwest.

Keywords: thermal mineral springs; groundwater; Sabatini Volcanic District; hydrogeology; geoarcheology; travertines

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1. Introduction

Water availability has influenced the location of human settlements worldwide since ancient times [1–3]. It was an indispensable requirement to support permanent settlements, especially for large communities [4,5], with springs often representing the only way to guarantee the essential water resource for the population [6], even during droughts or war periods.

Because of its vital value, water is connected to many religious rituals and faiths, regardless of geographical location, cultures, and historic periods [7]. Water-related symbolism has occurred across civilizations and religious cultures since ancient times to nowadays, with several meanings [8]. Temples and bath complexes from antiquity are particularly worth noting. They were commonly realized in correspondence with thermal and mineral springs, and their occurrence is helpful to identify the presence of both water resources and sacred areas [9,10].

Here, we report the case of the ancient city of Veii (*Veio*) near Rome (Italy), with a detailed focus on the Campetti Southwest site. The city was frequented during the protohistoric Etruscan period and later controlled and expanded by the Romans until the fall of the Empire, when Veii was progressively abandoned [11–13]. Archeological excavations discovered a high number of water-related structures (e.g., pools, tanks), mostly concentrated at the Campetti Southwest site. Highly relevant is also the presence of a *nymphaeum*, a rectangular, apsidal building with niches associated with water. Here, votive inscriptions strongly suggest the presence of sacred water-related structures. However, the lack of active springs or evidence of water supply systems strongly limited a fully archeological comprehension of this site [14].

Hydrogeological and petrological analyses were combined with the archeological findings to improve knowledge on the evolution of the local thermal mineral springs and their influence on the Veii settlement evolution. Hydrogeological surveys were conducted in the Veii area to detect active thermal–mineral springs. The chemical composition of the springs results from a mixing between hot mineralized groundwater coming from deep carbonate aquifers and cold groundwater from shallow volcanic aquifers. In addition, travertine and oxide layers were collected both inside and near the archeological site as proofs of ancient deposits produced by paleothermal mineral springs. Geochemical and mineralogical results define the chemical evolution that occurred in the thermal mineral springs since historical times and support the identification of a thermal mineral spring in the Campetti Southwest site at least during Roman times.

Hydrogeology and archeology findings can, therefore, be integrated into similar studies focusing on the assessment and evolution of human societies and water resources in ancient settlements.

2. Study Area

2.1. Geological Settings

The studied archeological site of Veii is in the southeastern sector of the Sabatini Volcanic District (SVD), one of the dormant Quaternary volcanic districts of the Roman Province [15,16] in Central Italy (Figure 1A). SVD lies on a sedimentary basement composed of four main units [17–20]: Triassic evaporites (I); Meso-Cenozoic carbonates (II); Cretaceous-Oligocene calcareous-pelitic calcarenites and arenaceous-pelitic turbidites (Ligurian units) (III); and Plio-Pleistocene continental to marine deposits (IV) (Figure 1B).

The sedimentary basement was affected by two main tectonic phases: the compressional stage leading to the construction of the Apennine orogen since the Eocene (i) and the post-orogen extensional stage linked with the opening of the Tyrrhenian Sea since the Late Miocene (ii) [21]. The latter extensional tectonics produced NNW-SSE horst-and graben structures that controlled the SVD volcanic evolution.

The SVD activity is dated between 0.60 and 0.08 Ma [22–24] and characterized by acid domes, lava flows, pyroclastic fall deposits, and, mostly during the final stage, phreatomagmatic deposits [25]. The volcanic stratigraphy in the Veii area can be summarized according to [26] (Figure 1C):

- "Pyroclastic fall deposits from Sacrofano" (PFS), which extensively outcrop over the SE sector of SVD;
- "Red tuff with black scoria" (RTBS) pyroclastic flow unit, interbedded in the PFS unit;
- "Sacrofano lower pyroclastic flow unit" (SLP), a tuff composed of centimetric pumices, sedimentary, and volcanic clasts, in a lithified ash matrix. SLP directly covers the sedimentary substratum.

As volcanic activity waned, most of the late craters and caldera basins were occupied by lakes; some of them are nowadays drained and filled by alluvial and lacustrine sediments. Peripheral fluvial valleys have developed along the SVD, mostly controlled by tectonic structures [27], driving the upwelling of deep mineralized fluids and the formation of travertines [28].

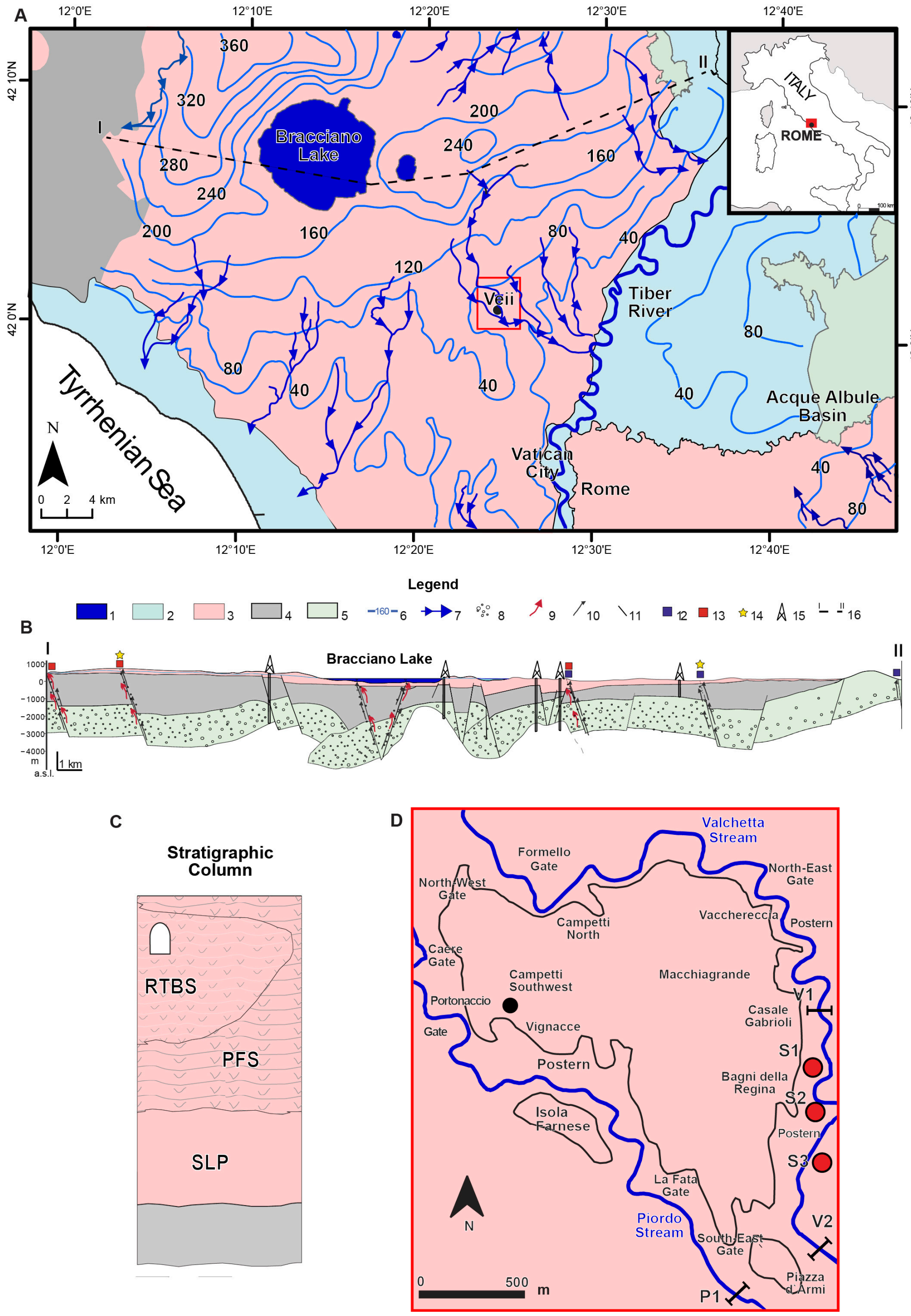

Figure 1. Location and geological contextualization of the SVD and Veii (i.e., Veio on Google Earth) area: Hydrogeological map of the Sabatini Volcanic District (modified from [29]) with water table map and major gaining streams (**A**); Hydrogeological cross section with trace in panel A (modified from [20]). (1) Lakes; (2) Alluvial deposits; (3) Volcanic units; (4) Low-permeability units; (5) Carbonate units; (6) Water level (elevation in m a.s.l.); (7) Gaining streams; (8) CO_2-rich fluids; (9) Rising hot fluids; (10) Rising CO_2-rich fluids; (11) Main faults; (12) CO_2-rich cold waters; (13) Thermal water; (14) Gas emission; (15) Geothermal boreholes, (16) Trace of cross section) (**B**). Stratigraphy of the Veii site: PFS: "Pyroclastic fall deposits from Sacrofano", RTBS: "Red Tuff with Black Scoria", and SLP: "Sacrofano lower pyroclastic flow unit"; location of artificial tunnels is shown (**C**). Detail of the Veii area and location of sampled springs (red dots) and discharge measurements (black bars) (**D**).

2.2. Hydrogeological Settings

Two aquifers can be detected at the regional scale: the shallow volcanic aquifer in the SVD deposits and the deep and confined aquifer in the Meso-Cenozoic carbonate units. The aquifers are separated by a thick aquitard composed of Plio-Pleistocene deposits and Ligurian units (Figure 1B). The shallow volcanic aquifer is multilayered, unconfined, and recharged by local rainfall [29–31]. In the northern and western sectors, it discharges into Bracciano Lake; in the southern and eastern sectors, groundwater discharge has a centrifugal pattern from the lake (Figure 1A) [29,31,32]. In the peripherical sectors of the SVD, groundwater is drained by gaining streams as the aquitard crops out at the bottom of the fluvial valleys [33]. In the Veii area, the volcanic aquifer corresponds to PFS and RTBS units, and it is sustained by the SLP aquitard. The water level decreases southeastward, driven by the Piordo and the Valchetta gaining streams [31] (Figure 1A).

The deep carbonate aquifer has been intercepted approximately at −1000 m a.s.l. by geothermal boreholes [34–36]. The deep groundwater has a temperature of at least 200 °C [37,38] and Ca-HCO_3(SO_4) to Na(Ca)-HCO_3(Cl) attributes. This aquifer is supposed to be recharged by deep inflow from the Apennines [20,39].

The two aquifers are locally in hydraulic connection through faults and fractures, mainly in correspondence with the borders of buried horst-graben structures (Figure 1B). Here, CO_2-rich thermal and cold fluids upraise (Figure 1B) as a result of mantle degassing and/or thermo-metamorphic processes [20,40,41].

This complex setting results in thermal and mineralized springs, characterized by intermediate compositions between the two mixing aquifers [20,42]. The fluid-rock interaction and the presence of endogenous CO_2 [43–45] produce Ca (Na, K)-HCO_3 and Ca (Mg)-HCO_3 waters [46], either cold or hypothermal (T < 30 °C) [42].

Among the thermal springs of the SVD, some of them correspond to the ancient Bagni della Regina spa, less than 1000 m from Veii (Figure 1D). The springs have temperatures between 27 and 32 °C and up to 4 mg/L of Fe and 1.3 mg/L of Mn, a higher concentration than the reference values of the cold volcanic aquifer [20,42].

2.3. Veii and Campetti Southwest Archeological Site

Veii is an archeological site located about 16 km northwest of Rome on a volcanic plain with a mean elevation of approximately 110 m a.s.l. (Figure 1A). The ancient boundaries of Veii are set along the Valchetta and Piordo streams [47,48] (Figure 1D). Historical sources testify to Veii cultural and water prosperity, at least from the Archaic period. For example, the Greek historian Dionysius of Halicarnassus reported the presence of abundant and excellent drinking waters that flow in the Veii neighborhood. At the same time, thermal mineral springs feed a Roman bath known as Bagni della Regina along the Valchetta Stream (Figure 2B,D) [49].

Campetti Southwest (42.0232° N, 12.3898° E) corresponds to the southwestern edge of the Veii settlement, facing the Piordo Stream (Figure 1D). This settlement is located between the Etruscan Portonaccio sanctuary [50] and the boundaries of the Roman settlements [51] (Figure 1D). It has been populated for many centuries since the Protohistoric Age [52]. Here, a higher number of water-related structures were discovered [53]. A dense network of tunnels was dug under Campetti Southwest in the Etruscan period, probably to transport freshwater collected from the Piordo Stream using a dam [14]. During Roman times, water infrastructures were improved for public functions with the realization of bathing pools, pits and tanks for water storage, underground plumbing networks, and a *nymphaeum* [54] (Figure 2A,C).

Campetti Southwest has been considered a bathing, therapeutic, and sacred site since the end of the first century BC [55]. The discovery of a Roman epigraph (Figure S1) mentioning the *Fontes* and the cult of Hercules suggested the presence of sacred waters, used for healing purposes [14,56]. The presence of water infrastructures used for public or sacred purposes testifies to the crucial role played by water in the socio-economic evolution of the site. The presence of a thermal mineral spring has been suggested by [57].

If confirmed, public or sacred buildings have been built at the Campetti Southwest site rather than private edifices.

Figure 2. Pictures and archeological schemes of the Campetti Southwest site and Bagni della Regina spa. Aerial view of Campetti Southwest (modified from [56]) (**A**); Picture of the ruins of Bagni della Regina spa (modified from [58]) (**B**); Map of the Campetti Southwest site (modified from [14]) (**C**); Map of the Bagni della Regina site (modified from [49]) (**D**). In (**C**,**D**) TV, ON, XX, TB, and FR, red dots correspond to the locations of the collected rock samples.

3. Materials and Methods

3.1. Waters

3.1.1. Hydrogeological Survey

The hydrogeological survey focused on the Valchetta and Piordo streams (Figure 1D). Two discharge measurements were performed by using a SEBA® Hydrometrie M1 mini current meter in the Valchetta Stream (Kaufbeuren, Germany) (V1 and V2) (Figure S2) and one in the Piordo Stream (P1). Several small springs were recognized between V1 and V2, but they were not considered due to their extremely low and diffuse flow. Temperature, pH, and electric conductivity (EC, with automatic compensation to 20 °C) were measured in situ in correspondence with the three discharge sections in the streams. The recognized presence of gas (as bubbles) and red oxides along the Valchetta Stream suggests an additional contribution of mineral fluids through the riverbed.

Three springs (S1, S2, and S3) (Figure S2) with a significant discharge rate (~1 L/s) were instead recognized near Bagni della Regina. Temperature, pH, and EC were measured in situ (Figure 1D) using portable probes (WTW pH/cond 340i, WTW, Weilheim Germany). Oxidation reduction potential (ORP) was measured using a Hanna HI991002 meter (Hanna Instruments, Padova, Italy). OTT Hydrolab Sonde 4a was used for dissolved oxygen (O_2) and total dissolved salts (TDS). The O_2 sensor is a Clark cell.

3.1.2. Water Sampling and Analysis

Groundwater samples were filtered in the field using 0.45 µm Minisart sterile cellulose acetate membranes. Two aliquots of water were collected, one of which was acidified with ultra-pure Merck HNO_3. The total alkalinity (as HCO_3^-) was determined in situ by titration with 0.1 M HCl against the methyl orange indicator. Major elements were analyzed by ion chromatography (Dionex DX-120, Sunnyvale, CA, USA) on the unacidified (F^-, Cl^-, NO_3^-, and SO_4^{2-}) and acidified (Na^+, K^+, Mg^{2+}, and Ca^{2+}) samples. The results show an error on the charge balance of less than ±5%. Minor element analysis was conducted using ICP-MS Agilent 7500ce-ORS technology (Agilent, Santa Clara, CA, USA). Internal standards (constant concentrations of ^{89}Y and ^{159}Tb) were used to monitor the instrumentation drift. External precision (errors < 5%) was monitored using a spike standard.

3.2. Rocks

3.2.1. Rock Sampling and Description

ON, TV, and XX samples were collected inside the Campetti Southwest site during the archeological excavations (Figure 2C). TB and FR samples were collected in the Valchetta Stream valley near the ruins of Bagni della Regina spa (Figure 2D).

ON (Figure 3A) is a dark deposit described in [57]. It fills the fractures detected within the tunnels dug at the end of the first century CE (US 8125) under Campetti Southwest. At a microscopic scale, it consists of juvenile fragments characterized by subspherical vesicles and porphyritic texture due to mostly euhedral plagioclase phenocrysts (Figure 4). The matrix is tiny, altered, and affected by oxidation.

TV was collected from a tank vault in Campetti Southwest, built during the second half of the 1st century CE (US 73). It is a dark grey and highly porous travertine with local reddish tones obtained by hydroxide mineralization (Figure 3B). The cavities are partially filled by calcite. The original depositional site of TV is unknown, but it is likely to be onsite because it was used as building material. Thus, TV might be considered a reference for the local mineral deposition in pre-Roman times.

XX (Figure 3C) is composed of alternating thin carbonate and oxide layers. It was deposited in a Roman tank in the second half of the first century CE (US 5907). Calcite crystals in clusters, in vugs, and locally in the substitution of fossil shells characterize the sample (Figure 4).

TB is a grey travertine (Figure 3D) covering a wall built during the Imperial Age to protect the spa from the floods of the Valchetta Stream [49]. The deposition of TB occurred probably after the disposal of the bath after the fall of the Roman Empire.

FR is a red, unconsolidated mud (Figure 3E), deposited from the S3 spring. It is characterized by thin depositional layers with encrusted fragments of vegetation.

TG is a white travertine (Figure 3F), collected from a borehole in the Acque Albule thermal basin approximately 25 km east of Veii (Figure 1A). It is included in this study as an external reference. In fact, it originates from a carbonate/sedimentary hydrothermal system [59], without volcanic contamination.

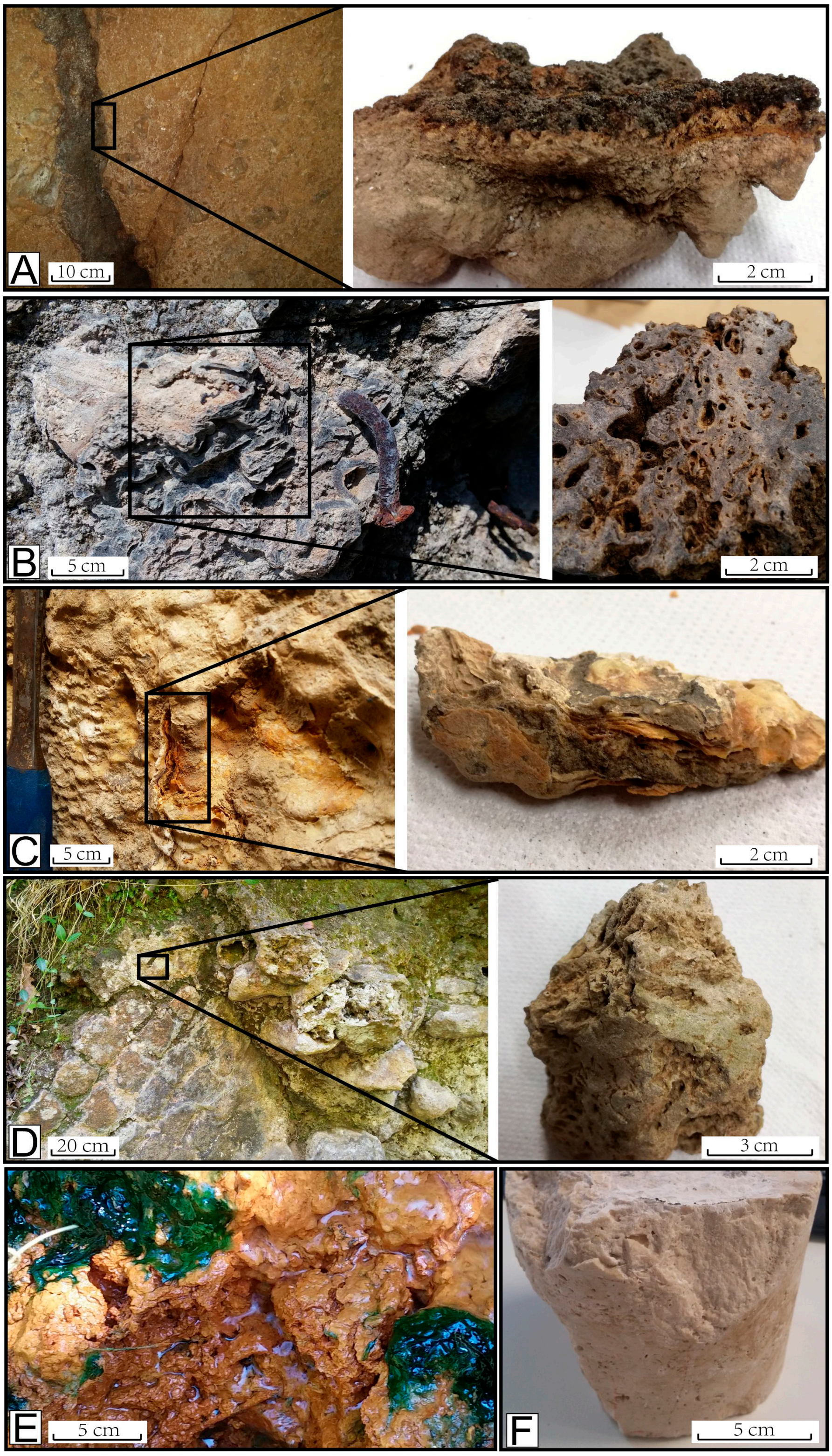

Figure 3. Pictures of sampled rocks in situ (**left**) and the related appearance of the sampled portions at the macroscopic scale (**right**): sample ON representing materials filling the tunnel rocks at the Campetti Southwest site (**A**); sample TV from a travertine tank vault in Campetti Southwest (**B**); sample XX from the carbonate Roman tank in Campetti Southwest (**C**); sample TB from a grey travertine coverture of an Imperial wall near the Bagni della Regina spa (**D**); sample FR representing sediments from the S3 spring in the Valchetta Stream (**E**); TG sample (**F**).

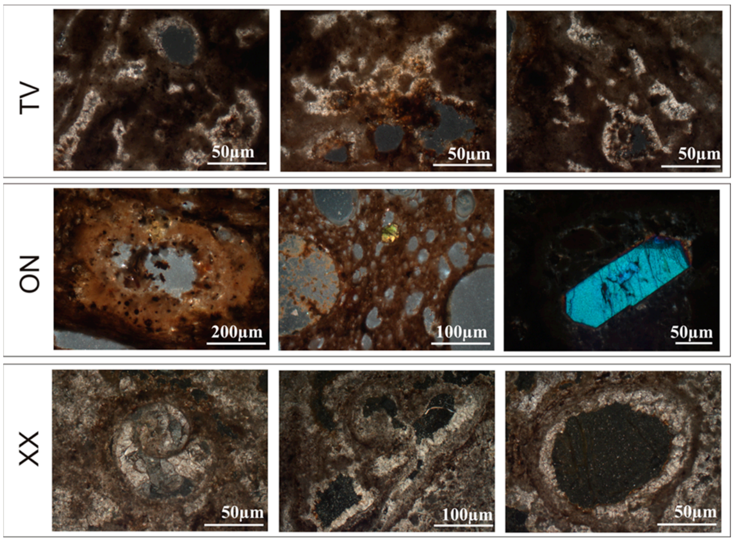

Figure 4. Rock samples in a thin section under the optical microscope. Textural and mineralogical details are visible. Refer to Figure 3 and the text for sample types and details.

3.2.2. Rock Geochemistry

Analysis of major and minor elements in rock samples was conducted using the ICP-MS Agilent 7500ce (Santa Clara, CA, USA). Rocks were powdered and pre-treated according to EPA Method 3015 [60] to dissolve them before ICP-MS analyses. Internal standards (constant concentrations of ^{89}Y and ^{159}Tb) were used to monitor the instrumentation drift. External precision was monitored by using an internal spike standard, which indicates errors of less than 10% for all reported analytes. The carbonate content ($CaCO_3$) was determined using a Dietrich–Fruhling calcimeter.

3.2.3. Mineralogical Analysis

Mineralogical characterization and semi-quantitative determination were performed by X-ray Powder Diffraction (XRPD) on micro-milled bulk rock samples. We used a Panalytical X'pert PRO PW 3040/60 diffractometer equipped with a pyrolitic graphite analyzer crystal. XRD spectra acquisitions contemplate unfiltered CuKα radiation (40 kV, 40 mA), 3°–100° 2θ range, steps of 0.02° 2θ, counting time in 30 s/step, 0.5 mm divergence slit, 0.1 mm receiving slit, and a 0.5° anti-scatter slit. Search–match software X'Pert HIGH Score Plus 4.9 and the ICDD PDF2 allow elaborating on acquired spectra identifying phases.

4. Results

4.1. Hydrogeological Results

The results of the discharge measurements and the chemical-physical parameters measured in situ are reported in Table 1.

Table 1. Discharge measurements and in situ parameters for the Valchetta Stream (V1 and V2), Piordo Stream (P1), and Bagni della Regina thermal springs (S1, S2, and S3).

ID	Discharge (L/s)	T (°C)	pH	EC (µS/cm)	O_2 (%)	O_2 (mg/L)	TDS (mg/L)	ORP (mV)
V1	186	17.8	7.92	599	n/a	n/a	n/a	n/a
V2	250	22.7	7.81	1426	n/a	n/a	n/a	n/a
P1	100	n/a	n/a	n/a	n/a	n/a	n/a	n/a
S1	~1	24.5	6.98	3245	48.8	4.1	2.08	56
S2	~1	28.8	6.2	2906	8.4	0.6	1.86	77
S3	~1	28.8	6.46	3097	14.4	1.1	1.98	51

Increases in discharge rate (~60 L/s), water temperature (~5 °C), and EC (~800 µS/cm) were observed in the Valchetta Stream between V1 and V2. S1, S2, and S3 are characterized by a higher temperature (>24 °C) and enrichment in dissolved ions (EC > 2900 µS/cm) (Table 1). The discharge rate at P1 (100 L/s) was partially affected by domestic sewers and therefore not further considered.

4.2. Mineralogical Results

Calcite is the most abundant mineral in XX, TV, and FR (Table 2), associated with hematite (sample FR) and fluoro-apatite (sample XX). ON is the unique sample without calcite, in agreement with the textural appearance observed under the microscope. This sample has an unstructured XRDP pattern, indicating the prevalence of the amorphous phase. Peaks associated with feldspar are absent even if a crystal was detected under the microscope (Figure 4), indicating that this phase has an extremely low abundance. The blackish color of the matrix is due to the goethite mineralization.

Table 2. Mineralogical results of the rock samples using XRDP.

ID	Calcite	Amorphous	Fluoro-Apatite	Goethite	Hematite
ON		x		x	
TV	x				
XX	x		x		
FR	x				x

4.3. Chemical Results of Water and Rock Samples

The results of the chemical analysis of S1, S2, and S3 are reported in Tables 3 and 4. Springs show similar Ca (44% of major metals) and Na+K (42% of major metals) content. Among the major anions, a slight predominance of HCO_3^- (48% of total major anions) on SO_4^{2-} (40%) is observed. Cl^- is the least abundant cation (12%). Groundwater is also saturated with calcite ($SI_{calcite} > 0$, calculated with the PHREEQC code [61]) (Table 3).

Table 3. Chemical composition of the Bagni della Regina thermal springs collected during this study.

ID	HCO_3^- mg/L	F^- mg/L	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	$SI_{calcite}$
S1	1242	1.9	184	3	751	195	299	69	346	0.82
S2	1356	1.7	190	0	926	218	348	74	380	0.41
S3	1347	1.7	189	0	896	226	348	77	383	0.14

Table 4. Trace metal concentrations of the Bagni della Regina thermal springs collected during this study.

ID	Li µg/L	B µg/L	Ti µg/L	Mn µg/L	Fe µg/L	As µg/L	Rb µg/L	Sr µg/L	Zr µg/L	Ba µg/L	U µg/L
S1	442	3407	5	1053	3793	41	300	3753	4	13	5
S2	517	3749	4	1146	4213	41	342	4185	3	17	4
S3	544	3998	4	1145	4043	42	344	5124	3	19	4

The abundance of major ions in the sampled springs is within the range of the composition of other thermal springs in SVD (Table S1) [20,43].

Sampled springs show high concentrations of B, Sr, and Fe (~4 mg/L each), F^-~2 mg/L, and Mn~1.1 mg/L, and abundant Rb (~300 µg/L) and Li (~550 µg/L), As (~40 µg/L), and Ba (~16 µg/L) (Table 4). Other minor elements with a concentration below the detection limit are not reported in Table 4. Detected concentrations are comparable with high mineral water types belonging to peri-Tyrrhenian mineralized aquifers in Central Italy [62–67]. On the contrary, the cold volcanic water of the SVD shows a smaller quantity of dissolved ions, especially Fe and Mn, that have concentrations of a few μg/L [20,42,43].

The chemical compositions of TG, TV, TB, XX, and FR (Table S2) confirm they are travertines, characterized by different amounts of oxides (Figure 5a,b).

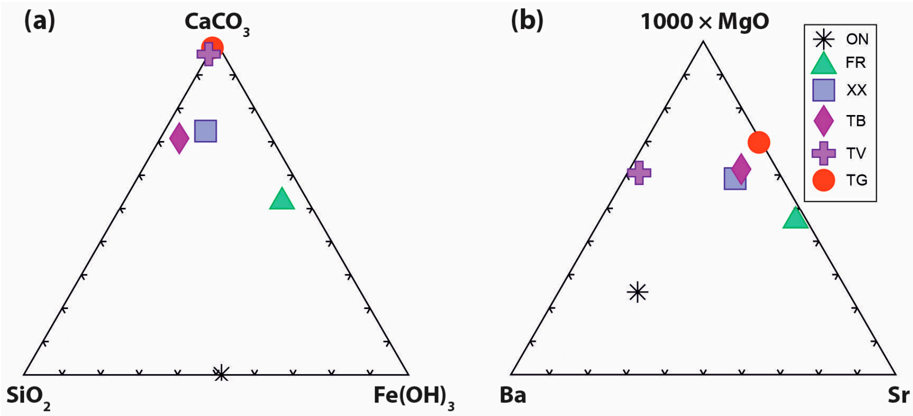

Figure 5. Relative compositions of major (**a**) and minor (**b**) elements in analyzed rocks. Location of the sample in Figure 2 and picture of the samples in Figures 3 and 4.

The chemical composition of TG confirms its origin in a carbonate system without a volcanic component. In fact, it is almost entirely composed of $CaCO_3$ (approximately 97 wt%) and lacks $Fe(OH)_3$, Mn, Ni, and U (Table S2).

TV and TB show differences in their compositions. In fact, TV has a high quantity of $CaCO_3$ (93 wt%), and it is not statistically different from TG. TB is composed of a lower amount of $CaCO_3$ (63 wt%) and almost an order of magnitude higher SiO_2, $Fe(OH)_3$, and trace element content. In particular, TB is rich in alkali earth metals, Ti, Rb, Sr, and Ba.

XX has a slightly similar composition to TB according to $CaCO_3$ amount (68 wt%), silica, alkali, and alkali ion content (Table S2). XX has a slightly higher amount of $Fe(OH)_3$ than TB.

The FR sample is almost totally composed of $CaCO_3$ and $Fe(OH)_3$. In agreement with the sample appearance and mineral paragenesis (Table 2). Silica, alkali, and alkali earth metals are less than 10% (w/w), and trace elements are compared to other local travertines (TV and TB), except for As, Sr, and Ba (Table S2).

Different from the other samples, ON does not contain $CaCO_3$, is rich in silica, and has a relevant abundance of major and trace metals, particularly Al_2O_3, Fe(OH), Ba, As, Ti, and V (Table S2). ON is classified as an altered amorphous material derived from a volcanic rock protolith, in agreement with chemical and mineralogical results.

5. Discussion

Hydrogeochemical and mineralogical results contribute to the characterization of thermal mineral springs in SVD and give insights on their evolution during the historical period. The chemical composition of the thermal mineral springs in fact depends on groundwater mixing between the deep carbonate-mineralized aquifer saturated in CO_2 and the shallow, cold volcanic aquifer [43]. Comparing travertine deposited at Roman times and active springs, a marked enrichment in the volcanic-related elements and a decrease in the $CaCO_3$ content are evident.

The relative compositions of major metals in the sampled springs and other groundwater samples in the study area [20,43] (Table S1) have been plotted together with the Sacrofano volcanic units [68] and the Meso–Cenozoic limestones (Figure 6), as references to the main aquifers. It appears that sampled thermal mineral springs match the composition of local volcanic deposits; they also align with a mixing trend between volcanites and limestones. The positive $SI_{calcite}$ supports the influence of carbonate hydrolysis, mainly from the deep aquifer, where the absorption of reactive gases (CO_2 and H_2S) [40,44] enhances water-host rock leaching dynamics.

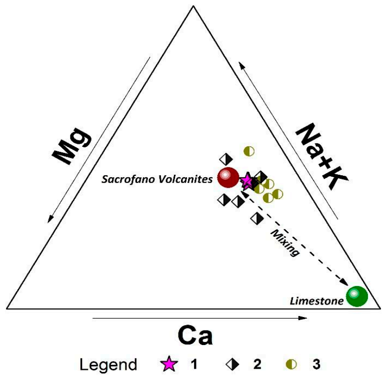

Figure 6. Relative compositions of major metals in local springs and for Sacrofano volcanites and limestone formations. Legend: (1) thermal mineral springs sampled in this study; (2) literature data from [20]; (3) literature data from [43]. Detailed data are reported in Table S1.

The relative abundance of major and minor elements in the travertine rocks is influenced by the chemical composition of the parental groundwater [69]. The chemical composition of ancient travertines cannot be linked to the actual composition of the groundwater. The gradual and relative high abundance of volcanic elements in the younger travertines may reflect the decreased contribution from the deep, hot, and carbonate endmember. In particular, the volcanic elements progressively increased through time up to the Roman period.

ON is not a travertine, and it has a different origin according to its petrological features. It is not formed by the precipitation of thermal waters, as previously supposed [57], but more likely by weathered volcanic material deposited inside fractures of the RTBS bedrock before the tunnel excavation.

TV is the most ancient travertine among the rocks collected near Veii. In fact, it is part of a Roman building, and its deposition must date from prior to the Romans. TV is poor in volcanic-derived elements, and its composition is more like TG (Figure 5a,b). Groundwater composition during the deposition of TV should be driven mostly by the carbonate endmember as a major factor in the mixing process.

XX is composed of alternated calcite and iron-hydroxide layers deposited on a tank at the Campetti Southwest site. It indicates the presence of a local thermal mineral spring active during Roman times, according to the archeological dating of the tank (first century CE [56]). This spring was probably characterized by water in reducing conditions and saturated with calcite. The rapid $CaCO_3$ and $Fe(OH)_3$ precipitation suggests that the paleo spring should be remarkably close to the XX deposit. XX could not have originated from the heating of the volcanic groundwater during the spa activities, because in that case, precipitation of $Fe(OH)_3$ should not occur. During this period, a *nymphaeum* and numerous tanks were built in Campetti Southwest to store water. This architectural switch suggests a flux reduction in Campetti Southwest, where the hydrothermal water was probably still present, as testified by XX, but was insufficient to support active use. The *nymphaeum* was presumably realized to compensate for the lower hydrothermal water supply or as a votive offer to the gods. In this context, we suppose that the former travertine deposits like TV were dismantled and reused for the *nymphaeum*.

Meanwhile, Bagni della Regina reached its maximum architectonical development, confirming that the thermal mineral springs still provided an adequate supply for the spa activities. After the fall of the Roman Empire, the Campetti Southwest site was occupied until the Middle Ages, when it was definitively abandoned, and the settlement was progressively ruined. Bagni della Regina spa faced the same fate.

TB is a travertine rich in volcanic-related elements, and it might have been dated after the Imperial Roman Period, when the travertine progressively encrusted the abandoned Roman structures. The discharge rate of the thermal springs continuously decreased up to the current extremely low flow conditions.

FR is a reference to the present hydrogeochemical conditions in the Valchetta Stream valley. Active thermal mineral springs are characterized by high concentrations of volcanic-related elements, resulting in FR. The comparable composition between TB and FR also suggests similarities in their parental groundwater.

Several factors, like prolonged droughts [70], seismic events [71], or their combination [72], may affect the springs discharge, even rendering them inactive. In addition, most thermal and mineralized springs are affected by the self-sealing of the feeding fractures due to mineral precipitation and argillification of silica minerals [73–76]. Similar dynamics have also been reported for other Tyrrhenian hydrothermal systems [77,78].

The most likely scenario for the hydrogeological evolution of the Veii area can be summarized as follows (Figure 7):

- Before the Roman period (Figure 7A), an abundant and prevalent contribution of deep thermal and mineralized fluids from the carbonate aquifer occurred. They produced travertine deposits with a low concentration of volcanic-related elements. During Roman times, the discharge of Bagni della Regina springs was presumably higher than currently, since it was essential for feeding the spa. In this phase, at least one small, thermal mineralized spring was active at the Campetti Southwest site with a similar chemical composition.
- Later (Figure 7B), the progressive sealing of the fractures due to the calcite precipitation induced the reduction of spring flow at Bagni della Regina and the interruption in Campetti Southwest. The decreased contribution of the deep mineralized carbonate component reflects a shift toward a more volcanic-derived composition, as observed in the active springs and actual travertine deposits in the Valchetta Stream valley.

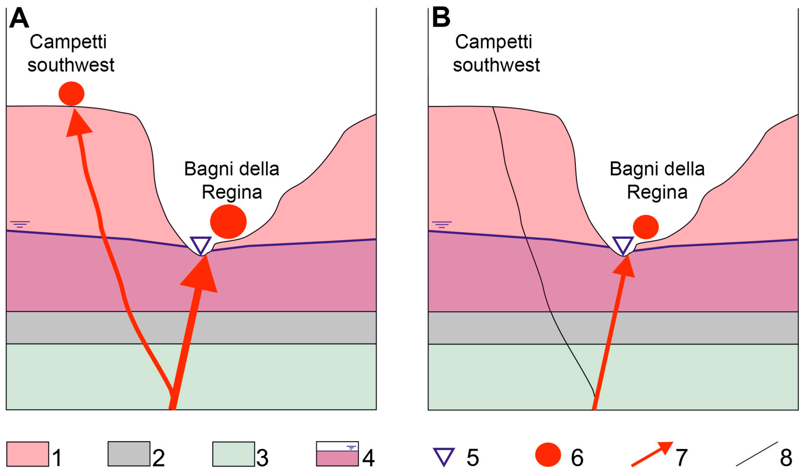

Figure 7. Scheme of the hydrogeological evolution of the thermal mineral springs at the Veii site (not to scale). First stage: presence of a thermal mineral spring in Campetti Southwest and higher flow in Bagni della Regina spa (**A**); Present stage: no active springs are present at Campetti Southwest, and the discharge rate of Bagni della Regina is significantly reduced (**B**). Legend: (1) Volcanic deposits; (2) Regional aquiclude; (3) Carbonate units; (4) Volcanic aquifer; (5) gaining stream; (6) Thermal mineral spring (discharge rate is proportional to the size); (7) Upflow of deep thermal mineral fluids (upflow rate is proportional to the thickness of the arrow); (8) Sealed fracture.

6. Conclusions

The combination of hydrogeological, petrological, and archeological data allowed us to define the evolution of thermal mineral springs in the southeastern sector of SVD and improved our knowledge of the history of the ancient Veii settlement.

The analyses of travertine samples revealed changes in chemical composition due to variations in groundwater mixing between the deep mineralized carbonate aquifer and the cold, shallow volcanic aquifer. Thanks to the archeological information of the encrusted structures, it was possible to indirectly date the travertines and, therefore, the changes in the parental groundwater composition. Prehistorical travertines are characterized by the almost exclusive contribution of the carbonate member. Travertines deposited during and after Roman time show a progressive increase in $Fe(OH)_3$ and in volcanic-related trace elements. This variation was induced by the reduction of the carbonate groundwater input. This also reflects a progressive decrease in the discharge rate, as actually recognized at the Bagni della Regina site.

In addition, the presence of a thermal mineral spring in Campetti Southwest, at least during the Imperial Roman Period, was demonstrated. Thin calcite and iron hydroxide layers were identified in a tank, suggesting that the mouth of the ancient spring was closest to the sampling site. The spring probably had a sacred meaning, as testified by the votive inscriptions found by the archeologists. The progressive reduction of the spring discharge imposed a structural reorganization of the site with the building of tanks and a *nymphaeum* to collect waters.

Anyway, some issues are still open; how the main drinking supply system at Veii operated is not yet known. Future archeological studies in the Veii settlements should, therefore, carefully pay attention to rock and mineral deposits that can help to ascertain the presence of other thermal mineral springs and can provide further useful information on the socio-economic development of ancient settlements. In the future, direct geochronological dates should be performed to closer define the age of the mineral deposits in Campetti Southwest and better constrain the time interval during which the spring was active.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16081113/s1, Figure S1: Votive inscription to Hercules and the Springs found in Campetti Southwest site (modified from [53]); Figure S2: Pictures and locations of the studied springs and the discharge measurements along the Valchetta River. Legend: (1) Discharge measurements; (2) Thermal–mineral springs; (3) Streams.; Table S1: Chemical composition of water sampled in the southeastern sector of Sabatini Volcanic District. * [43]; ** [20]; n.a.: not analyzed; Table S2: Chemical composition of the rock samples.

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