GEOCHEMICAL CONDITIONS AND ENVIRONMENTAL POLLUTION FROM HYDROTHERMAL WATERS OF THE ANTHEMOUS BASIN, THESSALONIKI DISTRICT, N. GREECE

M.K. NIMFOPoulos1, S.A. HADJISPYROU2, D.A. POLYA3, K.M. MICHAILIDIS4, G. TRONTSIOS4

ABSTRACT

The Anthemous basin of the Stip Axios belt, is a graben covered by Miocene-Pliocene, Pleistocene and Holocene sediments. Hydrothermal springs in the graben margins, discharge through WNW-ESE faults and deposit metalliferous (rich in As, Fe, REE, Ti, Cu, Zr, Rb, Ba, Sr, Li and Au) sediment and travertine (enriched in As, Fe, Ba and P) at their aprons. Spring waters have T 23-28ºC, pH 6.2-7.3, Eh -0.21 to -0.88 mV, E.C. 7.9-10.9 mS.cm⁻¹, TDS up to 5850 ppm and H₂S (60-70 vol%), CH₄ (0-30 vol%) and CO₂ (0-20 vol%) in the gas phase. They are saturated in H₂S, Na, K, Cl, F, Br, B and HCO₃⁻, enriched in pollutants (NO₂-, As, Mn), and Si, Li and depleted in Fe, Cu, Zn and other metals due to prior sulphide deposition. The spring waters have an alkali-chloride-bicarbonate composition.

KEYWORDS: Anthemous, hydrothermal, water, travertine, geochemistry, pollution

I. INTRODUCTION AND GEOLOGICAL SETTING

The Anthemous basin is located some 15 km SE of the Thessaloniki town (latitude 40°30', longitude 23°00') and encloses the Anthemous river and the villages Thermi, Souroti, Agia Paraskevi, besides those of Tagarades, Vasilika, Monopigado, Lakkia, Nea Redestos and Triadi (Fig. 1) and extends SE up to Chalkidiki district (Vavdos village). The former areas contain natural springs which have been used for curative purposes or for water bottling in the past 30 years period (Minissale et al., 1989).

The research area geotectonically belongs to the Stip Axios belt. The Anthemous Neogene-Quaternary basin formed over a graben with a NW-SE alignment and overlies Mesozoic metamorphic rocks, gabbroic intrusive bodies, ultrabasic rocks and a Late Jurassic limestone, which forms a considerable hydrogeothermal reservoir. The basin is dominated by Holocene (loose sediments: grit), Pleistocene (terrace, fanglomerates) and Late Miocene-Pliocene, 500-600 m thick terrestrial to marine sediments (conglomerates, red clays, sandstones, marls, clayey limestones of terrestrial, fluvial or lacustrine origin, travertine and sandstones-marls. The faulting of the basin strikes N-S, NE-SW and WNW-ESE (IGME, 1978; Shterev and Meladiotis, 1993).

The studied geothermal springs (T 23-28°C) eject through chemical sediments of travertine composition and are closely related to the active WNW-ESE trending faults. In the spring pool of Agia Paraskevi, a black metalliferous mud has precipitated containing abundant frambooidal pyrite and minor chalcopyrite (Michailidis et al., 2000).

The aim of this paper is to determine the geochemical conditions which have prevailed during hydrothermal activity and how these affected the quality of spring and groundwaters by enriching them in pollutants and other elements.

II. SAMPLING AND ANALYSIS

Over 5 metalliferous sediment (ore mud), 20 travertine sediment samples and 20 geothermal water samples (including dissolved gases) from 5 established sites (area of Agia Paraskevi to Souroti) were collected in different seasons in order

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Fig. 1. Geological setting of the Anthemous basin study area.
to reveal any significant seasonal variations in the spring water composition. In addition, more than 30 water samples from basinal irrigation boreholes were collected from the center of the basin (Holocene deposits in the area enclosed by Tagarades, Souroti, Nea Redestos and Lakkia; Fig. 1) in order to compare geothermal water composition with that of irrigation water from the basin.

Thin sections and XRD diagrams were made of the chemical sediments in order to normalize their chemical composition with that of the contained minerals. Water and chemical sediment samples were analyzed by Atomic Absorption Spectrophotometry-Graphite Furnace (AAS-GF) and High Performance liquid chromatography-Ion chromatography (HPLC-IC), the dissolved gases in hydrothermal waters by Gas Chromatography-Thermal Conductivity Detection (GC-TCD), the chemical metalliferous sediment by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and the quantitative valency determination of As in the hydrothermal waters by the new method of Ion Chromatography-ICP-Hexapole Collision Cell-Mass Spectrometry (IC-ICP-HEX-MS) (Polya et al., 2002). Temperature, pH, electric conductivity, as well as Ca\(^{2+}\), HCO\(_3\)\(^{-}\), NH\(_4\)\(^{+}\) and SiO\(_2\) were determined in the field, since these chemical species may undergo precipitation (calcite, amorphous silica), or oxidation in the case of ammonium. Besides field analysis, the above parameters and elements were re-analyzed in the lab to check possible changes during storage.

III. RESULTS

III.A. METALLIFEROUS SEDIMENT

The metalliferous sediment (Table 1) from the bottom of the spring pool contains sulphides (framboidal pyrite, chalcopyrite) and actually represents a chemical-clastic material containing skeletal crystals of calcite, quartz, feldspar and mica. It is chemically enriched in Si (up to 23.23 wt%), Ca (up to 10.21 wt%), Al (up to 6.89 wt%) and Fe (up to 3.95 wt%). Fe and As (up to 160 ppm) are mainly contained in pyrite. Significant contents of Zr (up to 174 ppm), Cs (up to 37 ppm), Rb (up to 78 ppm), a series of other metals (e.g. Hf, Th) and Rare Earth Elements (REE) also occur.

<table>
<thead>
<tr>
<th>TABLE 1. REPRESENTATIVE CHEMICAL ANALYSES OF THE METALLIFEROUS SEDIMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major elements (wt%)</strong></td>
</tr>
<tr>
<td>n=5  SiO(_2)  Al(_2)O(_3)  CaO  FeO  Fe(_2)O(_3)  Na(_2)O  K(_2)O  TiO(_2)  MgO  MnO  P(_2)O(_5)  LOI</td>
</tr>
<tr>
<td>mean 49.19  11.87  13.36  1.18  3.94  1.76  1.61  0.61  0.91  0.05  0.72  13.83</td>
</tr>
<tr>
<td>min  48.93  10.50  11.80  1.22  3.74  1.62  1.44  0.49  0.83  0.04  0.11  11.64</td>
</tr>
<tr>
<td>max  49.71  13.02  14.29  1.31  4.19  1.83  1.72  0.67  0.98  0.05  1.05  15.65</td>
</tr>
<tr>
<td><strong>Trace elements (ppm)</strong></td>
</tr>
<tr>
<td>n=5  As  Ba  Sr  Zr  Cr  Ni  Cu  Pb  Zn  Rb  Ce  Nd  La  Sc  Cs  Th  V</td>
</tr>
<tr>
<td>mean  147  916  329  168  82  53  35  17  46  51  56  30  28  17  20  10  25</td>
</tr>
<tr>
<td>min  140  358  274  162  35  24  17  13  20  7  45  20  22  10  3  8  3</td>
</tr>
<tr>
<td>max  160  998  384  174  135  99  68  24  76  78  66  40  35  25  37  15  66</td>
</tr>
</tbody>
</table>

Note: Also found Au=195 ppb), Co(mean 13 ppm), Li(mean 12 ppm), Y=31 ppm), Hf=4 ppm), U=2 ppm), W=5 ppm), Sm=7 ppm) and Be=3 ppm).

Det. limits: major elements=0.01 wt%; trace elements=0.1-1 ppm, Pb-Rb=2 ppm

III.B. Travertine chemical sediments

Travertine is mainly composed of variably crystalline calcite, aragonite, amorphous silica and Fe-oxides in variable proportions, depending on sample location. Representative analyses of the travertine chemical sediment (Table 2)
reveal variable Si, directly related to Al, reflecting the presence of aluminosilicates (kaolinite) and silica against calcite. Ca is negatively correlated to Fe, reflecting the presence of amorphous Fe-oxides instead of CaCO₃. The presence of higher Fe-contents in travertine rather than in the metalliferous sediment is somewhat erroneous. However, this can easily be explained by the presence of abundant amorphous Fe-oxides (determined by a background rise at ~10-18°2θ in the XRD patterns) in the travertine samples. Thus, in contrast to the metalliferous sediment, the main Fe-content in travertine is in the oxidised form (Fe³⁺) and the total Fe-oxide (FeO+Fe₂O₃) content can be as high as 19.45 wt%. Na, K, P, Li and base metal contents are directly related to silica, while As shows a preference to the carbonate phase.

### TABLE 2. REPRESENTATIVE CHEMICAL ANALYSES OF THE TRAVERTINE

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MgO</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>LOI</th>
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<tr>
<td>mean</td>
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<td>0.73</td>
<td>45.07</td>
<td>0.58</td>
<td>5.96</td>
<td>0.35</td>
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<td>0.06</td>
<td>1.09</td>
<td>39.45</td>
</tr>
<tr>
<td>min</td>
<td>0.65</td>
<td>0.00</td>
<td>28.00</td>
<td>0.14</td>
<td>1.13</td>
<td>0.03</td>
<td>0.01</td>
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<td>0.18</td>
<td>0.03</td>
<td>0.23</td>
<td>34.85</td>
</tr>
<tr>
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<td>15.98</td>
<td>1.15</td>
<td>53.40</td>
<td>1.36</td>
<td>18.08</td>
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<td>0.25</td>
<td>bd</td>
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<td>0.10</td>
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<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Li</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Rb</th>
<th>Co</th>
<th>V</th>
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<td>6</td>
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<td>21</td>
<td>14</td>
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<td>1</td>
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<tr>
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<td>5</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
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<td>10</td>
<td>98</td>
<td>54</td>
<td>6</td>
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</table>

*Note: bd=below detection*

**Det. limits:** major elements=0.01 wt%; trace elements=0.1-1 ppm, Pb-Rb=2 ppm

### III.C. SPRING WATER CHARACTERISTICS

Spring waters (Table 3) have T 23-28°C, relatively low pH (6.2-7.3) and Eh (-21 to -88 mV), high E.C. (7.9 to 10.9 mS.cm⁻¹) and TDS (up to 5850 ppm), characteristic smell of hydrogen sulphide, and contain H₂S (60 to 70 vol.%), CH₄ (0 to 30 vol.%) and CO₂ (0 to 20 vol.%) in the gas phase. They are saturated in Na (0.11 to 0.16 wt%), K (58 to 88 ppm), Cl (1507 to 2445 ppm), F (0.7 to 2.0 ppm), Br (60 to 480 ppb), NO₂ (up to 24.4 ppm), B (69 to 105 ppm) and HCO₃ (805 to 1037 ppm) which are several times above the E.U. drinking limits of potable water (HGN, 2001). They are also enriched in toxic elements, such as As (up to 50 ppb) and Mn (up to 295 ppb), Si (up to 27 ppm SiO₂) and Li (up to 5 ppm), while, in contrast to irrigation water (Table 4), Fe, Cu, Zn, and the other metals have probably been removed by the process of sulphide precipitation (Michailidis et al., 2000). Al was also detected.

During the dry season, the Na, Cl, F, As, Mn and NO₂ contents increase to maximum levels in the spring waters (Table 3), thus causing further degradation of their quality and environmental pollution to the surrounding ecosystem. This shows that there may be an important influx of shallow meteoric water in the springs in the wet period by a process of water mixing in the fault zones near the surface and dilution of the spring water. In order to study this in more detail, water samples from a geothermal borehole (>500 m) were collected and analysed. They have lower pH (6.02-7.29), and Fe (3-12 ppb), Mn (10-15 ppb), Cu (9-14 ppb), Zn (up to 21 ppb), Al (<5 ppb), SO₄ (<0.1 ppm), F (0.22-0.60 ppm) and NO₃ (<0.1-3.0 ppm) contents, but higher T (32°C), E.C. (10.5-11.0 mS.cm⁻¹), TDS (0.6 to 1.17 wt%), and Ca (161-533 ppm), Mg (85-135 ppm), Na (2930-3320 ppm), K (175-200 ppm), HCO₃ (1635-3315 ppm), Cl (4201-4963 ppm), Br (250-300 ppb), NO₂ (24.5-28 ppm), NH₄ (0.36-16.00 ppm), As (60-85 ppb), Li (4.2-8.5 ppm) and SiO₂ (95-110 ppm) contents. A similar geochemistry has been observed in
active geothermal fields elsewhere (Karpov and Naboko, 1990). The high NO\textsubscript{2} contents reflect either the oxidation of the emitted N\textsubscript{2} gas from the hot water (Karpov and Naboko, 1990) or high concentrations of organic substances. Spring water and borehole water composition is alkali-chloride-bicarbonate. The composition of borehole water strongly resembles to that of an undiluted hypogene (hydrothermal) fluid possibly heated by the geothermal field of the Monopigado granodiorite (Michard et al., 1998) or by thermal gradient (3°C/100 m). It probably originated from the Late Jurassic limestone (Fig. 1) and the underlying ultrabasic rocks (Traganos and Bibou, 1989) and had previously deposited its metal load at depth. On the contrary, the composition of hot spring water designates a process of element scavenging during its ascending course and infiltration through the overlying host rocks (sandy conglomerate-red clays-sandstones-marls).

### TABLE 3. REPRESENTATIVE CHEMICAL ANALYSES OF THERMAL SPRING AND BOREHOLE WATERS

#### SPRING

<table>
<thead>
<tr>
<th>n=20</th>
<th>T °C</th>
<th>pH units</th>
<th>Eh mV</th>
<th>T.DS ppm</th>
<th>Ca ppm</th>
<th>Mg ppm</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>Σ\textsubscript{ca+} ppm</th>
<th>T.H ppm</th>
<th>Σ\textsubscript{anion} ppm</th>
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</thead>
<tbody>
<tr>
<td>mean</td>
<td>26</td>
<td>7.15</td>
<td>-55</td>
<td>8900</td>
<td>124</td>
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<td>1314</td>
<td>74</td>
<td>1546</td>
<td>423</td>
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<tr>
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<td>67</td>
<td>24</td>
<td>1084</td>
<td>58</td>
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<td>290</td>
<td>2747</td>
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<tr>
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<td>7.30</td>
<td>-88</td>
<td>10900</td>
<td>160</td>
<td>49</td>
<td>1606</td>
<td>88</td>
<td>1860</td>
<td>532</td>
<td>3271</td>
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#### BOREHOLE

<table>
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<tr>
<th>n=5</th>
<th>T °C</th>
<th>pH units</th>
<th>Eh mV</th>
<th>T.DS ppm</th>
<th>Ca ppm</th>
<th>Mg ppm</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>Σ\textsubscript{ca+} ppm</th>
<th>T.H ppm</th>
<th>Σ\textsubscript{anion} ppm</th>
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<tbody>
<tr>
<td>mean</td>
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<td>6.60</td>
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<td>3120</td>
<td>190</td>
<td>3767</td>
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<tr>
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#### SPRING

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<th>HCO\textsubscript{3} ppm</th>
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<th>SO\textsubscript{4} ppm</th>
<th>NO\textsubscript{2} ppm</th>
<th>NO\textsubscript{3} ppm</th>
<th>F ppm</th>
<th>NH\textsubscript{4} ppm</th>
<th>PO\textsubscript{4} ppm</th>
<th>B ppm</th>
<th>SiO\textsubscript{2} ppm</th>
<th>Br ppm</th>
<th>Mn ppm</th>
<th>Fe ppm</th>
<th>As ppm</th>
<th>Cu ppm</th>
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<tr>
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#### BOREHOLE

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<th>Cl ppm</th>
<th>SO\textsubscript{4} ppm</th>
<th>NO\textsubscript{2} ppm</th>
<th>NO\textsubscript{3} ppm</th>
<th>F ppm</th>
<th>NH\textsubscript{4} ppm</th>
<th>PO\textsubscript{4} ppm</th>
<th>B ppm</th>
<th>SiO\textsubscript{2} ppm</th>
<th>Br ppm</th>
<th>Mn ppm</th>
<th>Fe ppm</th>
<th>As ppm</th>
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<td>102</td>
<td>280</td>
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<td>min</td>
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</table>

**Note:** bd=below detection, tr.=traces of element were detected. Al and Zn are also present. Al is present in spring waters only.

**Det. limits:** Cl, SO\textsubscript{4}, NO\textsubscript{2} = 10 ppb; all other elements = 1 ppb.
III.D. Irrigation water characteristics

Irrigation waters were sampled from different depths (80 to 250 m) by using farmers’ boreholes during the irrigation period. These waters have higher pH (up to 8.15), but much lower electric conductivity (up to 2060 mS.cm⁻¹). They generally contain much less Na, K, B, Cl and NO₃, less Ca, HCO₃, F, Mn, PO₄ and SiO₂ but more SO₄ and Fe (Table 4). This has been probably caused by mixing and dilution of the ascending hydrothermal water with descending meteoric fresh water in the fault zones at phreatic levels. On the other hand, SO₄ and Fe contents are higher because no prior sulphide precipitation took place from the meteoric irrigation water, in contrast to spring water.

IV. DISCUSSION

The borehole water is probably the initial hydrothermal fluid which originates through the process of descending meteoric waters from fracture zones in the, 500-800 m thick, Late Jurassic Katsika limestone formation and the underlying pre-Alpine ultrabasic metamorphic basement (Jackelen et al., 1986; Traganos and Bibou, 1989). In the Anthemous basin, this process takes place at depths below 1-1.5 km, while between 0.5 and 1 km depth, a 200-600 m thick basal Miocene sandy conglomerate exists and may have acted as a reservoir containing huge volumes of geothermal water with T 30-60°C (Fytikas and Taktikos, 1988).

### TABLE 4. REPRESENTATIVE CHEMICAL ANALYSES OF IRRIGATION GROUNDWATERS

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<tr>
<th>n=30 unit</th>
<th>T °C</th>
<th>pH units</th>
<th>Eh mV</th>
<th>E.C. µS/cm</th>
<th>TDS ppm</th>
<th>Ca ppm</th>
<th>Mg ppm</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>Σ cat. ppm</th>
<th>T.H ppm</th>
<th>Σ anion ppm</th>
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<tr>
<td>mean</td>
<td>18</td>
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<td>80</td>
<td>710</td>
<td>380</td>
<td>75</td>
<td>43</td>
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<td>184</td>
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<td>531</td>
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<tr>
<td>min</td>
<td>16</td>
<td>7.75</td>
<td>60</td>
<td>440</td>
<td>275</td>
<td>24</td>
<td>11</td>
<td>15</td>
<td>1</td>
<td>80</td>
<td>260</td>
<td>433</td>
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<tr>
<td>max</td>
<td>19</td>
<td>8.15</td>
<td>110</td>
<td>1640</td>
<td>460</td>
<td>127</td>
<td>91</td>
<td>122</td>
<td>6</td>
<td>230</td>
<td>440</td>
<td>756</td>
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<table>
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<tr>
<th>n=30 unit</th>
<th>HCO₃ ppm</th>
<th>Cl ppm</th>
<th>SO₄ ppm</th>
<th>NO₃ ppm</th>
<th>NO₂ ppm</th>
<th>F ppm</th>
<th>NH₄ ppm</th>
<th>PO₄ ppm</th>
<th>B ppm</th>
<th>SiO₂ ppm</th>
<th>Al ppm</th>
<th>Mn ppm</th>
<th>Fe ppm</th>
<th>As ppm</th>
<th>Zn ppm</th>
<th>Sb ppm</th>
<th>Li ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>384</td>
<td>82</td>
<td>58</td>
<td>7</td>
<td>0.01</td>
<td>0.4</td>
<td>0.05</td>
<td>0.50</td>
<td>1</td>
<td>21</td>
<td>40</td>
<td>100</td>
<td>290</td>
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<tr>
<td>min</td>
<td>222</td>
<td>23</td>
<td>30</td>
<td>1 tr.</td>
<td>0.2 tr.</td>
<td>0.2 tr.</td>
<td>0.16 tr.</td>
<td>0.6 tr.</td>
<td>tr.</td>
<td>6 tr.</td>
<td>tr.</td>
<td>10 tr.</td>
<td>18 tr.</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
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<tr>
<td>max</td>
<td>600</td>
<td>152</td>
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<td>0.7</td>
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<td>1.85</td>
<td>4</td>
<td>28</td>
<td>300</td>
<td>400</td>
<td>830</td>
<td>tr.</td>
<td>tr.</td>
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</table>

Note: tr.=traces of element. The element I is also present (50-820 ppb).
Det. limits: Cl, SO₄, NO₃, and NO₂ = 10 ppb; all other elements = 1 ppb.

This clastic rock and the Late Jurassic limestone have probably controlled the composition of the hosted hydrothermal water.

In places where active faults cross these reservoirs, at WNW-ESE direction (borders of the tectonic depression), an ascending course of the reservoir hot water begins and hot springs may discharge at surface. Before reaching the surface, the hot water appears to deposit a large part of its metallic content, probably along fracture zones at depth, as it is evident by its very low sulphate content. Spring waters contain significant gas concentrations such as H₂S, CH₄ and CO₂. Hydrogen sulphide originates probably from organic matter reduction of sulphate contained in the salty connate waters, which flooded the carbonate Jurassic reservoir and the overlying Neogene clayey sediments during the Neogene marine transgression (Shterev and Meladiotis, 1993). The elevated values of nitrites in spring waters (Table 3) also suggest the organic matter sulphate reduction. Methane and carbon dioxide are the reduced and oxidised form of carbon, which predominates in the carbonate reservoir. At pH >6, CO₂ favours the enrichment of spring waters in bicarbonates by which Ca, Na, Mg and Fe, Mn, Zn, Pb, Cu and other elements are transported. This has also been observed in the karst environment of Kato Nevrokopi, where the mobilities of the above metals have also been studied (Nimfopoulos, 1988). The presence of CH₄ and CO₂ in
the spring water indicates favourable conditions for base metal-Au deposition (Naden and Shepherd, 1989), as it is evident from the metalliferous sediment.

In the course of approaching the surface, the reservoir hot water is restricted to follow active faults at the margins of the basin (Fig. 2). Thus, it interacts with the Miocene-Pliocene clayey sediments, dissolving Al, Fe, Mn and other metals, which brings to the surface (hot springs). At the same time, a
Anthropogenic modern hydrothermal system.

Fig. 2. Evolutionary sketch model for the development of the

\[ + \]

Ophiolite

\[ + \]

Mesozoic

\[ + \]

(140 Ma)

Granodiorite

\[ + \]

Upper Jurassic

Limestone

\[ + \]

Miocene

Basal sandy conglomerate

\[ + \]

Miocene-Pliocene

Clayey sediments

\[ + \]

Thermal spring

Borehole

\[ + \]

Fault

\[ + \]

\[ \rightarrow \]

Decrease in NO\textsubscript{2}

\[ \rightarrow \]

CO\textsubscript{2}, CH\textsubscript{4}

\[ \rightarrow \]

H\textsubscript{2}S, CH\textsubscript{4}

\[ \rightarrow \]

Enrichment in Al, Fe, etc.

\[ \rightarrow \]

Enrichment

\[ \rightarrow \]

Water

\[ \rightarrow \]

Meteoritic water

\[ \rightarrow \]

Descending meteoric water

through fracture zones

\[ \rightarrow \]

Water

\[ \rightarrow \]

SAT enrichment

Water

\[ \rightarrow \]

HCO\textsubscript{3} enrichment

\[ \rightarrow \]

T \textsubscript{60} \textdegree C

\[ \rightarrow \]

Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}

Rich in Na

\[ \rightarrow \]

Hydrothermal

\[ \rightarrow \]

Micodidal

\[ \rightarrow \]

SO\textsubscript{4}, CO\textsubscript{2}, H\textsubscript{2}S, CH\textsubscript{4}

\[ \rightarrow \]

Reduction of
process of spring water dilution begins to take place at the phreatic level by progressive mixing with shallow meteoric water, cooling, and oxidation of part of the contained hydrogen sulphide to sulphate. This explains the sulphate enrichment of irrigation water contrary to the hydrothermal borehole water.

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V. REFERENCES