



## The chemistry and isotopic composition of waters in the low-enthalpy geothermal system of Cimino-Vico Volcanic District, Italy

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

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11

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  $\delta D$ ,  $\delta^{18}O$ ,  
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  $\delta^{18}O$  ( $-6.6\text{‰}$  to  $-5.9\text{‰}$ ) and  $\delta D$  ( $-$   
23  $40.60\text{‰}$  to  $-36.30\text{‰}$ ) 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  $6.12\text{‰}$ ) is similar to those of the volcanic cover, but  
29 the  $\delta^{11}B$  of thermal waters ( $-8.37\text{‰}$  to  $-4.12\text{‰}$ ) 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

36 **1. Introduction**

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

48 Geothermal energy exploration is based in large part on the characterization of water, gas, and  
49 rock chemistry, reservoir permeability, and the rates of water recharge into the reservoir. In the past  
50 several decades many geochemical indicators have been developed to assess the state of the  
51 geothermal reservoir to reduce the high costs of exploratory drilling (e.g. Arnórsson, 2000;  
52 Boschetti, 2013; Capaccioni et al., 2014; Fournier, 1981; Fournier and Truesdell, 1973; Fournier,  
53 1977; Giggenbach, 1988, 1992; Spycher et al., 2011). In geothermal resource exploration and  
54 assessment, the stable isotopes of water ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) have been widely used as tracers for the  
55 origin of groundwater and for water-rock interaction, and as indicators for mixing of waters from  
56 different sources. The isotopic composition of strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) provides information on flow  
57 paths and mixing of waters because strontium is readily leached from rocks (e.g. Boschetti et al.,  
58 2005; Dotsika et al., 2010; Lee et al., 2011; ; Negrel et al., 1999; Peiffer et al., 2011; Pennisi et al.,  
59 2006). Boron stable isotopes are applied in geothermal exploration, because boron is highly  
60 incompatible during the water-rock interaction and because incorporation of boron into secondary

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

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

## 74 **2. Geological framework**

75 Volcanic activity which gave rise to the Cimino and Vico complexes started at 1.35 Ma with  
76 explosive and effusive activity of the Cimino complex. Between 0.8 and 0.3 Ma, the Vico complex  
77 was active, with a central caldera that now hosts Vico Lake (Figure 1). The Cimino volcanic  
78 products include rhyodacites, latitic ignimbrites and olivine-latitic lavas, and are mostly covered by  
79 the K-alkaline pyroclastic deposits from the Vico volcanics, consisting of undersaturated trachytes,  
80 phonolites, tephritic phonolites, tephrites, and subordinate tuffs (Arnone, 1979; Gambardella et al.,  
81 2005; Sollevanti, 1983). Northwest and northeast striking extensional faults divide the substratum  
82 rocks and control the horst and graben pattern (Baiocchi et al., 2013). Ongoing magmatic activity is  
83 manifested by several geothermal anomalies, thermal springs, CO<sub>2</sub>-rich vents and active travertine  
84 deposition.

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

86 hydrostratigraphic sequence was defined (Angelone et al., 2008; Arnone, 1979; Baiocchi et al.,  
87 2013; Chiocchini et al., 2010; Piscopo et al., 2006) (Figure 2). The high permeability Mesozoic  
88 limestone in Central Italy is the primary regional groundwater aquifer which hosts numerous  
89 geothermal reservoirs with temperatures ranging between 48°C and 115°C (Minissale, 2004). The  
90 reservoir temperature of Cimino-Vico geothermal system is ~94°C, based on multicomponent  
91 geothermometry (Battistel et al., 2014). Abundant CO<sub>2</sub> from active metamorphism is dissolved in  
92 the aquifer (Chiodini et al., 1999; Duchi et al., 1987; Minissale and Duchi, 1988). The shallow  
93 (<200 m) fresh-water aquifer in the volcanic products of Cimino and Vico and the deep regional  
94 aquifer are separated by low-permeability Pliocene-Pleistocene sediments and Cretaceous-  
95 Oligocene flysch deposits (Ligurian Units) (Figure 2). Thermal groundwater from the deep  
96 reservoir ascends through fractures and faults in the sedimentary substratum (Angelone et al., 2008;  
97 Arnone, 1979; Baiocchi et al., 2012; Chiocchini et al., 2010; Piscopo et al., 2006). The aquifer  
98 system is bounded laterally by the Pliocene- Pleistocene sedimentary complex and Cretaceous-  
99 Oligocene flysch units.

### 100 **3. Sampling and laboratory analysis**

101 Twenty-three water samples from springs and private wells (Figure 1) used for agricultural  
102 water supply were sampled between October 2011 and August 2012. Samples for major element  
103 chemistry were collected in 50 ml high-density polyethylene bottles and filtered in the field with a  
104 0.45 µm filter. Water temperature, electrical conductivity (EC) and pH were measured in the field.  
105 Alkalinity was determined in the field by titration with 0.1 N HCl. Major element concentrations  
106 were determined at the Geochemistry laboratory of Sapienza University in Rome with a Dionex  
107 DX-120 ion chromatograph (precision ±2%) with a Dionex CS-12 column for cations and a Dionex  
108 AS9-SC column for anions. Nine samples were collected in 50 ml cleaned glass bottles and  
109 analysed for δ<sup>18</sup>O and δD compositions at the U.S. Geological Survey Stable Isotope Laboratory in  
110 Reston, Virginia. δ<sup>18</sup>O values were determined using the CO<sub>2</sub> equilibration technique of Epstein and

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

116 Fourteen additional filtered samples were collected in 15 ml high-density polyethylene bottles  
117 for strontium and boron concentrations and isotope analyses. The samples were acidified with ultra-  
118 pure nitric acid to a pH of about 2 in the field. Strontium and boron concentrations were measured  
119 at the Geochemistry laboratory of Sapienza University in Rome using ICP-MS (X Serie 2 Thermo  
120 Fisher Scientific) with an analytical accuracy of 2% to 5%. The strontium isotope ratios were  
121 measured on a Finnigan MAT 261 Thermal Ionization Mass Spectrometer (TIMS) at the USGS  
122 Metal and Metalloid Isotope Laboratory in Menlo Park, CA. Reported values have been corrected  
123 for natural and analytical stable isotope fractionation to  $^{88}\text{Sr}/^{86}\text{Sr} = 8.37515$  and then adjusted to the  
124 NBS987 standard value of 0.71024. The values are precise to 0.00002 at the 95% confidence level.  
125 Boron isotope analysis were carried out by negative TIMS (Vengosh et al., 1989; Zeininger and  
126 Heumann, 1983) at the USGS Metal and Metalloid Isotope Laboratory in Menlo Park, CA.  
127 Sufficient water to supply 2 ng of B was loaded directly onto degassed, zone-refined Re filaments.  
128 The B isotopes were measured as the  $\text{BO}_2$  species at masses 42 and 43. The typical agreement of  
129 replicate analyses of a sample is within 1%. Isotope ratios are reported as permil deviation ( $\delta^{11}\text{B}$ ) in  
130 the  $^{11}\text{B}/^{10}\text{B}$  ratios relative to the standard NBS SRM 951 and the analytical precision is  $\pm 0.5\%$  as  
131  $\delta^{11}\text{B}$ .

#### 132 **4. Results**

133 The chemical composition of groundwater samples from Cimino-Vico thermal area is reported  
134 in Table 1. The charge balance of all samples is within  $\pm 4\%$ . The waters sampled are classified as  
135 either  $\text{HCO}_3^-$ -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  $\text{SO}_4^-$ -

136 rich thermal waters ( $T > 25^{\circ}\text{C}$ ,  $5.8 > \text{pH} > 7.0$ ,  $\text{HCO}_3/\text{SO}_4$  of 0.3-1.7 equivalent) (Figures 3-6, Table 1).  
137 The thermal waters have  $\text{Cl}/\text{SO}_4$  and  $\text{Na}/\text{Cl}$  equivalent ratios ranging from 0.01 to 0.02 and 2.52 to  
138 5.83 respectively, which considerably differ from the values of other thermal waters in Central Italy  
139 (e.g. Minissale et al., 2002). The  $\text{B}/\text{Cl}$  equivalent ratio ranges from 0.003 to 0.04 in the fresh waters  
140 and from 0.02 to 0.38 in the thermal samples.

141 The cation composition of thermal waters ranges between the composition in geothermal well  
142 Vetralla 001 VET1 drilled to a depth of 1117 m within the Mesozoic units ~20 km south of the  
143 study area (<http://unmig.sviluppoeconomico.gov.it/unmig/geotermia/pozzi/dettaglio.asp?cod=136>)  
144 and the NaK-rich composition of the Vico rocks (Figure 4). Few thermal water samples bear the  
145 signature of the  $\text{Na}^+$ - and  $\text{K}^+$ -rich volcanic substrate of the Cimino-Vico area (Arnone, 1979;  
146 Gambardella et al., 2005; Sollevanti, 1983). The high concentration of  $\text{Ca}^{2+}$  (<881 mg/L) and  $\text{SO}_4$   
147 (<1,826 mg/L) in thermal waters traces the interaction with gypsum constituting the Mesozoic units.  
148 There is only a weak correlation between water temperature and dissolved ions concentrations,  
149 suggesting rapid cooling of the ascending waters.

#### 150 *Isotopic composition of waters*

151 The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of all samples range between -6.6‰ to -5.9‰ and from -40.60‰ to -  
152 36.30 ‰, respectively (Table 1, Figure 7) and strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) range between  
153 0.70797 and 0.71026 (Table 1, Figure 8). The  $^{87}\text{Sr}/^{86}\text{Sr}$  values of thermal waters have a narrow  
154 range (0.70797-0.70805) and are similar to those of the Mesozoic evaporite-carbonate units  
155 ( $0.70778 \pm 0.000110$ ; Boschetti et al. 2005). The cold fresh waters have a wider range of values  
156 (0.71086-0.70852) which are generally higher than the ratios in thermal waters, and extend to the  
157 values of the volcanic rocks from the Cimino-Vico district, 0.7107-0.7136 (Hurley et al., 1966; Poli  
158 et al., 1984; Vollmer, 1976).  $\delta^{11}\text{B}$  in thermal waters ranges from -8.37‰ to -4.12‰, and in fresh  
159 waters between -5.00 and 6.12‰ (Table 1, Figures 9,10). Samples #14 and #15 have positive  $\delta^{11}\text{B}$   
160 values of 3.25 and 6.12‰, respectively.



161 **5. Discussion**

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

167 *5.1 Processes controlling water chemistry*

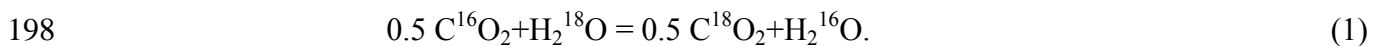
168 The relatively high temperature of groundwater ascending from depth, the high rate of CO<sub>2</sub>  
169 degassing, and the mixing between thermal and fresh waters are reflected in the chemical  
170 composition of spring waters in the Cimino-Vico District (Figures 3 and 4). The chemical  
171 composition of the thermal waters suggests that in the geothermal reservoir, fluids are in  
172 equilibrium with gypsum, quartz, aragonite and calcite (Battistel et al., 2014). The dissolution of  
173 sulphate minerals results from groundwater flow in the Mesozoic evaporite-carbonate sequence as  
174 inferred from the positive correlation between Ca<sup>2+</sup>+Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. The enrichment in Ca<sup>2+</sup>+Mg<sup>2+</sup>  
175 compared with Na<sup>+</sup>+K<sup>+</sup> (Figures 4, 5) suggests insignificant contributions from silicate weathering  
176 in thermal waters.

177 High HCO<sub>3</sub><sup>-</sup> concentrations in fresh waters reflect the dissolution of carbonates and CO<sub>2</sub>  
178 degassing from the deep geothermal reservoir through the local fault system. The (Ca<sup>2+</sup>+Mg<sup>2+</sup>)/  
179 HCO<sub>3</sub><sup>-</sup> ≈ 1 also implies that carbonate dissolution is significant (Figure 5). Silicate weathering is  
180 evident in the chemistry of fresh water samples. The dissolution of Na-K-bearing silicate minerals  
181 such as leucite and plagioclase, likely resulting from the ingress of CO<sub>2</sub> in the volcanic aquifer  
182 increases the ratio Na<sup>+</sup>+K<sup>+</sup>/ Ca<sup>2+</sup>+Mg<sup>2+</sup>. Similar to other low-enthalpy geothermal systems, the  
183 chemistry of low enthalpy thermal waters of Cimino-Vico system is mainly lithology-dependent and  
184 controlled by rock dissolution. In contrast, the chemical composition of high enthalpy thermal fluids  
185 is mainly controlled by temperature-dependent reactions between primary and secondary, alteration

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

188 The uniform  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of Cimino-Vico volcanic waters that plot along the Meteoric  
189 Water Line (Figure 7) suggest a meteoric origin for thermal waters. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  show a  
190 progressive isotope lightening from the Tyrrhenian Sea to the Apennines Chain. The proposed  
191 vertical isotope gradient for Central Italy (-0.3‰ per 100 m; Cinti et al., 2014; Longinelli and  
192 Selmo, 2003; Minissale and Vaselli, 2011; Zuppi et al., 1974,) suggests that recharge is at an  
193 elevation of 400 m to 700 m on the summit of Mount Cimino, consistent with previous studies  
194 (Baiocchi et al., 2006; Cinti et al., 2014; Piscopo et al., 2006). A slight negative shift in  $\delta^{18}\text{O}$  values  
195 of thermal waters likely results from oxygen exchange between water and  $\text{CO}_2$  derived from  
196 geothermal activity (Negrel et al., 1999):

197



199

200 The relatively low temperature in the geothermal reservoir (Battistel et al., 2014) and the relatively  
201 large effect of the  $\text{CO}_2$  on the  $\delta^{18}\text{O}$  value imply that fluid-rock interaction has a minimal effect on  
202 the isotope ratio (Figure 7).

### 203 *5.2 Processes controlling B and Sr systematics*

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

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

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

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

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

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

## 253 **6. Conclusions**

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

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

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

264 • SO<sub>4</sub>/Cl, Na/Cl and B/Cl of thermal waters differ from other hydrothermal systems in Central  
265 Italy, probably implying a lack of hydraulic continuity across the region.

266 • Based on the the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of spring water, we infer that the recharge area for both the  
267 fresh and thermal aquifers is the summit region of Mount Cimino.

268 • Both  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{11}\text{B}$  can be used as tracer of groundwater mixing and circulation since  
269 they behave as conservative tracers in low-enthalpy thermal systems. The boron isotope  
270 composition of fresh waters is similar to those of the volcanic rocks constituting the aquifer,  
271 whereas the  $\delta^{11}\text{B}$  values of thermal waters reflect dissolution of borosilicate minerals during  
272 fluid ascent from the deep aquifer.

273 • The  $\delta^{11}\text{B}$  signature shows that thermal waters rising to the surface circulate within the low  
274 permeability flysch units.

275 • The thermal water flow path dictated by our geochemistry data (slow upflow) results in low  
276 spring temperatures that partially mask the heat resource of the reservoir. Our data are  
277 consistent with a large energy potential in this system.

278

## 279 **References**

280 Aggarwal, J. K., Palmer, M. R., Bullen, T. D., Arnórsson, S., & Ragnarsdóttir, K. V. (2000). The  
281 boron isotope systematics of Icelandic geothermal waters: 1. Meteoric water charged  
282 systems. *Geochimica et Cosmochimica Acta*, 64(4), 579-585.

283 Aggarwal, J. K., Sheppard, D., Mezger, K., & Pernicka, E. (2003). Precise and accurate  
284 determination of boron isotope ratios by multiple collector ICP-MS: origin of boron in the  
285 Ngawha geothermal system, New Zealand. *Chemical Geology*, 199(3), 331-342.

- 286 Angelone, M., Cremisini, C., Piscopo, V., Proposito, M., & Spaziani, F. (2008). Influence of  
287 hydrostratigraphy and structural setting on the arsenic occurrence in groundwater of the  
288 Cimino-Vico volcanic area (Central Italy). *Hydrogeology Journal*, 17(4), 901–914.  
289 doi:10.1007/s10040-008-0401-3
- 290 Arnone, G. (1979). Studio delle sorgenti termali del Lazio settentrionale. *Rend. Soc. It. Min. E Pet*,  
291 5(2), 647–666.
- 292 Arnórsson, S. (2000). *Isotopic and chemical techniques in geothermal exploration, development*  
293 *and use*. Vienna: International Atomic Energy Agency.
- 294 Arnórsson, S., & Andréðóttir, A. (1995). Processes controlling the distribution of boron and  
295 chlorine in natural waters in Iceland. *Geochimica et Cosmochimica Acta*, 59(20), 4125-4146  
296 doi:10.1016/0016-7037(95)00278-8
- 297 Baiocchi, A., Dragoni, W., Lotti, F., Luzzi, G., & Piscopo, V. (2006). Outline of the hydrogeology  
298 of the Cimino and Vico volcanic area and of the interaction between groundwater and Lake  
299 Vico (Lazio Region, Central Italy). *Bollettino Della Societa Geologica Italiana*, 125(2), 187–  
300 202.
- 301 Baiocchi, A., Lotti, F., & Piscopo, V. (2012). Conceptual Hydrogeological Model and Groundwater  
302 Resource Estimation in a Complex Hydrothermal Area: The Case of the Viterbo Geothermal  
303 Area (Central Italy). *Journal of Water Resource and Protection*, 04(04), 231–247.  
304 doi:10.4236/jwarp.2012.44026
- 305 Baiocchi, A., Lotti, F., & Piscopo, V. (2013). Impact of groundwater withdrawals on the interaction  
306 of multi-layered aquifers in the Viterbo geothermal area (Central Italy). *Hydrogeology*  
307 *Journal*, 21(6), 1339–1353. doi:10.1007/s10040-013-1000-5
- 308 Barbieri, M., Masi, U., & Tolomeo, L. (1979). Origin And Distribution Of Strontium In The  
309 Travertines, 24, 181–188.

- 310 Barth, S. (1993). Boron isotope variations in nature: a synthesis. *Geologische Rundschau*,  
311 (January), 640–651. doi: 10.1007/BF00191491
- 312 Battistel, M., Hurwitz, S., Evans, W., & Barbieri, M. (2014). Multicomponent Geothermometry  
313 Applied to a Medium-low Enthalpy Carbonate-evaporite Geothermal Reservoir. *Energy*  
314 *Procedia*, 59, 359–365. doi:10.1016/j.egypro.2014.10.389
- 315 Boschetti, T. (2013). Oxygen isotope equilibrium in sulfate–water systems: A revision of  
316 geothermometric applications in low-enthalpy systems. *Journal of Geochemical Exploration*,  
317 124, 92–100. doi:10.1016/j.gexplo.2012.08.011
- 318 Boschetti, T., Etiope, G., Pennisi, M., Romain, M., & Toscani, L. (2013). Boron, lithium and  
319 methane isotope composition of hyperalkaline waters (Northern Apennines, Italy): Terrestrial  
320 serpentinization or mixing with brine? *Applied Geochemistry*, 32, 17–25.  
321 doi10.1016/j.apgeochem.2012.08.018
- 322 Boschetti, T., Venturelli, G., Toscani, L., Barbieri, M., & Mucchino, C. (2005). The Bagni di Lucca  
323 thermal waters (Tuscany, Italy): an example of Ca-SO<sub>4</sub> waters with high Na/Cl and low  
324 Ca/SO<sub>4</sub> ratios. *Journal of Hydrology*, 307(1-4), 270–293. doi:10.1016/j.jhydrol.2004.10.015
- 325 Capaccioni, B., Franco, T., Alberto, R., Orlando, V., Marco, M., & Salvatore, I. (2014).  
326 Geochemistry of thermal fluids in NW Honduras: New perspectives for exploitation of  
327 geothermal areas in the southern Sula graben. *Journal of Volcanology and Geothermal*  
328 *Research*, 280, 40–52. doi:10.1016/j.jvolgeores.2014.04.004
- 329 Chiocchini, U., Castaldi, F., Barbieri, M., & Eulilli, V. (2010). A stratigraphic and geophysical  
330 approach to studying the deep-circulating groundwater and thermal springs, and their recharge  
331 areas, in Cimino Mountains–Viterbo area, Central Italy. *Hydrogeology Journal*, 18(6), 1319–  
332 1341. doi:10.1007/s10040-010-0601-5

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



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

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

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

364 Epstein, S., & Mayeda, T. (1953). Variation of O<sup>18</sup> content of waters from natural sources.  
365 *Geochimica et Cosmochimica Acta*, 4(5), 213–224. doi:10.1016/0016-7037(53)90051-9

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

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

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

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

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

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

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

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

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

409 Minissale, A. (2004). Origin, transport and discharge of  $\text{CO}_2$  in Central Italy. *Earth-Science*  
410 *Reviews*, 66(1-2), 89–141. doi:10.1016/j.earscirev.2003.09.001

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

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

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

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

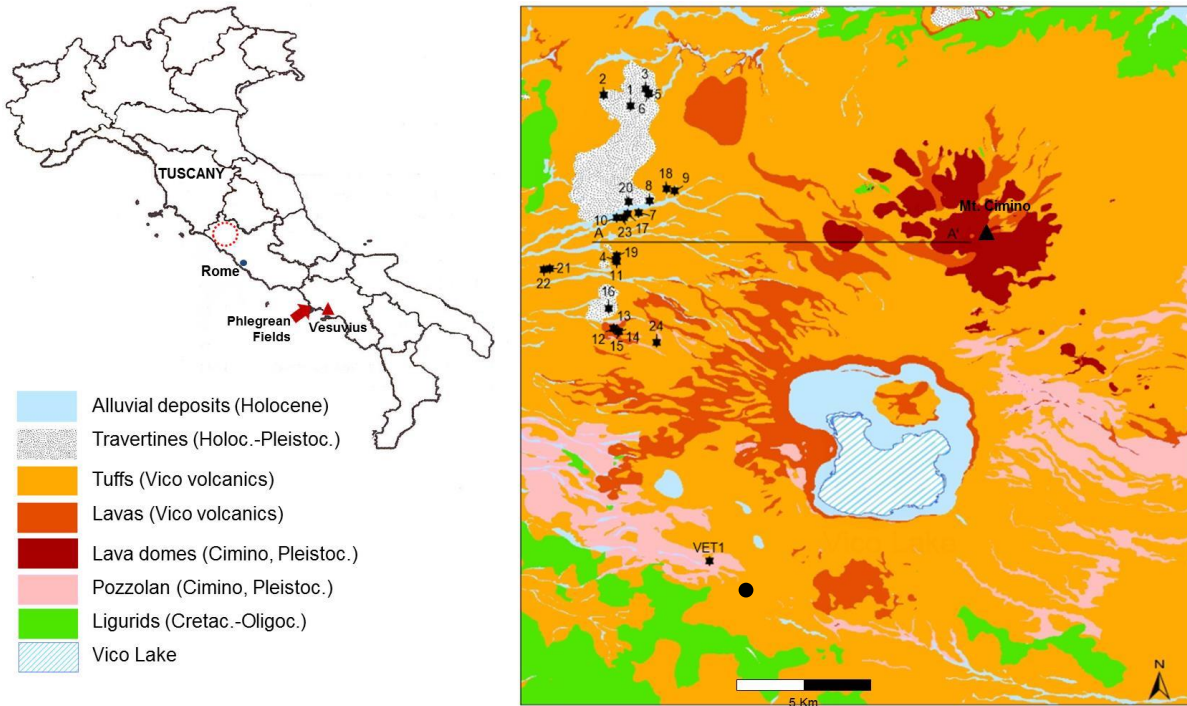
424 Moore, J. N., & Simmons, S. F. (2013). More power from below. *Science*, 340(6135), 933-934.  
425 doi:10.1126/science.1235640

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

- 447 Piscopo, V., Barbieri, M., Monetti, V., Pagano, G., Pistoni, S., Ruggi, E., & Stanzione, D. (2006).  
448 Hydrogeology of thermal waters in Viterbo area, Central Italy. *Hydrogeology Journal*, 14(8),  
449 1508–1521. doi:10.1007/s10040-006-0090-8
- 450 Poli, G., Frey, F. A., & Ferrara, G. (1984). Geochemical characteristics of the south Tuscany (Italy)  
451 volcanic province: Constraints on lava petrogenesis. *Chemical Geology*, 43(3-4), 203–221.  
452 doi:10.1016/0009-2541(84)90049-4
- 453 Reed, M. J. (1983). *Assessment of low-temperature geothermal resources of the United States;*  
454 *1982* (No. 892). US Geological Survey,.
- 455 Révész, K., & Coplen, T. B. (2008). Determination of the  $\delta(\text{H}/\text{H})$  of Water: RSIL Lab Code 1574.  
456 In Révész & T. Kinga, and Coplen (Eds.), *Methods of the Reston Stable Isotope Laboratory:*  
457 *U.S. Geological Survey Techniques and Methods 10–C1* US Geological Survey, 2008.
- 458 Sollevanti, F. (1983). Geologic, volcanologic, and tectonic setting of the Vico-Cimino area, Italy.  
459 *Journal of Volcanology and Geothermal Research*, 17(1-4), 203–217. doi:10.1016/0377-  
460 0273(83)90068-9
- 461 Spycher, N., Sonnenthal, E., & Kennedy, B. M. (2011). Integrating multicomponent chemical  
462 geothermometry with parameter estimation computations for geothermal exploration. In  
463 *Transactions - Geothermal Resources Council* (Vol. 35 1, pp. 663–666).
- 464 Thompson, J. M., & DeMonge, J. M. (1996). Chemical analyses of hot springs, pools, and geysers  
465 from Yellowstone National Park, Wyoming, and vicinity, 1980-1993. *US Geological Survey;*  
466 *Earth Science Information Center, Open-File Reports Section*
- 467 Tonarini, S., Forte, C., Petrini, R., & Ferrara, G. (2003). Melt/biotite  $^{11}\text{B}/^{10}\text{B}$  isotopic fractionation  
468 and the boron local environment in the structure of volcanic glasses. *Geochimica et*  
469 *Cosmochimica Acta*, 67(10), 1863–1873. doi:10.1016/S0016-7037(02)00987-0

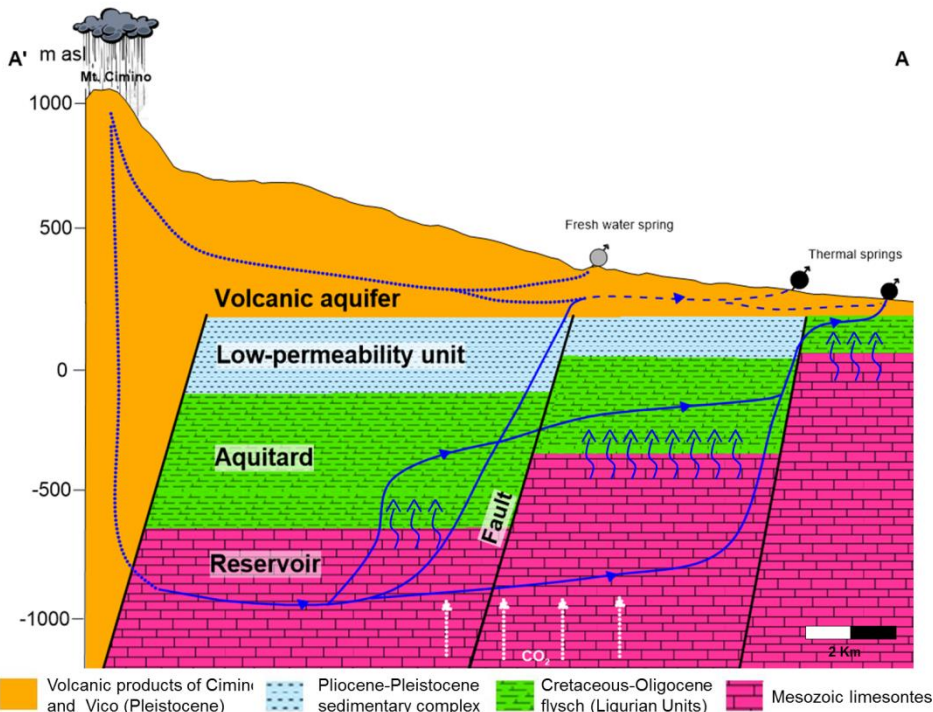
- 470 Tonarini, S., Pennisi, M., & Gonfiantini, R. (2009). Boron isotope determinations in waters and  
471 other geological materials: analytical techniques and inter-calibration of measurements.  
472 *Isotopes in Environmental and Health Studies*, 45(2), 169–83.  
473 doi:10.1080/10256010902931210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

491



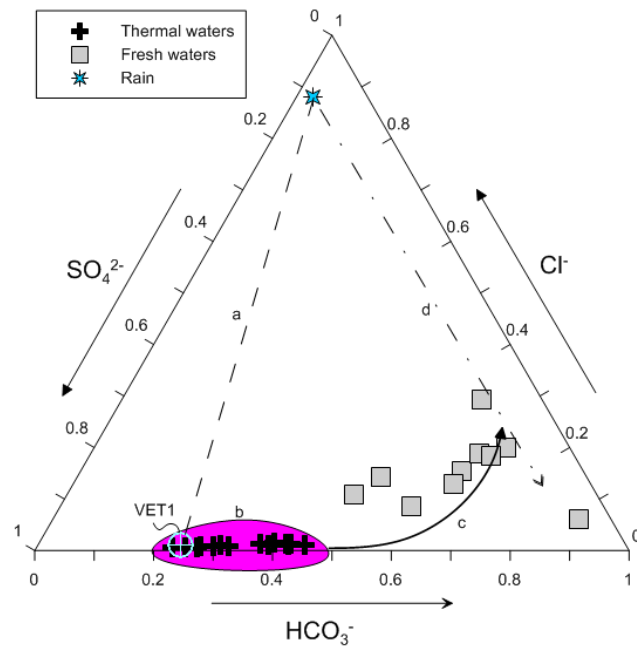
492

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



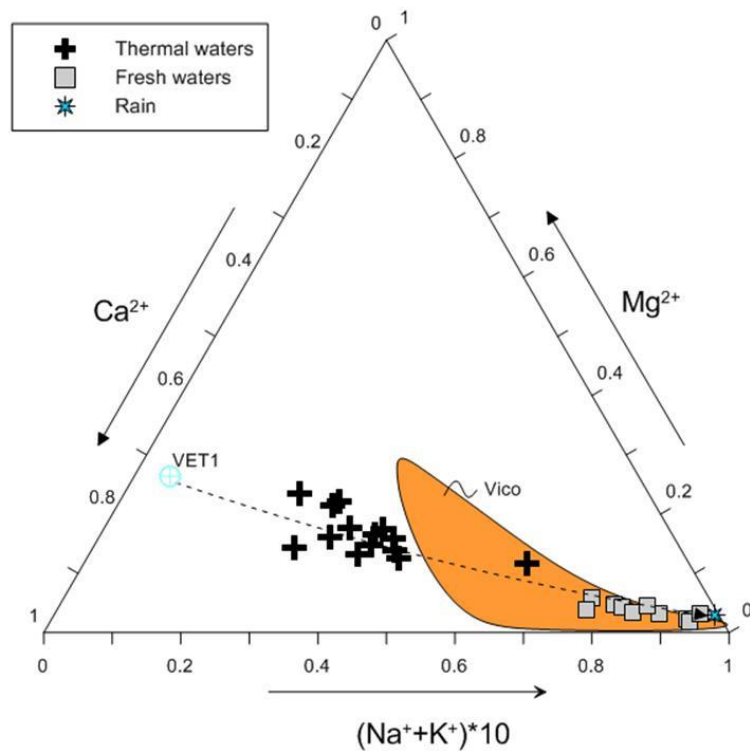
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498 Figure 2. Sketch of the hydrogeological setting of Cimino-Vico hydrothermal system and the  
 499 groundwater circulation along the A-A' section showed in Figure 1. Dotted lines represent fresh  
 500 water, solid lines thermal waters and dashed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



501

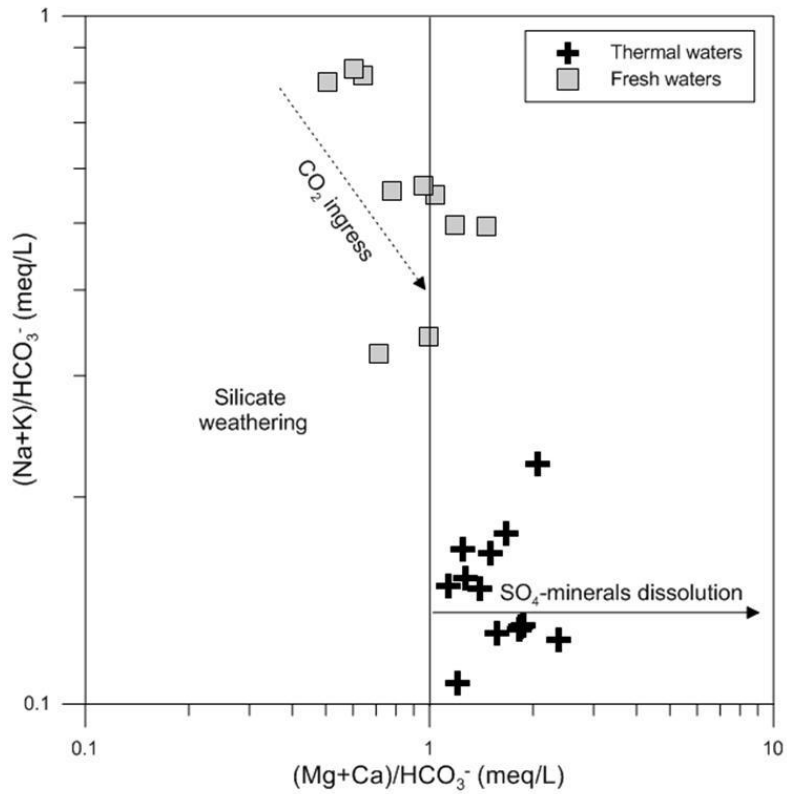
502 Figure 3. Anion composition of water samples (Equivalent/L) of fresh and thermal water: Dashed  
 503 line (a) represents the enrichment in  $\text{SO}_4^{2-}$  content of rainwater that penetrates down into the  
 504 geothermal reservoir. Grey area (b) is the interaction with carbonate minerals in the reservoir. Solid  
 505 line (c) represents the mixing between thermal and fresh waters. Dashed dotted line (d) is the direct  
 506 recharge of rain water to the shallow aquifer. VET 1 is the composition of the geothermal well  
 507 Vetralla 001 (Figure 1).



508

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

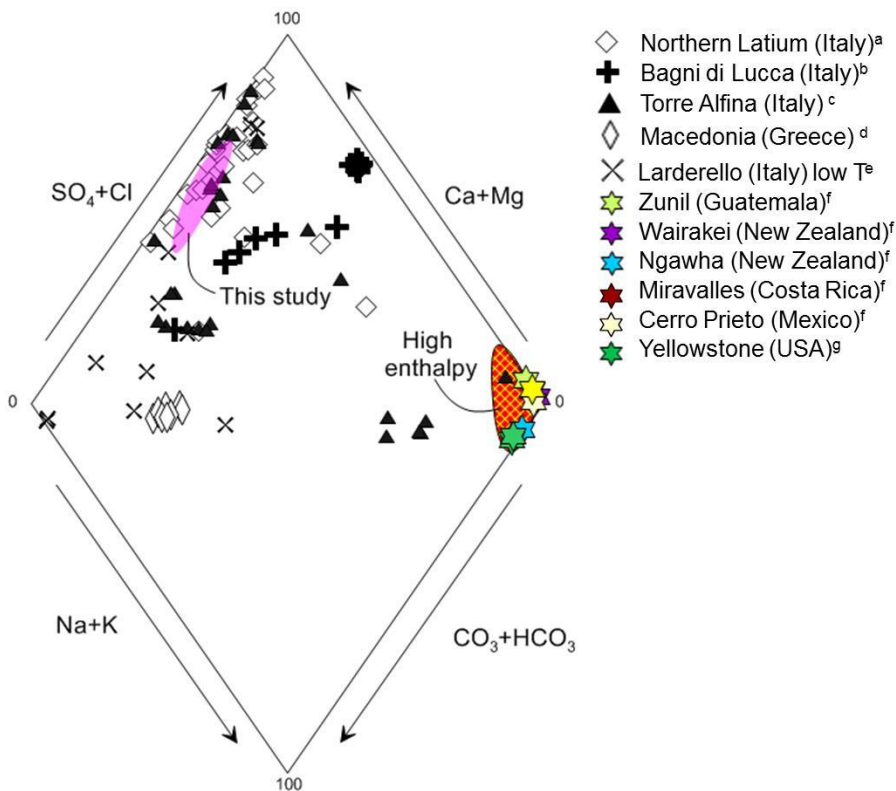




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Figure 5. Plot of  $(\text{Na}+\text{K})/\text{HCO}_3^-$  versus  $(\text{Ca}+\text{Mg})/\text{HCO}_3^-$ . For details see text



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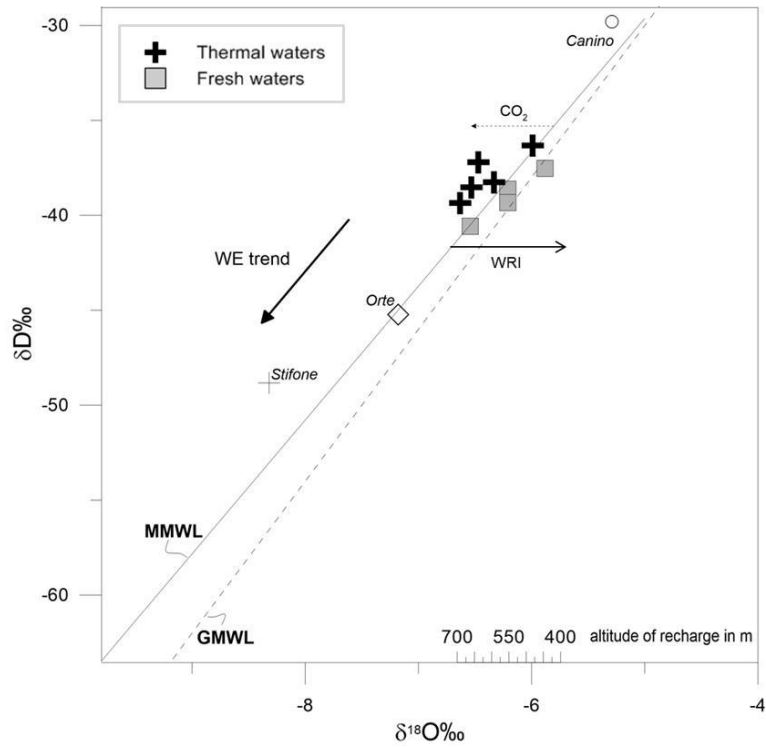
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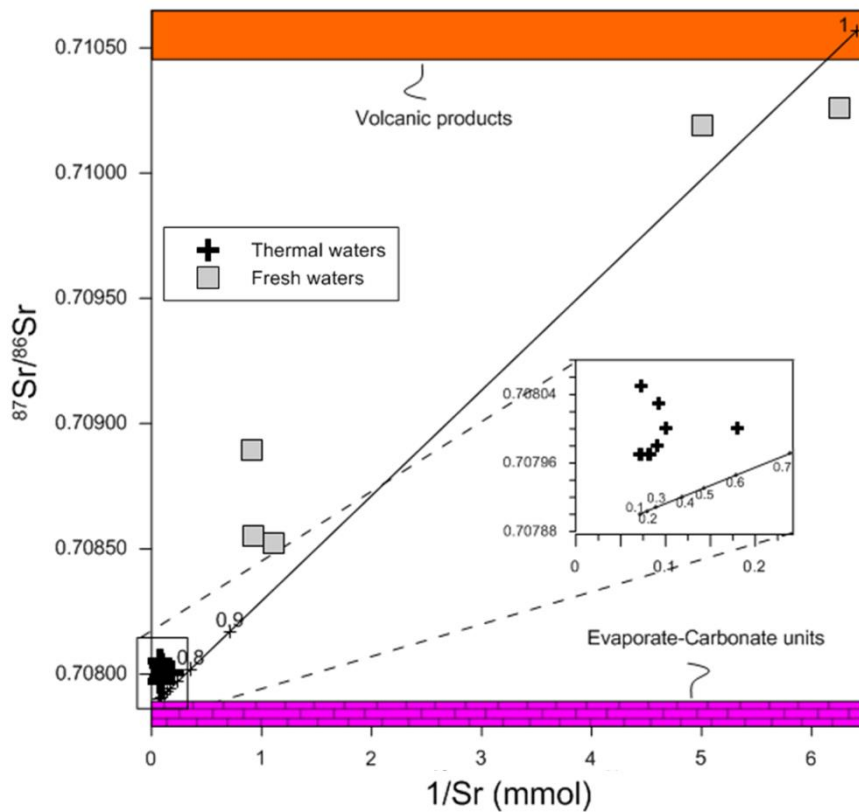
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Figure 6. Composition (Equivalent) of thermal waters from different geothermal systems. The colored star symbols represent the water with  $T > 100^\circ\text{C}$ . a- Minissale et al., 2002; b- Boschetti et al., 2005; c- Duchi et al., 1987; d- Dotsika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



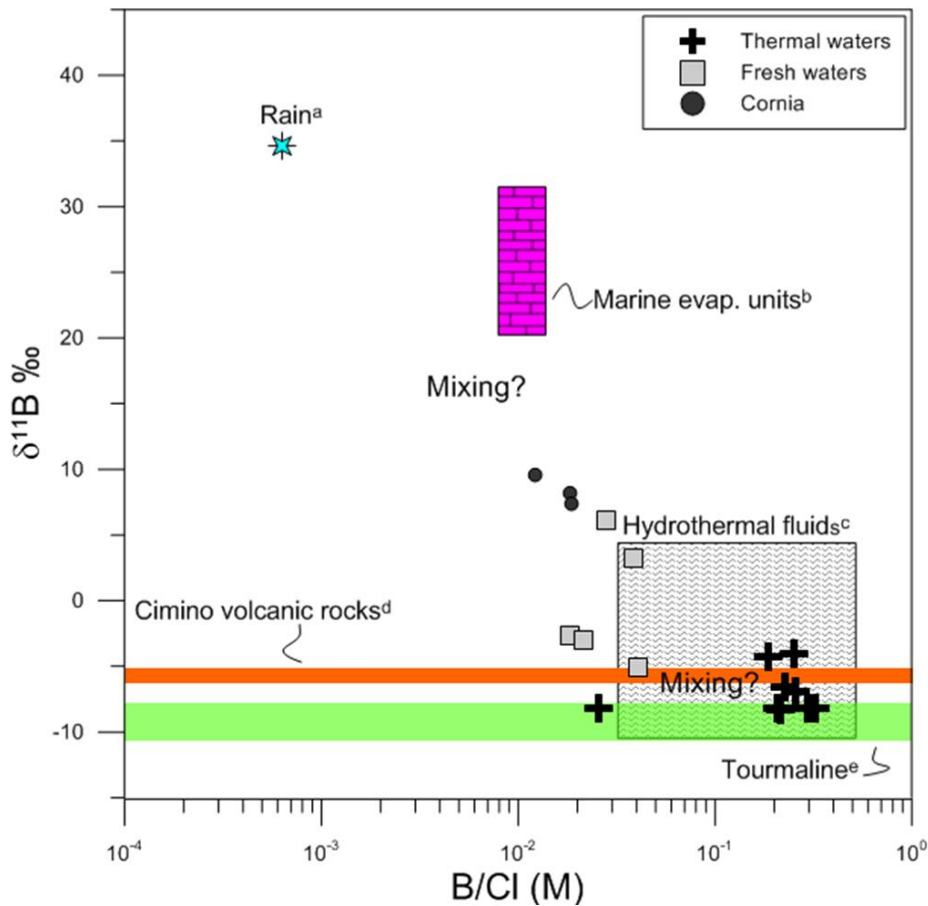
520  
 521 Figure 7. Water stable isotopes of the Cimino-Vico groundwater compared to the Global Meteoric  
 522 Water Line (GMWL) (Craig, 1961), the Mediterranean Meteoric Water Line (MMWL) (Longinelli  
 523 and Selmo, 2003) and other springs from Central Italy (Minissale, 2004). The black arrow indicates  
 524 the geographical trend from West to East. WRI - Water-Rock Interaction.

525



526  
 527 Figure 8.  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$  in the Cimino-Vico groundwater. The solid line is the calculated  
 528 theoretical mixing line between the volcanic shallow aquifer end member and the evaporite-

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



532  
 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).

539 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 <sub>3</sub> mg/L	Cl mg/L	SO <sub>4</sub> mg/L	SiO <sub>2</sub> mg/L	Sr mg/L	B mg/L	δ <sup>18</sup> O ‰	δD ‰	<sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>11</sup> 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