The Chemistry and Isotopic Composition of Waters in the Low-Enthalpy Geothermal System of Cimino-Vico Volcanic District, Italy

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12 **ABSTRACT**

13 Geothermal energy exploration is based in part on interpretation of the chemistry, temperature, and
14 discharge rate of thermal springs. Here we present the major element chemistry and the δD , $\delta^{18}O$,
15 $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ of groundwater from the low-enthalpy geothermal system near the city of Viterbo
16 in the Cimino-Vico volcanic district of west-Central Italy. The geothermal system hosts many
17 thermal springs and gas vents, but the resource is still unexploited. Water chemistry is controlled by
18 mixing between low salinity and HCO_3 -rich fresh waters ($<24.2^\circ C$) flowing in shallow volcanic
19 rocks and SO_4 -rich thermal waters ($25.3^\circ C$ to $62.2^\circ C$) ascending from deep, high permeability
20 Mesozoic limestones. The (equivalent) SO_4/Cl (0.01-0.02), Na/Cl (2.82-5.83) and B/Cl (0.02-0.38)
21 of thermal waters differs from the ratios in other geothermal systems in Central Italy, probably
22 implying a lack of hydraulic continuity across the region. The $\delta^{18}O$ (-6.6‰ to -5.9‰) and δD ($-$
23 40.60‰ to -36.30‰) of spring water suggest that the recharge area for the geothermal system is the
24 summit region of Mount Cimino. The strontium isotope ratios ($^{87}Sr/^{86}Sr$) of thermal waters
25 (0.70797-0.70805) are consistent with dissolution of the Mesozoic evaporite-carbonate units that
26 make up the reservoir, and the ratios of cold fresh waters mainly reflect shallow circulation through
27 the volcanic cover but some admixture ($<10\%$) of thermal water as well. The boron isotope
28 composition ($\delta^{11}B$) of fresh waters (-5.00 and 6.12‰) is similar to those of the volcanic cover, but
29 the $\delta^{11}B$ of thermal waters (-8.37‰ to -4.12‰) is a mismatch for the Mesozoic reservoir rocks and
30 instead reflects dissolution of secondary boron minerals during fluid ascent through flysch units that
31 overlie the reservoir. A slow and tortuous ascent enhances extraction of boron but also promotes
32 conductive cooling, partially masking the heat present in the reservoir. Overall data from this study
33 is consistent with previous studies that concluded that the geothermal system has a large energy
34 potential.

35 *Keywords: Low-enthalpy geothermal system; Fluid geochemistry; Boron isotopes; Strontium*
36 *isotopes; Central Italy.*

1. Introduction

In the past few decades the development of geothermal energy resources has expanded worldwide as a sustainable and renewable source for electricity generation and heating applications (e.g. Moore and Simmons, 2013). Geothermal systems are classified based on the reservoir temperature and there are various criteria for their classification (Williams et al., 2011). Low-enthalpy (or low-temperature) geothermal systems have been classified by the U.S. Geological Survey as those with reservoir temperatures of less than 90 °C (Reed, 1983; Williams et al., 2008) and by others at <125 °C (Hochstein, 1988), and <150 °C (e.g. Nicholson, 1993). In many countries low-enthalpy geothermal resources are typically used for bathing, heating, greenhouses, and ground source heat pumps (Lund et al., 2011; Moore and Simmons, 2013); they can also be exploited for electric power generation if sufficiently low temperatures are available for cooling the working fluid in a binary power plant (Williams et al., 2008).

Geothermal energy exploration is based in large part on the characterization of water, gas, and rock chemistry, reservoir permeability, and the rates of water recharge into the reservoir. In the past several decades many geochemical indicators have been developed to assess the state of the geothermal reservoir to reduce the high costs of exploratory drilling (e.g. Arnórsson, 2000; Boschetti, 2013; Capaccioni et al., 2014; Fournier, 1981; Fournier and Truesdell, 1973; Fournier, 1977; Giggenbach, 1988, 1992; Spycher et al., 2011). In geothermal resource exploration and assessment, the stable isotopes of water ($\delta^{18}\text{O}$ and δD) have been widely used as tracers for the origin of groundwater and for water-rock interaction, and as indicators for mixing of waters from different sources. The isotopic composition of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) provides information on flow paths and mixing of waters because strontium is readily leached from rocks (e.g. Boschetti et al., 2005; Dotsika et al., 2010; Lee et al., 2011; ; Negrel et al., 1999; Peiffer et al., 2011; Pennisi et al., 2006). Boron stable isotopes are applied in geothermal exploration, because boron is highly incompatible during the water-rock interaction and because incorporation of boron into secondary

minerals fractionates its isotopes (e.g. Ellis and Mahon, 1964, 1967; Leeman et al., 2005; Millot et al., 2012; Palmer and Sturchio, 1990).

In this study we present the major element chemistry and the δD , $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ of groundwater from the low-enthalpy geothermal system near the city of Viterbo in the Cimino-Vico volcanic district of west-Central Italy (Figure 1). The region hosts many thermal springs and gas vents and is a part of a larger thermally anomaly that extends from southern Tuscany in the north to the active volcanic areas of Phlegrean Fields and Vesuvius (Figure 1). The geothermal resource in the area is still unexploited despite its large potential (Cinti et al., 2014, 2015). The specific goals of this study are to (1) characterize the processes controlling water chemistry in the Cimino-Vico area, (2) characterize the processes controlling the isotopic systematics of boron and strontium in low enthalpy hydrothermal systems, and (3) use the geochemical and isotopic data to provide new insights on the groundwater circulation in the area, which in turn, provide information on the potential for geothermal energy production.

2. Geological framework

Volcanic activity which gave rise to the Cimino and Vico complexes started at 1.35 Ma with explosive and effusive activity of the Cimino complex. Between 0.8 and 0.3 Ma, the Vico complex was active, with a central caldera that now hosts Vico Lake (Figure 1). The Cimino volcanic products include rhyodacites, latitic ignimbrites and olivine-latitic lavas, and are mostly covered by the K-alkaline pyroclastic deposits from the Vico volcanics, consisting of undersaturated trachytes, phonolites, tephritic phonolites, tephrites, and subordinate tuffs (Arnone, 1979; Gambardella et al., 2005; Sollevanti, 1983). Northwest and northeast striking extensional faults divide the substratum rocks and control the horst and graben pattern (Baiocchi et al., 2013). Ongoing magmatic activity is manifested by several geothermal anomalies, thermal springs, CO₂-rich vents and active travertine deposition.

The hydrogeology of the Cimino-Vico geothermal area has been widely studied and the

hydrostratigraphic sequence was defined (Angelone et al., 2008; Arnone, 1979; Baiocchi et al., 2013; Chiocchini et al., 2010; Piscopo et al., 2006) (Figure 2). The high permeability Mesozoic limestone in Central Italy is the primary regional groundwater aquifer which hosts numerous geothermal reservoirs with temperatures ranging between 48°C and 115°C (Minissale, 2004). The reservoir temperature of Cimino-Vico geothermal system is ~94°C, based on multicomponent geothermometry (Battistel et al., 2014). Abundant CO₂ from active metamorphism is dissolved in the aquifer (Chiodini et al., 1999; Duchi et al., 1987; Minissale and Duchi, 1988). The shallow (<200 m) fresh-water aquifer in the volcanic products of Cimino and Vico and the deep regional aquifer are separated by low-permeability Pliocene-Pleistocene sediments and Cretaceous-Oligocene flysch deposits (Ligurian Units) (Figure 2). Thermal groundwater from the deep reservoir ascends through fractures and faults in the sedimentary substratum (Angelone et al., 2008; Arnone, 1979; Baiocchi et al., 2012; Chiocchini et al., 2010; Piscopo et al., 2006). The aquifer system is bounded laterally by the Pliocene- Pleistocene sedimentary complex and Cretaceous-Oligocene flysch units.

3. Sampling and laboratory analysis

Twenty-three water samples from springs and private wells (Figure 1) used for agricultural water supply were sampled between October 2011 and August 2012. Samples for major element chemistry were collected in 50 ml high-density polyethylene bottles and filtered in the field with a 0.45 µm filter. Water temperature, electrical conductivity (EC) and pH were measured in the field. Alkalinity was determined in the field by titration with 0.1 N HCl. Major element concentrations were determined at the Geochemistry laboratory of Sapienza University in Rome with a Dionex DX-120 ion chromatograph (precision ±2%) with a Dionex CS-12 column for cations and a Dionex AS9-SC column for anions. Nine samples were collected in 50 ml cleaned glass bottles and analysed for δ¹⁸O and δD compositions at the U.S. Geological Survey Stable Isotope Laboratory in Reston, Virginia. δ¹⁸O values were determined using the CO₂ equilibration technique of Epstein and

112 Mayeda (1953), which has been automated (Révész and Coplen, 2008). δD compositions were
113 determined using a hydrogen equilibration technique (Coplen et al., 1991; Révész and Coplen,
114 2008). The 2σ uncertainties of oxygen and hydrogen isotopic results are 0.2‰ and 2‰, respectively
115 and the results are reported in per mill (‰) relative to VSMOW (Vienna Standard Mean Ocean
116 Water).

117 Fourteen additional filtered samples were collected in 15 ml high-density polyethylene bottles
118 for strontium and boron concentrations and isotope analyses. The samples were acidified with ultra-
119 pure nitric acid to a pH of about 2 in the field. Strontium and boron concentrations were measured
120 at the Geochemistry laboratory of Sapienza University in Rome using ICP-MS (X Serie 2 Thermo
121 Fisher Scientific) with an analytical accuracy of 2% to 5%. The strontium isotope ratios were
122 measured on a Finnigan MAT 261 Thermal Ionization Mass Spectrometer (TIMS) at the USGS
123 Metal and Metalloid Isotope Laboratory in Menlo Park, CA. Reported values have been corrected
124 for natural and analytical stable isotope fractionation to $^{88}\text{Sr}/^{86}\text{Sr} = 8.37515$ and then adjusted to the
125 NBS987 standard value of 0.71024. The values are precise to 0.00002 at the 95% confidence level.
126 Boron isotope analysis were carried out by negative TIMS (Vengosh et al., 1989; Zeininger and
127 Heumann, 1983) at the USGS Metal and Metalloid Isotope Laboratory in Menlo Park, CA.
128 Sufficient water to supply 2 ng of B was loaded directly onto degassed, zone-refined Re filaments.
129 The B isotopes were measured as the BO_2 species at masses 42 and 43. The typical agreement of
130 replicate analyses of a sample is within 1‰. Isotope ratios are reported as permil deviation ($\delta^{11}\text{B}$) in
131 the $^{11}\text{B}/^{10}\text{B}$ ratios relative to the standard NBS SRM 951 and the analytical precision is $\pm 0.5\text{‰}$ as
132 $\delta^{11}\text{B}$.

133 4. Results

134 The chemical composition of groundwater samples from Cimino-Vico thermal area is reported
135 in Table 1. The charge balance of all samples is within $\pm 4\%$. The waters sampled are classified as
136 either HCO_3^- -rich fresh waters ($T < 25^\circ\text{C}$, $6.4 < \text{pH} < 7.4$, $\text{HCO}_3^-/\text{SO}_4$ of 1.1-16.4 equivalent) or SO_4^- -

rich thermal waters ($T > 25^{\circ}\text{C}$, $5.8 < \text{pH} < 7.0$, HCO_3/SO_4 of 0.3-1.7 equivalent) (Figures 3-6, Table 1). The thermal waters have Cl/SO_4 and Na/Cl equivalent ratios ranging from 0.01 to 0.02 and 2.52 to 5.83 respectively, which considerably differ from the values of other thermal waters in Central Italy (e.g. Minissale et al., 2002). The B/Cl equivalent ratio ranges from 0.003 to 0.04 in the fresh waters and from 0.02 to 0.38 in the thermal samples.

The cation composition of thermal waters ranges between the composition in geothermal well Vetralla 001 VET1 drilled to a depth of 1117 m within the Mesozoic units ~20 km south of the study area (<http://unmig.sviluppoeconomico.gov.it/unmig/geotermia/pozzi/dettaglio.asp?cod=136>) and the NaK-rich composition of the Vico rocks (Figure 4). Few thermal water samples bear the signature of the Na^+ - and K^+ -rich volcanic substrate of the Cimino-Vico area (Arnone, 1979; Gambardella et al., 2005; Sollevanti, 1983). The high concentration of Ca^{2+} (<881 mg/L) and SO_4 (<1,826 mg/L) in thermal waters traces the interaction with gypsum constituting the Mesozoic units. There is only a weak correlation between water temperature and dissolved ions concentrations, suggesting rapid cooling of the ascending waters.

Isotopic composition of waters

The $\delta^{18}\text{O}$ and δD values of all samples range between -6.6‰ to -5.9‰ and from -40.60‰ to -36.30 ‰, respectively (Table 1, Figure 7) and strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) range between 0.70797 and 0.71026 (Table 1, Figure 8). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of thermal waters have a narrow range (0.70797-0.70805) and are similar to those of the Mesozoic evaporite-carbonate units (0.70778 ± 0.000110 ; Boschetti et al. 2005). The cold fresh waters have a wider range of values (0.71086-0.70852) which are generally higher than the ratios in thermal waters, and extend to the values of the volcanic rocks from the Cimino-Vico district, 0.7107-0.7136 (Hurley et al., 1966; Poli et al., 1984; Vollmer, 1976). $\delta^{11}\text{B}$ in thermal waters ranges from -8.37‰ to -4.12‰, and in fresh waters between -5.00 and 6.12‰ (Table 1, Figures 9,10). Samples #14 and #15 have positive $\delta^{11}\text{B}$ values of 3.25 and 6.12‰, respectively.

5. Discussion

The chemical and isotopic data we have acquired provide new insights on the low-enthalpy Cimino-Vico hydrothermal system. We first discuss the processes that control the groundwater chemistry and then the systematics of strontium and boron isotopes. The data help us resolve groundwater flowpaths, mixing relations, and ultimately energy resource available. The approach we use may be applicable to other, similar low-enthalpy systems in central Italy and elsewhere.

5.1 Processes controlling water chemistry

The relatively high temperature of groundwater ascending from depth, the high rate of CO₂ degassing, and the mixing between thermal and fresh waters are reflected in the chemical composition of spring waters in the Cimino-Vico District (Figures 3 and 4). The chemical composition of the thermal waters suggests that in the geothermal reservoir, fluids are in equilibrium with gypsum, quartz, aragonite and calcite (Battistel et al., 2014). The dissolution of sulphate minerals results from groundwater flow in the Mesozoic evaporite-carbonate sequence as inferred from the positive correlation between Ca²⁺+Mg²⁺ and SO₄²⁻. The enrichment in Ca²⁺+Mg²⁺ compared with Na⁺+K⁺ (Figures 4, 5) suggests insignificant contributions from silicate weathering in thermal waters.

High HCO₃⁻ concentrations in fresh waters reflect the dissolution of carbonates and CO₂ degassing from the deep geothermal reservoir through the local fault system. The (Ca²⁺+Mg²⁺)/HCO₃⁻ ≈ 1 also implies that carbonate dissolution is significant (Figure 5). Silicate weathering is evident in the chemistry of fresh water samples. The dissolution of Na-K-bearing silicate minerals such as leucite and plagioclase, likely resulting from the ingress of CO₂ in the volcanic aquifer increases the ratio Na⁺+K⁺/Ca²⁺+Mg²⁺. Similar to other low-enthalpy geothermal systems, the chemistry of low enthalpy thermal waters of Cimino-Vico system is mainly lithology-dependent and controlled by rock dissolution. In contrast, the chemical composition of high enthalpy thermal fluids is mainly controlled by temperature-dependent reactions between primary and secondary, alteration

187 minerals and by cation exchange processes that result in ion ratios much different from those in the
188 host rock (Figure 6).

189 The uniform $\delta^{18}\text{O}$ and δD values of Cimino-Vico volcanic waters that plot along the Meteoric
190 Water Line (Figure 7) suggest a meteoric origin for thermal waters. The $\delta^{18}\text{O}$ and δD show a
191 progressive isotope lightening from the Tyrrhenian Sea to the Apennines Chain. The proposed
192 vertical isotope gradient for Central Italy (-0.3‰ per 100 m; Cinti et al., 2014; Longinelli and
193 Selmo, 2003; Minissale and Vaselli, 2011; Zuppi et al., 1974,) suggests that recharge is at an
194 elevation of 400 m to 700 m on the summit of Mount Cimino, consistent with previous studies
195 (Baiocchi et al., 2006; Cinti et al., 2014; Piscopo et al., 2006). A slight negative shift in $\delta^{18}\text{O}$ values
196 of thermal waters likely results from oxygen exchange between water and CO_2 derived from
197 geothermal activity (Negrel et al., 1999):

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200

201 The relatively low temperature in the geothermal reservoir (Battistel et al., 2014) and the relatively
202 large effect of the CO_2 on the $\delta^{18}\text{O}$ value imply that fluid-rock interaction has a minimal effect on
203 the isotope ratio (Figure 7).

204 *5.2 Processes controlling B and Sr systematics*

205 The $^{87}\text{Sr}/^{86}\text{Sr}$ values in the thermal waters show that the major source of strontium is the
206 Mesozoic formations hosting evaporite deposits (Figure 8). Overall, the $^{87}\text{Sr}/^{86}\text{Sr}$ values show that
207 both thermal and fresh waters are actually variable mixtures of the two end-member fluids. The
208 isotopic ratio of fresh waters samples implies that the fraction of water that circulates only through
209 the Vico volcanic rocks is 0.9-1 (Figure 8); up to 10% of the water is from the thermal reservoir.
210 The presence of faults cutting the intervening low-permeability units facilitates the ascent of the
211 thermal fluids to the surface and the connection between the two aquifers.

212 In hydrothermal systems, both boron and chloride are readily leached from rocks (Ellis and
213 Mahon 1964, 1967), although high Cl content can also be derived from magma degassing of HCl.
214 Boron concentrations in water higher than 1 mg/L are generally attributable to hydrothermal
215 influence (Hem, 1985), and the Cimino-Vico thermal waters mostly meet this criterion. However
216 the Cimino-Vico hydrothermal system shows a lower chloride content compared to other
217 geothermal systems (e.g. Central Italy: Boschetti et al., 2005; Minissale et al., 1997; Minissale et
218 al., 2002; Pennisi et al., 2006. Rest of the world: Arnórsson and Andréðóttir, 1995; Dotsika et al.,
219 2010; Millot and Négrel, 2007; Palmer and Sturchio, 1990). Such low Cl concentrations suggest a
220 highly permeable reservoir that has been flushed repeatedly with water and a reservoir that is
221 isolated from inputs of magmatic brine or sources of chloride from adjacent geothermal systems. So
222 the question arises as to why so much boron is still being leached from the subsurface.

223 We propose that boron, like chloride, has already been removed from the Mesozoic reservoir
224 rocks and the elevated B content in the thermal waters is attributable to the dissolution of the
225 borosilicate minerals making up the Ligurid units. Flysch rocks are naturally rich in boron (Pennisi
226 et al., 2000) and in this setting could have been further enriched if the boron removed from the
227 underlying Mesozoic rocks was redeposited into secondary formation minerals like tourmaline,
228 during perhaps a previous stage of high enthalpy hydrothermal activity. The aggressiveness of the
229 presently ascending thermal fluids promotes boron-mineral dissolution, increasing boron
230 concentration in thermal waters that discharge from the springs.

231 This scenario is confirmed by the $\delta^{11}\text{B}$ values of thermal waters samples that are
232 anomalously low with respect to their principal circulation in the Mesozoic units (Figure 9). Indeed,
233 if the thermal waters of meteoric origin (as the water isotopes suggest) circulated only in evaporate
234 minerals units of marine origin, the value of $\delta^{11}\text{B}$ would range from 18‰ to 32‰ (Barth, 1993).
235 The values of $\delta^{11}\text{B}$ of several of the thermal waters are even lower than the -5‰ characteristic of the
236 Cimino volcanic rocks (Tonarini et al., 2003) or attributed to the flysch rock (Pennisi et al., 2000)
237 but are rather comparable to those of hydrothermal tourmalines (Palmer, 1991) and local

tourmalines from Central Italy (Figure 9). Coupling the major ion content and $\delta^{11}\text{B}$ values, it is possible to show that thermal waters during their rising circulate within the flysch Ligurids (Figure 2). Because of the low permeability of these flysch units, the flow is very slow, giving the hot waters time to react and dissolve the borosilicate minerals within the flysch. A slow and tortuous path through the flysch units, with attendant conductive cooling, can explain the large temperature range of the thermal springs despite their relatively uniform chemical composition. Despite the presence of boron-rich minerals such as tourmaline in the Cimino-Vico province, the low boron concentration of the fresh waters circulating in the volcanics indicates the poor reactivity of these minerals in dilute waters and the relatively short water-rock interaction. The fresh waters acquire a boron isotopic signature which is a combination between the negative $\delta^{11}\text{B}$ of the volcanic products and the positive $\delta^{11}\text{B}$ of the recharge water (the rain water value approaches 40‰ near the coast; Pennisi et al., 2000), Figure 9.

Thus, in low enthalpy geothermal systems both strontium and boron isotopes can be used as conservative tracers since their chemistry is controlled more by the dissolution of the associated rocks and less by temperature-dependent fractionation into alteration minerals. Sr traces the interaction with the parent rocks and can be used to evaluate the mixing.

6. Conclusions

Chemical and multi-isotope data of fresh and thermal waters, sampled in the medium-low enthalpy hydrothermal system located in the Cimino-Vico volcanic district, have been studied. Water chemistry is controlled by mixing between fresh groundwater flowing in shallow volcanic rocks and thermal waters ascending from deep, high permeability Mesozoic limestones. Based on major element chemistry and the $\delta^{18}\text{O}$, δD , $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of waters we conclude the following:

- The chemical composition of thermal waters (ranging from 25.3°C and 62.2°C) reflect long-term circulation within the deep geothermal reservoir in the Mesozoic evaporate-carbonate

formations. The chemistry of fresh waters (<24.2°C) differs from the composition of thermal waters and reflects interaction with the Na-K-rich Cimino-Vico volcanics.

- SO_4/Cl , Na/Cl and B/Cl of thermal waters differ from other hydrothermal systems in Central Italy, probably implying a lack of hydraulic continuity across the region.
- Based on the $\delta^{18}\text{O}$ and δD of spring water, we infer that the recharge area for both the fresh and thermal aquifers is the summit region of Mount Cimino.
- Both $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$ can be used as tracer of groundwater mixing and circulation since they behave as conservative tracers in low-enthalpy thermal systems. The boron isotope composition of fresh waters is similar to those of the volcanic rocks constituting the aquifer, whereas the $\delta^{11}\text{B}$ values of thermal waters reflect dissolution of borosilicate minerals during fluid ascent from the deep aquifer.
- The $\delta^{11}\text{B}$ signature shows that thermal waters rising to the surface circulate within the low permeability flysch units.
- The thermal water flow path dictated by our geochemistry data (slow upflow) results in low spring temperatures that partially mask the heat resource of the reservoir. Our data are consistent with a large energy potential in this system.

References

- Aggarwal, J. K., Palmer, M. R., Bullen, T. D., Arnórsson, S., & Ragnarsdóttir, K. V. (2000). The boron isotope systematics of Icelandic geothermal waters: 1. Meteoric water charged systems. *Geochimica et Cosmochimica Acta*, 64(4), 579-585.
- Aggarwal, J. K., Sheppard, D., Mezger, K., & Pernicka, E. (2003). Precise and accurate determination of boron isotope ratios by multiple collector ICP-MS: origin of boron in the Ngawha geothermal system, New Zealand. *Chemical Geology*, 199(3), 331-342.

287 Angelone, M., Cremisini, C., Piscopo, V., Proposito, M., & Spaziani, F. (2008). Influence of
 288 hydrostratigraphy and structural setting on the arsenic occurrence in groundwater of the
 289 Cimino-Vico volcanic area (Central Italy). *Hydrogeology Journal*, 17(4), 901–914.
 290 doi:10.1007/s10040-008-0401-3

291 Arnone, G. (1979). Studio delle sorgenti termali del Lazio settentrionale. *Rend. Soc. It. Min. E Pet*,
 292 5(2), 647–666.

293 Arnórsson, S. (2000). *Isotopic and chemical techniques in geothermal exploration, development*
 294 *and use*. Vienna: International Atomic Energy Agency.

295 Arnórsson, S., & Andréðóttir, A. (1995). Processes controlling the distribution of boron and
 296 chlorine in natural waters in Iceland. *Geochimica et Cosmochimica Acta*, 59(20), 4125-4146
 297 doi:10.1016/0016-7037(95)00278-8

298 Baiocchi, A., Dragoni, W., Lotti, F., Luzzi, G., & Piscopo, V. (2006). Outline of the hydrogeology
 299 of the Cimino and Vico volcanic area and of the interaction between groundwater and Lake
 300 Vico (Lazio Region, Central Italy). *Bollettino Della Societa Geologica Italiana*, 125(2), 187–
 301 202.

302 Baiocchi, A., Lotti, F., & Piscopo, V. (2012). Conceptual Hydrogeological Model and Groundwater
 303 Resource Estimation in a Complex Hydrothermal Area: The Case of the Viterbo Geothermal
 304 Area (Central Italy). *Journal of Water Resource and Protection*, 04(04), 231–247.
 305 doi:10.4236/jwarp.2012.44026

306 Baiocchi, A., Lotti, F., & Piscopo, V. (2013). Impact of groundwater withdrawals on the interaction
 307 of multi-layered aquifers in the Viterbo geothermal area (Central Italy). *Hydrogeology*
 308 *Journal*, 21(6), 1339–1353. doi:10.1007/s10040-013-1000-5

309 Barbieri, M., Masi, U., & Tolomeo, L. (1979). Origin And Distribution Of Strontium In The
 310 Travertines, 24, 181–188.

- 311 Barth, S. (1993). Boron isotope variations in nature: a synthesis. *Geologische Rundschau*,
312 (January), 640–651. doi: 10.1007/BF00191491
- 313 Battistel, M., Hurwitz, S., Evans, W., & Barbieri, M. (2014). Multicomponent Geothermometry
314 Applied to a Medium-low Enthalpy Carbonate-evaporite Geothermal Reservoir. *Energy*
315 *Procedia*, 59, 359–365. doi:10.1016/j.egypro.2014.10.389
- 316 Boschetti, T. (2013). Oxygen isotope equilibrium in sulfate–water systems: A revision of
317 geothermometric applications in low-enthalpy systems. *Journal of Geochemical Exploration*,
318 124, 92–100. doi:10.1016/j.gexplo.2012.08.011
- 319 Boschetti, T., Etiope, G., Pennisi, M., Romain, M., & Toscani, L. (2013). Boron, lithium and
320 methane isotope composition of hyperalkaline waters (Northern Apennines, Italy): Terrestrial
321 serpentinization or mixing with brine? *Applied Geochemistry*, 32, 17–25.
322 doi:10.1016/j.apgeochem.2012.08.018
- 323 Boschetti, T., Venturelli, G., Toscani, L., Barbieri, M., & Mucchino, C. (2005). The Bagni di Lucca
324 thermal waters (Tuscany, Italy): an example of Ca-SO₄ waters with high Na/Cl and low
325 Ca/SO₄ ratios. *Journal of Hydrology*, 307(1-4), 270–293. doi:10.1016/j.jhydrol.2004.10.015
- 326 Capaccioni, B., Franco, T., Alberto, R., Orlando, V., Marco, M., & Salvatore, I. (2014).
327 Geochemistry of thermal fluids in NW Honduras: New perspectives for exploitation of
328 geothermal areas in the southern Sula graben. *Journal of Volcanology and Geothermal*
329 *Research*, 280, 40–52. doi:10.1016/j.jvolgeores.2014.04.004
- 330 Chiocchini, U., Castaldi, F., Barbieri, M., & Eulilli, V. (2010). A stratigraphic and geophysical
331 approach to studying the deep-circulating groundwater and thermal springs, and their recharge
332 areas, in Cimini Mountains–Viterbo area, Central Italy. *Hydrogeology Journal*, 18(6), 1319–
333 1341. doi:10.1007/s10040-010-0601-5

- 334 Chiodini, G., Frondini, F., Kerrick, D., & Rogie, J. (1999). Quantification of deep CO₂ fluxes from
 335 Central Italy. Examples of carbon balance for regional aquifers and of soil diffuse degassing.
 336 *Chemical Geology*, 159, 205–222.
- 337 Cinti, D., Tassi, F., Procesi, M., Bonini, M., Capecchiacci, F., Voltattorni, N., & Quattrocchi, F.
 338 (2014). Fluid geochemistry and geothermometry in the unexploited geothermal field of the
 339 Vicano–Cimino Volcanic District (Central Italy). *Chemical Geology*, 371, 96–114.
 340 doi:10.1016/j.chemgeo.2014.02.005
- 341 Cinti, D., Procesi, M., Poncia, P., Tassi, F., Vaselli, O., & Quattrocchi, F. (2015). Application of the
 342 Revised Volume Method for the Evaluation of the Geothermal Potential in the Vicano-Cimino
 343 Hydrothermal Reservoir (Central Italy). In *Proceedings World Geothermal Congress 2015*.
 344 Melbourne.
- 345 Coplen, T. B., Wildman, J. D., & Chen, J. (1991). Improvements in the gaseous hydrogen-water
 346 equilibration technique for hydrogen isotope-ratio analysis. *Analytical Chemistry*, 63(9), 910–
 347 912. doi:10.1021/ac00009a014
- 348 Craig, H. (1961). Isotopic Variations in Meteoric Waters. *Science (New York, N.Y.)*, 133(3465),
 349 1702–3. doi:10.1126/science.133.3465.1702
- 350 Dotsika, E., Poutoukis, D., Kloppmann, W., Guerrot, C., Voutsas, D., & Kouimtzis, T. H. (2010).
 351 The use of O, H, B, Sr and S isotopes for tracing the origin of dissolved boron in groundwater
 352 in Central Macedonia, Greece. *Applied Geochemistry*, 25(11), 1783–1796.
 353 doi:10.1016/j.apgeochem.2010.09.006
- 354 Duchi, V., Minissale, A. A., Ortino, S., & Romani, L. (1987). Geothermal prospecting by
 355 geochemical methods on natural gas and water discharges in the vulsini mts volcanic district
 356 (Central Italy). *Geothermics*, 16(2), 147–157. doi:10.1016/0375-6505(87)90062-9
- 357 Duchi, V., Minissale, A. A., & Rossi, R. (1986) Chemistry of thermal springs in the Larderello-

358 Travale geothermal region, southern Tuscany, Italy. *Applied geochemistry* 1(6): 659-667.

359 Ellis, A. J., & Mahon, W. A. J. (1964). Natural hydrothermal systems and experimental hot-
 360 water/rock interactions. *Geochimica et Cosmochimica Acta*, 28(8), 1323–1357.
 361 doi:10.1016/0016-7037(64)90132-2

362 Ellis, A., & Mahon, W. A. J. (1967). Natural hydrothermal systems and experimental hot water/rock
 363 interactions (Part II). *Geochimica et Cosmochimica Acta*, 31(4), 519–538. doi:10.1016/0016-
 364 7037(67)90032-4

365 Epstein, S., & Mayeda, T. (1953). Variation of O¹⁸ content of waters from natural sources.
 366 *Geochimica et Cosmochimica Acta*, 4(5), 213–224. doi:10.1016/0016-7037(53)90051-9

367 Fournier, R. O. (1977). Chemical geothermometers and mixing models for geothermal systems.
 368 *Geothermics*, 5(1-4), 41–50. doi:10.1016/0375-6505(77)90007-4

369 Fournier, R. O. (1981). Application of Water Geochemistry to Geothermal Exploration and
 370 Reservoir Engineering. In L.Rybach and L.J.P. Muffler (Ed.), *Geothemal Systems: Principles*
 371 *and Case Histories*. John Wiley & Sons Ltd.

372 Fournier, R. O., & Truesdell, A. H. (1973). An empirical Na-K-Ca geothermometer for natural
 373 waters. *Geochimica et Cosmochimica Acta*, 37(5), 1255–1275.

374 Gambardella, B., Marini, L., & Baneschi, I. (2005). Dissolved potassium in the shallow
 375 groundwaters circulating in the volcanic rocks of central-southern Italy. *Applied Geochemistry*,
 376 20(5), 875–897. doi:10.1016/j.apgeochem.2004.12.001

377 Giggenbach, W. F. (1988). Geothermal solute equilibria. derivation of Na-K-Mg-Ca geoindicators.
 378 *Geochimica et cosmochimica acta*, 52(12), 2749-2765. doi:10.1016/0016-7037(88)90143-3

379 Giggenbach, W. F. (1992). Isotopic shifts in waters from geothermal and volcanic systems along
 380 convergent plate boundaries and their origin. *Earth and Planetary Science Letters*.
 381 doi:10.1016/0012-821X(92)90127-H

- 382 Hem, D. (1985). *Study and Interpretation the Chemical of Natural of Characteristics Water*. (U. G.
383 S. Department of the Interior, Ed.) (3rd ed.). Alexandria: Department of the Interior, US
384 Geological Survey.
- 385 Hochstein, M. P. (1988). Assessment and modelling of geothermal reservoirs (small utilization
386 schemes). *Geothermics*, 17(1), 15-49.
- 387 Hurley, P. M., Fairbairn, H. W., & Pinson, W. H. (1966). RbSr isotopic evidence in the origin of
388 potash-rich lavas of Western Italy. *Earth and Planetary Science Letters*, 1(5), 301–306.
389 doi:10.1016/0012-821X(66)90012-4
- 390 Lee, S.G., Kim, T.K., & Lee, T. J. (2011). Strontium isotope geochemistry and its geochemical
391 implication from hot spring waters in South Korea. *Journal of Volcanology and Geothermal*
392 *Research*, 208(1-2), 12–22. doi:10.1016/j.jvolgeores.2011.09.004
- 393 Leeman, W. P., & Tonarini, S. (2001). Boron Isotopic Analysis of Proposed Borosilicate Mineral
394 Reference Samples. *Geostandards and Geoanalytical Research*, 25(2-3), 399–403.
395 doi:10.1111/j.1751-908X.2001.tb00614.x
- 396 Leeman, W. P., Tonarini, S., Pennisi, M., & Ferrara, G. (2005). Boron isotopic variations in
397 fumarolic condensates and thermal waters from Vulcano Island, Italy: Implications for
398 evolution of volcanic fluids. *Geochimica et Cosmochimica Acta*, 69(1), 143–163.
399 doi:10.1016/j.gca.2004.04.004
- 400 Longinelli, A., & Selmo, E. (2003). Isotopic composition of precipitation in Italy: a first overall
401 map. *Journal of Hydrology*, 270(1-2), 75–88. doi:10.1016/S0022-1694(02)00281-0
- 402 Lund, J. W., Freeston, D. H., & Boyd, T. L. (2011). Direct utilization of geothermal energy 2010
403 worldwide review. *Geothermics*, 40(3), 159-180. doi:10.1016/j.geothermics.2011.07.004
- 404 Millot, R., Hegan, A., & Négrel, P. (2012). Geothermal waters from the Taupo Volcanic Zone, New

405 Zealand: Li, B and Sr isotopes characterization. *Applied Geochemistry*, 27(3), 677-688.
 406 doi:10.1016/j.apgeochem.2011.12.015

407 Millot, R., & Négrel, P. (2007). Multi-isotopic tracing ($\delta^7\text{Li}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$) and chemical
 408 geothermometry: evidence from hydro-geothermal systems in France. *Chemical Geology*,
 409 244(3-4), 664–678. doi:10.1016/j.chemgeo.2007.07.015

410 Minissale, A. (2004). Origin, transport and discharge of CO_2 in Central Italy. *Earth-Science*
 411 *Reviews*, 66(1-2), 89–141. doi:10.1016/j.earscirev.2003.09.001

412 Minissale, A., & Duchi, V. (1988). Geothermometry on fluids circulating in a carbonate reservoir in
 413 north-Central Italy. *Journal of Volcanology and Geothermal Research*, 35(3), 237–252.
 414 doi:10.1016/0377-0273(88)90020-0

415 Minissale, A., Magro, G., Vaselli, O., Verrucchi, C., & Perticone, I. (1997). Geochemistry of water
 416 and gas discharges from the Mt. Amiata silicic complex and surrounding areas (Central Italy).
 417 *Journal of Volcanology and Geothermal Research*, 79(3-4), 223–251. doi:10.1016/S0377-
 418 0273(97)00028-0

419 Minissale, A., & Vaselli, O. (2011). Karst springs as “natural” pluviometers: Constraints on the
 420 isotopic composition of rainfall in the Apennines of Central Italy. *Applied Geochemistry*,
 421 26(5), 838–852. doi:10.1016/j.apgeochem.2011.02.005

422 Minissale, A., Vaselli, O., Tassi, F., Magro, G., Grechi, G. P., & Pira, V. La. (2002). Fluid mixing
 423 in carbonate aquifers near Rapolano (Central Italy): chemical and isotopic constraints. 17,
 424 1329–1342. doi:10.1016/S0883-2927(02)00023-9

425 Moore, J. N., & Simmons, S. F. (2013). More power from below. *Science*, 340(6135), 933-934.
 426 doi:10.1126/science.1235640

- 427 Negrel, P., Casanova, J., Azaroual, M., Guerrot, C., Cocherie, A., & Fouillac, C. (1999). Isotope
428 Geochemistry of Mineral Spring Waters in the Massif Central France. In H. Armannsson (Ed.),
429 *Geochemistry of Earth's Surface*. Rotterdam, The Netherlands.
- 430 Nicholson, K. (1993). *Geothermal Fluids* Springer Verlag, Berlin, XVIII, 264 p.
- 431 Palmer, M. R. (1991). Boron isotope systematics of hydrothermal fluids and tourmalines: A
432 synthesis. *Chemical Geology*, 94(2), 111–121. doi:10.1016/S0009-2541(10)80023-3
- 433 Palmer, M. R., & Sturchio, N. C. (1990). The boron isotope systematics of the Yellowstone
434 National Park (Wyoming) hydrothermal system : A reconnaissance, 54(10). 2811-2815.
435 doi:10.1016/0016-7037(90)90015-D
- 436 Palmer, R., Sturchio, N. C., & Kemp, A. J. (1997). The rare earth element geochemistry of acid-
437 sulphate and acid-sulphate-chloride geothermal systems from Yellowstone National Park,
438 Wyoming, USA. *Geochimica*, 61(4), 695–706.
- 439 Peiffer, L., Taran, Y. A., Lounejeva, E., Solis-Pichardo, G., Rouwet, D., & Bemard-Romero, R. A.
440 (2011). Tracing thermal aquifers of El Chichón volcano-hydrothermal system (México) with
441 $^{87}\text{Sr}/^{86}\text{Sr}$, Ca / Sr and REE, 205, 55–66. doi:10.1016/j.jvolgeores2011.06.004
- 442 Pennisi, M., Bianchini, G., Muti, A., Kloppmann, W., & Gonfiantini, R. (2006). Behaviour of boron
443 and strontium isotopes in groundwater–aquifer interactions in the Cornia Plain (Tuscany,
444 Italy). *Applied Geochemistry*, 21(7), 1169–1183. doi:10.1016/j.apgeochem.2006.03.001
- 445 Pennisi, M., Leeman, W. P., Tonarini, S., Pennisi, A., & Nabelek, P. (2000). Boron, Sr, O, and H
446 isotope geochemistry of groundwaters from Mt. Etna (Sicily)-hydrologic implications.
447 *Geochimica et Cosmochimica Acta*, 64(6), 961–974. doi:10.1016/S0016-7037(99)00382-8

448 Piscopo, V., Barbieri, M., Monetti, V., Pagano, G., Pistoni, S., Ruggi, E., & Stanzione, D. (2006).
 449 Hydrogeology of thermal waters in Viterbo area, Central Italy. *Hydrogeology Journal*, 14(8),
 450 1508–1521. doi:10.1007/s10040-006-0090-8

451 Poli, G., Frey, F. A., & Ferrara, G. (1984). Geochemical characteristics of the south Tuscany (Italy)
 452 volcanic province: Constraints on lava petrogenesis. *Chemical Geology*, 43(3-4), 203–221.
 453 doi:10.1016/0009-2541(84)90049-4

454 Reed, M. J. (1983). *Assessment of low-temperature geothermal resources of the United States;*
 455 *1982* (No. 892). US Geological Survey,.

456 Révész, K., & Coplen, T. B. (2008). Determination of the $\delta(\text{H}/\text{H})$ of Water: RSIL Lab Code 1574.
 457 In Révész & T. Kinga, and Coplen (Eds.), *Methods of the Reston Stable Isotope Laboratory:*
 458 *U.S. Geological Survey Techniques and Methods 10–C1* US Geological Survey, 2008.

459 Sollevanti, F. (1983). Geologic, volcanologic, and tectonic setting of the Vico-Cimino area, Italy.
 460 *Journal of Volcanology and Geothermal Research*, 17(1-4), 203–217. doi:10.1016/0377-
 461 0273(83)90068-9

462 Spycher, N., Sonnenthal, E., & Kennedy, B. M. (2011). Integrating multicomponent chemical
 463 geothermometry with parameter estimation computations for geothermal exploration. In
 464 *Transactions - Geothermal Resources Council* (Vol. 35 1, pp. 663–666).

465 Thompson, J. M., & DeMonge, J. M. (1996). Chemical analyses of hot springs, pools, and geysers
 466 from Yellowstone National Park, Wyoming, and vicinity, 1980-1993. *US Geological Survey;*
 467 *Earth Science Information Center, Open-File Reports Section*

468 Tonarini, S., Forte, C., Petrini, R., & Ferrara, G. (2003). Melt/biotite $^{11}\text{B}/^{10}\text{B}$ isotopic fractionation
 469 and the boron local environment in the structure of volcanic glasses. *Geochimica et*
 470 *Cosmochimica Acta*, 67(10), 1863–1873. doi:10.1016/S0016-7037(02)00987-0

- 471 Tonarini, S., Pennisi, M., & Gonfiantini, R. (2009). Boron isotope determinations in waters and
 472 other geological materials: analytical techniques and inter-calibration of measurements.
 473 *Isotopes in Environmental and Health Studies*, 45(2), 169–83.
 474 doi:10.1080/10256010902931210
- 475 Vengosh, A., Chivas, A. R., & McCulloch, M. T. (1989). Direct determination of boron and
 476 chlorine isotopic compositions in geological materials by negative thermal-ionization mass
 477 spectrometry. *Chemical Geology: Isotope Geoscience Section*, 79(4), 333–343.
 478 doi:10.1016/0168-9622(89)90039-0
- 479 Vollmer, R. (1976). Rb-Sr and U-Th-Pb systematics of alkaline rocks: the alkaline rocks from Italy.
 480 *Geochimica et Cosmochimica Acta*, 40(3), 283–295. doi:10.1016/0016-7037(76)90205-2
- 481 Williams, C. F., Reed, M. J., & Anderson, A. F. (2011, January). Updating the classification of
 482 geothermal resources. In *Proceedings, Thirty-Sixth Workshop on Geothermal Reservoir*
 483 *Engineering*.
- 484 Williams, C. F., Reed, M. J., & Mariner, R. H. (2008). A review of methods applied by the US
 485 Geological Survey in the assessment of identified geothermal resources. *US Geological Survey*
 486 *Open-File Report*, 1296(2008), 27.
- 487 Zeininger, H., & Heumann, K. G. (1983). Boron isotope ratio measurement by negative thermal
 488 ionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Physics*,
 489 48, 377–380. doi:10.1016/0020-7381(83)87106-X
- 490 Zuppi, G.M., Fontes, J.C., Letolle, R., 1974. Isotopes du milieu et circulations d’eaux sulfurees
 491 dans le Latium. *Isotope Techniques in Groundwater Hydrology*, IAEA, Wien, pp. 341–361.

492

Figure 1. Study area. The dotted circle in the map on the top left represents the enlarged area from where samples for this study were collected. The stars represent the sampling points and A-A' is the location of the hydrogeological section in figure 2. The circle represents the geothermal well VET1, see text for references.

Figure 2. Sketch of the hydrogeological setting of Cimino-Vico hydrothermal system and the groundwater circulation along the A-A' section showed in Figure 1. Dotted lines represent fresh water, solid lines thermal waters and dashed lines the mixing waters.

502

503 Figure 3. Anion composition of water samples (Equivalent/L) of fresh and thermal water: Dashed
 504 line (a) represents the enrichment in SO_4^{2-} content of rainwater that penetrates down into the
 505 geothermal reservoir. Grey area (b) is the interaction with carbonate minerals in the reservoir. Solid
 506 line (c) represents the mixing between thermal and fresh waters. Dashed dotted line (d) is the direct
 507 recharge of rain water to the shallow aquifer. VET 1 is the composition of the geothermal well
 508 Vetralla 001 (Figure 1).

509

510 Figure 4. Cation composition of water samples (Equivalent) of fresh and thermal water: VET 1 is
 511 the composition of the geothermal well Vetralla 001 (Figure 1). Dashed line represents the mixing
 512 between thermal samples and rain water. Grey area shows the composition for the volcanic rocks
 513 related to the Vico volcanic activity (Gambardella et al., 2005).

Figure 5. Plot of $(\text{Na}+\text{K})/\text{HCO}_3^-$ versus $(\text{Ca}+\text{Mg})/\text{HCO}_3^-$. For details see text

Figure 6. Composition (Equivalent) of thermal waters from different geothermal systems. The colored star symbols represent the water with $T > 100^\circ\text{C}$. a- Minissale et al., 2002; b- Boschetti et al., 2005; c- Duchi et al., 1987; d- Dotsika et al., 2010; e- Duchi et al., 1986; f- Giggenbach 1988; g- Thompson and DeMonge 1996.

Figure 7. Water stable isotopes of the Cimino-Vico groundwater compared to the Global Meteoric Water Line (GMWL) (Craig, 1961), the Mediterranean Meteoric Water Line (MMWL) (Longinelli and Selmo, 2003) and other springs from Central Italy (Minissale, 2004). The black arrow indicates the geographical trend from West to East. WRI - Water-Rock Interaction.

Figure 8. $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$ in the Cimino-Vico groundwater. The solid line is the calculated theoretical mixing line between the volcanic shallow aquifer end member and the evaporite-

530 carbonate units end member. The ratio of the Vico volcanic rocks is from Barbieri et al. (1979) and
 531 Hurley et al. (1966). The Sr concentrations of the evaporate-carbonate end member are from Cinti
 532 et al. (2014) and Minissale (2004).

533 Figure 9. $\delta^{11}\text{B}$ vs B/Cl Molar ratio showing samples from this study and from: a- Rain water
 534 (Tonarini et al., 2009), b- Marine evaporite minerals (Barth, 1993), c- Hydrothermal fluids
 535 (Aggarwal et al., 2000; Aggarwal et al., 2003; Boschetti et al., 2013; Millot et al., 2012; Palmer et
 536 al., 1997), d-Cimino volcanics (Tonarini et al., 2003), e-Tourmaline (Leeman and Tonarini, 2001;
 537 Tonarini et al., 2003; Tonarini et al., 2009). References for thermal samples of Cornia (Pennisi et al.,
 538 2006).

540 Table 1. Physical parameters and chemical concentrations of groundwater in the Cimino-Vico district

Id	T°C	pH	EC μS	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO ₃ mg/L	Cl mg/L	SO ₄ mg/L	SiO ₂ mg/L	Sr mg/L	B mg/L	δ ¹⁸ O ‰	δD ‰	⁸⁷ Sr/ ⁸⁶ Sr	δ ¹¹ B ‰
<i>Fresh waters</i>																	
2	17.3	7.4	719	58.2	17.0	49.3	15.9	275	76.5	35.9	-	-	-	-	-	-	-
9	20.0	7.0	603	64.6	12.8	27.2	23.5	160	35.6	117	75.4	0.90	0.15	-6.2	-38.6	0.70852	-2.62
13	24.2	6.4	446	67.0	13.8	24.7	17.0	186	24.1	123	63.5	1.10	0.26	-6.2	-39.3	0.70889	-3.00
14	19.4	7.8	305	9.32	6.71	15.9	25.5	122	20.4	14.8	61.2	0.20	0.22	-6.5	-40.6	0.71019	6.12
15	18.7	6.9	303	17.8	6.20	18.5	15.9	150	23.4	24.2	-	0.16	0.02	-	-	0.71026	3.25
15	19.5	7.2	476	25.3	5.80	33.7	37.4	177	29.6	33.6	-	-	-	-	-	-	-
18	18.1	6.8	753	107	13.8	36.0	25.6	397	45.8	112	78.1	1.08	0.26	-5.9	-37.5	0.70855	-5.00
22	18.7	7.1	771	82.1	13.7	37.1	45.0	308	26.1	133	-	-	-	-	-	-	-
23	19.9	6.7	749	85.3	17.3	28.2	52.8	488	19.2	23.4	-	-	-	-	-	-	-
24	20.3	7.6	342	18.5	5.10	15.9	29.9	128	17.9	32.0	-	-	-	-	-	-	-
<i>Thermal waters</i>																	
1	62.2	6.1	3170	558	146	33.8	31.5	1071	14.2	1968	49.4	12.3	1.12	-6.5	-37.2	0.70797	-6.99
3	60.0	6.3	2980	535	126	41.8	39.3	1129	14.5	1200	-	-	-	-	-	-	-
4	27.3	6.0	2460	473	120	34.2	32.9	638	9.01	1497	55.1	9.94	1.05	-6.0	-36.3	0.70800	-4.12
5	62.0	6.5	3010	585	143	34.5	32.1	1105	17.6	2268	49.7	11.0	1.12	-6.5	-38.5	0.70798	-4.25
6	57.0	6.5	2720	520	120	31.0	26.0	1145	14.5	1080	-	12.0	0.25	-	-	0.70797	-6.58
7	25.3	7.0	1720	243	73.5	33.4	71.1	619	12.4	727	-	5.61	1.08	-	-	0.70800	-8.24
8	54.7	6.5	2680	500	91.9	36.1	43.6	976	16.8	1051	-	-	-	-	-	-	-
10	41.1	6.3	3030	616	125	40.6	41.1	1037	14.2	1265	-	-	-	-	-	-	-
11	37.6	6.7	3400	608	141	41.8	39.6	976	12.8	1589	-	13.5	0.06	-	-	0.70805	-8.24
12	57.9	6.2	3190	681	149	32.5	31.1	1086	17.0	2845	48.3	13.7	1.15	-6.6	-39.3	0.70797	-8.37
16	59.6	6.1	3160	559	94.8	30.8	36.9	946	17.1	1228	-	-	-	-	-	-	-
17	31.1	5.8	2660	524	98.5	31.1	31.5	1040	19.0	1820	64.8	10.8	1.15	-6.3	-38.3	0.70803	-8.24
19	48.4	6.0	2700	474	95.9	36.6	37.4	1050	16.7	1099	-	-	-	-	-	-	-
20	51.4	6.1	3270	1003	155	32.8	46.0	1220	16.5	2579	-	14.0	1.56	-	-	0.70797	-8.24