

**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 23-28°C, 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 reasearch 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 framboidal 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 srpring 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

1:IGME, Division of Geochemistry and Environment, 1 Fragon street, 546-26 Thessaloniki, Greece

2:Aristotle University, Chemical Engineering Department, Laboratory of Inorganic Chemistry, 540-06 Thessaloniki, Greece

3:The Victoria University of Manchester, Earth Sciences Department, Manchester M13 9PL, England, U.K.

4:Aristotle University, School of Geology, Department of Mineralogy-Petrology-Economic Geology, 540-06 Thessaloniki, Greece

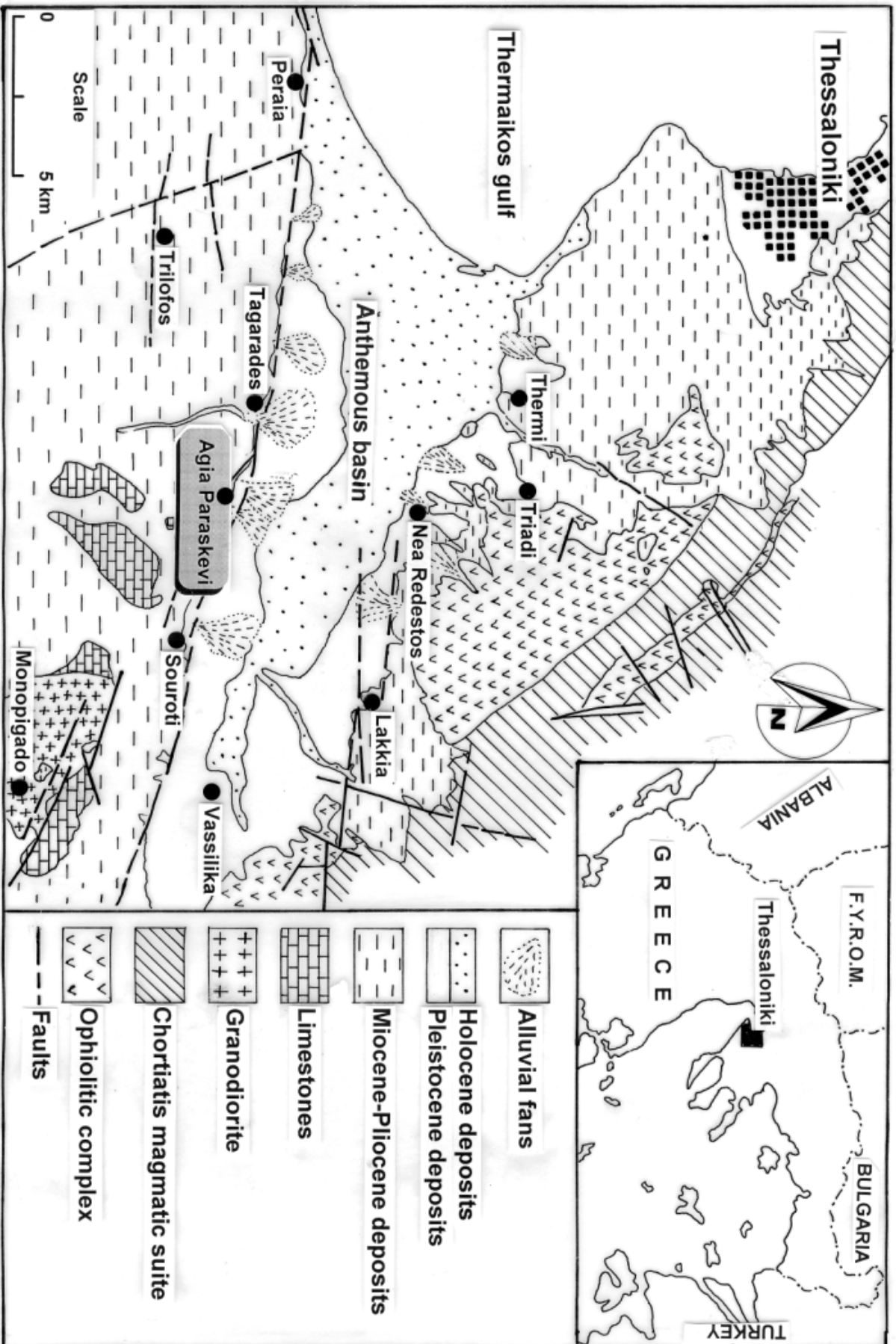


Fig. 1. Geological setting of the Anthemous basin study area.

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 1. REPRESENTATIVE CHEMICAL ANALYSES OF THE METALLIFEROUS SEDIMENT

Major elements (wt%)												
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
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
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
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

Trace elements (ppm)																	
n=5	As	Ba	Sr	Zr	Cr	Ni	Cu	Pb	Zn	Rb	Ce	Nd	La	Sc	Cs	Th	V
mean	147	916	329	168	82	53	35	17	46	51	56	30	28	17	20	10	25
min	140	358	274	162	35	24	17	13	20	7	45	20	22	10	3	8	3
max	160	998	384	174	135	99	68	24	76	78	66	40	35	25	37	15	66

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

Major elements (wt%)												
n=20	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
mean	5.79	0.73	45.07	0.58	5.96	0.35	0.12	bd	0.26	0.06	1.09	39.45
min	0.65	0.00	28.00	0.14	1.13	0.03	0.01	bd	0.18	0.03	0.23	34.85
max	15.98	1.15	53.40	1.36	18.08	0.65	0.25	bd	0.38	0.10	3.27	43.00
Trace elements (ppm)												
n=20	As	Ba	Li	Cr	Ni	Cu	Pb	Zn	Rb	Co	V	Sb
mean	235	1000	18	13	7	6	8	21	14	2	2	1
min	180	50	5	8	2	4	6	5	2	bd	bd	bd
max	270	2000	47	19	15	12	10	98	54	6	5	4

Note: bd=below detection
Det. limits: major elements=0.01 wt%; trace elements=0.1-1 ppm, Pb=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 NO₂ contents reflect either the oxidation of the emitted N₂ 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												
n=20 unit	T °C	pH pH units	Eh mV	E.C. µS/cm	TDS ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Σ _{cat.} ppm	T.H ppm	Σ _{anion.} ppm
mean	26	7.15	-55	8900	5325	124	34	1314	74	1546	423	3026
min	23	6.20	-21	7900	4760	67	24	1084	58	1324	290	2747
max	28	7.30	-88	10900	5850	160	49	1606	88	1860	532	3271

BOREHOLE												
n=5 unit	T °C	pH pH units	Eh mV	E.C. µS/cm	TDS ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Σ _{cat.} ppm	T.H ppm	Σ _{anion.} ppm
mean	32	6.60	-91	10750	8800	347	110	3120	190	3767	820	7081
min	31	6.02	-82	10500	6000	161	85	2930	175	3500	751	6600
max	32	7.29	-99	11000	11660	533	135	3320	200	3850	850	7545

SPRING																	
n=20 unit	HCO ₃ ppm	Cl ppm	SO ₄ ppm	NO ₃ ppm	NO ₂ ppm	F ppm	NH ₄ ppm	PO ₄ ppm	B ppm	SiO ₂ ppm	Br ppb	Mn ppb	Fe ppb	As ppb	Cu ppb	Sb ppb	Li ppm
mean	956	2055	1.4	14	12.1	1.2	.17	.70	86	26	168	119	138	36	15	2	2
min	805	1507	bd	8	tr.	0.7	.11	.42	69	24	60	10	20	15	10	1	0
max	1037	2445	1.9	21	24.4	2.0	.21	.99	105	27	480	295	450	50	25	5	5

BOREHOLE																	
n=5 unit	HCO ₃ ppm	Cl ppm	SO ₄ ppm	NO ₃ ppm	NO ₂ ppm	F ppm	NH ₄ ppm	PO ₄ ppm	B ppm	SiO ₂ ppm	Br ppb	Mn ppb	Fe ppb	As ppb	Cu ppb	Sb ppb	Li ppm
mean	2500	4580	bd	1	26.3	0.5	8.1	.80	115	102	280	13	10	70	11	2	7
min	1635	4201	bd	bd	24.5	0.2	0.4	.60	72	95	250	10	3	60	9	1	4
max	3315	4963	bd	3	28.1	0.6	16.0	.90	160	110	300	15	12	85	14	5	9

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, SO₄, NO₃ and NO₂ = 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 NO₂, 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).

n=30 unit	T °C	pH pH units	Eh mV	E.C. µS/cm	TDS ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Σ _{cat.} ppm	T.H ppm	Σ _{anion} ppm
mean	18	7.88	80	710	380	75	43	63	3	184	350	531
min	16	7.75	60	440	275	24	11	15	1	80	260	433
max	19	8.15	110	1640	460	127	91	122	6	230	440	756

n=30 unit	HCO ₃ ppm	Cl ppm	SO ₄ ppm	NO ₃ ppm	NO ₂ ppm	F ppm	NH ₄ ppm	PO ₄ ppm	B ppm	SiO ₂ ppm	Al ppb	Mn ppb	Fe ppb	As ppb	Zn ppb	Sb ppb	Li ppm
mean	384	82	58	7	0.01	0.4	0.05	0.50	1	21	40	100	290	tr.	180	tr.	tr
min	222	23	30	1	tr.	0.2	tr.	0.16	tr.	6	tr.	tr.	10	tr.	18	tr.	tr
max	600	152	365	20	0.02	0.7	0.35	1.85	4	28	300	400	830	tr.	900	tr.	tr

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

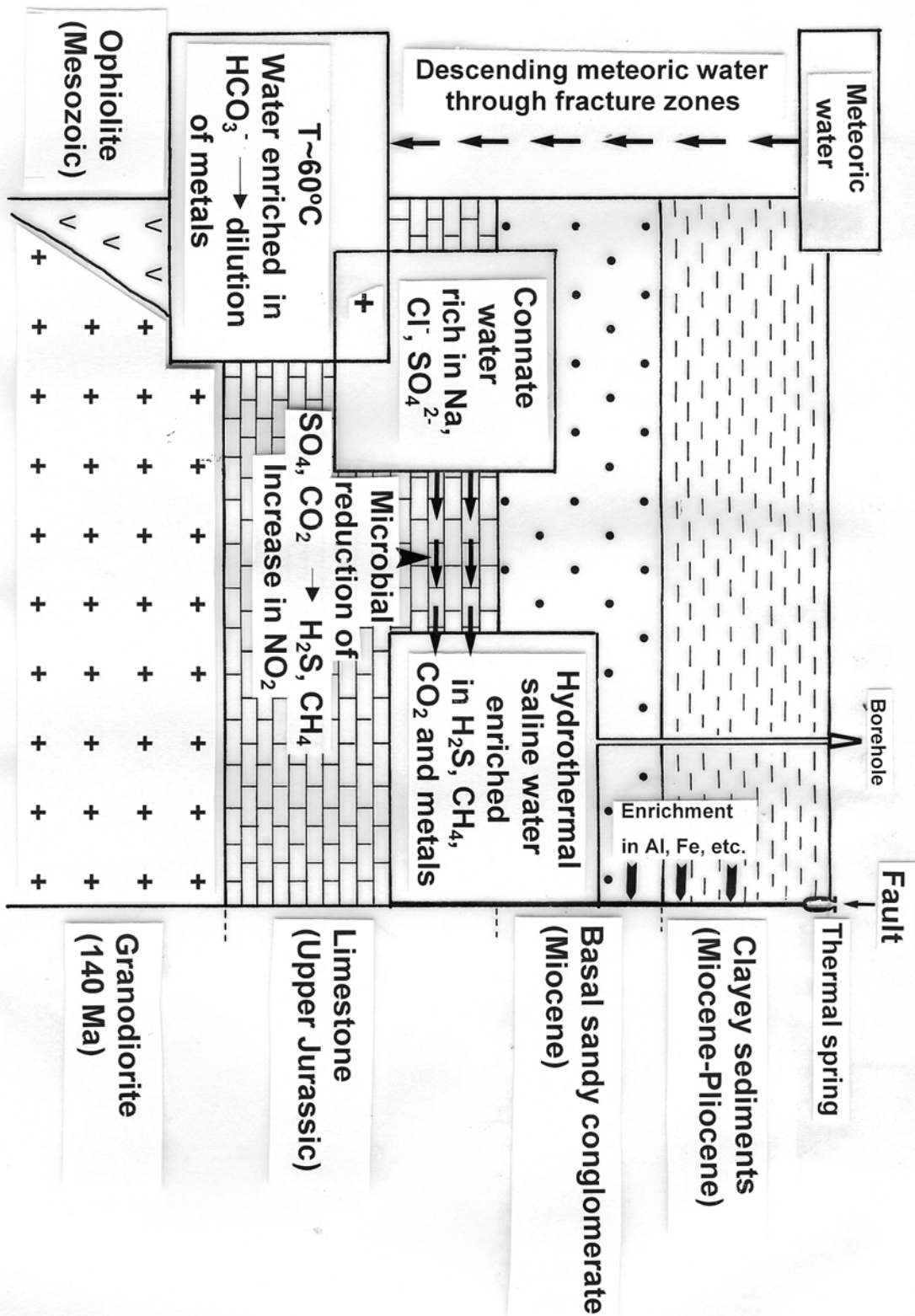


Fig. 2. Evolutionary sketch model for the development of the Anthemous modern hydrothermal system.

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.

ACKNOWLEDGEMENTS

We would like to thank the Director General of IGME for his permission to publish this paper, Professors Ananias Tsirambides and Georgios Karakaisis for assistance with the presentation and two anonymous referees of the 6th Congress of the Geographical Society of Greece for constructive criticism.

V. REFERENCES

- [1] FYTIKAS, M. and TAKTIKOS, S. (1988) Geothermal resource assessment of Greece. In HAENEL, R. and STAROSTE, E. (eds): *Atlas of the geothermal resources of the European Community*, 25-28.
- [2] HGN (2001) Quality of water for human consumption: *In accordance with the Directive 98/83/EC of the Council of the EU (3/11/1998)*. Hellenic Government Newspaper (HGN), Section 2, Sheet 892, 10865-10880.
- [3] IGME (1978) Geological map to Greece-Scale 1:50000, Sheet Vasilika.
- [4] JACKELEN, H.P., LOEHNERT, E.P. and PAPAKONSTANTINOY, A. (1986) Natural tracers in groundwaters of the western Chalkidiki Peninsula. *5th International Symposium on underground water tracing*, Athens, 59-73.
- [5] KARPOV, G.A. and NABOKO, S.I. (1990) Metal contents of recent thermal waters, mineral precipitates and hydrothermal alteration in active geothermal fields, Kamchatka. *Journal of Geochemical Exploration*, 36, 57-71.
- [6] MICHARD, A., FEINBERG, H. and MONTIGNY, R. (1998) The chalkidiki supra-ophiolitic formations, and their bearing on the Vardarian obduction process. *Bull. Geol. Soc. Of Greece*, 32(1), 59-64.
- [7] MICHAILIDIS, K.M., NIMFOPOULOS, M.K., ANAGNOSTOPOULOS, A. and HADJISPYROU, S.A. (2000) Present day frambooidal pyrite deposition from the active geothermal system in the Agia Paraskevi area, Thessaloniki, N. Greece. In PANAYIDES, I., XENOPHONTOS, C. and MALPAS, J. (eds): *Poster of the 3rd International Conference on the Geology of the Eastern Mediterranean (ICGEM)*, Geological Survey of Cyprus, 12 pp.
- [8] MINISSALE, A., DUCHI, V., KOLIOS, N. and TOTARO, G. (1989) Geochemical characteristics of Greek thermal springs. *J. Volcan. Geotherm. Research*, 39, 1-16.
- [9] NADEN, J. and SHEPHERD, T.J. (1989) The role of methane and carbon dioxide in gold deposition. *Nature*, 342, 793-795.
- [10] NIMFOPOULOS, M.K. (1988) Manganese mineralization near Kato Nevrokopi, Drama, Greece. *Ph.D. thesis, Victoria University of Manchester*, 259 pp.
- [11] POLYA, D.A., LYTHGOE, P.R., ABOU-SHAKRA, F., GAULT, A.G., BRYDIE, J.R., WEBSTER, J.G., BROWN, K.L., NIMFOPOULOS, M.K. and MICHAILIDIS, K.M. (2002) IC-ICP-MS and IC-ICP-HEX-MS determination of arsenic speciation in surface and groundwaters: Preservation and analytical issues. *Mineralogical Magazine*, 66(4), 52 pp. (In press).
- [12] SHTEREV, K. and MELADIOTIS, J. (1993) Thermomineral waters and hydrothermal resources in the western part of the Chalkidiki Peninsula. *Geol. Balcanica*, 23(6), 73-85.
- [13] TRAGANOS, G. and BIBOU, C. (1989) The present situation and the geothermal research prospects in the basin of Thessaloniki. *Tech. Chamb. Greece, Congress* (In Greek), Athens, April 1989.