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The geochemistry of Boron-rich groundwater of the Karlovassi Basin, Samos Island, Greece

Research Article

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Abstract: The upper Miocene of Karlovassi Basin, Samos Island, Greece, contain continental evaporites such as colemanite, ulexite, celestite, gypsum and thenardite. These evaporites are related with volcanic tuffs, diagenetically altered in a saline-alkaline lake environment. The aim of the present paper is to: a) define the impact of the already known and possible buried borates and other evaporites to the geochemistry of the hydrogeological system of Karlovassi Basin, and; b) to assess the correlation between surface and underground evaporite deposits considering the spatial changes in the concentrations of the examined physicochemical parameters. Fieldwork, laboratory measurements and literature data revealed elevated boron values (2136-33012 µg/L) in the central part of Karlovassi Basin. In the same area, high amounts of strontium, sodium, lithium and sulfates also occur. It is proposed that these ions originate from the leaching of evaporites and authigenic minerals such as the Sr-rich clinoptilolite and the boron-bearing potassium feldspar. Boron values are abnormally high for freshwater aquifers, and are indicative of the presence of buried evaporites in the basin with unknown significance.

Keywords: Boron • Samos Island • Karlovassi Basin • hydrogeochemistry • evaporites

1. Introduction

Boron is a non-metallic trace element that is found in the environment, naturally occurring in over 150 minerals [1]. Boron is never found in the elemental state in nature. It is among the less abundant elements in lithosphere with an average content of 10 ppm [2–5]. Boron chemistry is complex and resembles that of silicon [6]. It forms borosilicate minerals such as datolite ($CaB[OH]SiO_4$) and howlite ($Ca_2B_5SiO_9[OH]_5$), but mainly Na, Ca, Na-Ca and/or Mg-borates such as borax ($Na_2B_4O_7{\cdot}10H_2O$), colemanite ($Ca_2B_8O_{11}{\cdot}5H_2O$), ulexite ($NaCaB_5O_9{\cdot}8H_2O$), kernite ($Na_2[B_4O_6(OH)_2{\cdot}3H_2O]$), inderite ($Mg[B_3O_3(OH)_5]{\cdot}5H_2O$), szaibelyite ($Mg_2[(OH)(B_2O_4(OH))]$) and probertite ($NaCaB_5O_9{\cdot}5H_2O$) [1, 5, 7–9].

Seawater has a boron content of 4.5-5 ppm, whereas freshwater has a boron content of 0.1 ppm. In contrast, saline-alkaline lake waters have boron concentrations of several hundreds to thousands ppm [3, 7, 10–12]. Boron is present in aqueous solutions as $B(OH)^{4-}$ and undissociated boric acid (H_3BO_3) [13, 14].

Boron can be found in water systems as a result of natural or anthropogenic sources. Natural boron is derived from geothermal discharges, leaching from a large variety of rocks, or the mixing of groundwater with oil field water or connate or fossil brines [9]. Boron-rich thermal waters

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may influenced groundwater and surface waters [15, 16]. Anthropogenic boron sources include: boron-containing washing powders, municipal wastewaters, industrial residues, pesticides and fertilizers [2, 17]. Case studies in the Mediterranean Region have shown that high boron content in groundwater is mostly geogenic, related to hydrothermal or saline water resources, water–rock interaction processes and seawater invasion [14, 18, 19].

According to Watanabe [20], during the differentiation and crystallization process of a basaltic magma, boron is concentrated at the magmatic residuals. When the magmatic fluids reach the surface, they may be dissolved and led to marine or lacustrine basins. In the latter case, under arid climatic conditions boron forms borate deposits, due to strong evaporation [20–22]. In general, the borate deposits contain soluble Na and Na-Ca-borate salts [5] where they dissolute by meteoric or groundwater, while a great amount of the dissolved ions bonds to organic matter or clay minerals [23, 24]. In borate districts (i.e Western Turkey), groundwater geochemistry is significantly influenced by the dissolution of borate salts [15, 25] as can be assessed by the elevated values of boron which reach up to 391 mg/L [9, 26].

In Samos Island, borate mineral occurrences have been located in the central part of the Karlovassi Basin of the Upper Miocene age. The surface exposed borate lenses have a spongy texture due to their partial dissolution and the deposition of secondary carbonates [27]. The aim of the present paper is to define the impact of the already known and possible buried borates and other evaporites to the geochemistry of the hydrogeological system of Karlovassi Basin, and to assess the correlation between surface and underground evaporite deposits considering the spatial changes in the concentrations of the examined physico-chemical parameters.

2. Geological and hydrogeological setting

Karlovassi Basin (Figure 1) is located in the western part of Samos Island (Eastern Aegean sea, Greece) and extends with a N-S direction between latitudes 37°42′ and 37°48′ and longitudes 26°40′ and 26°45′.

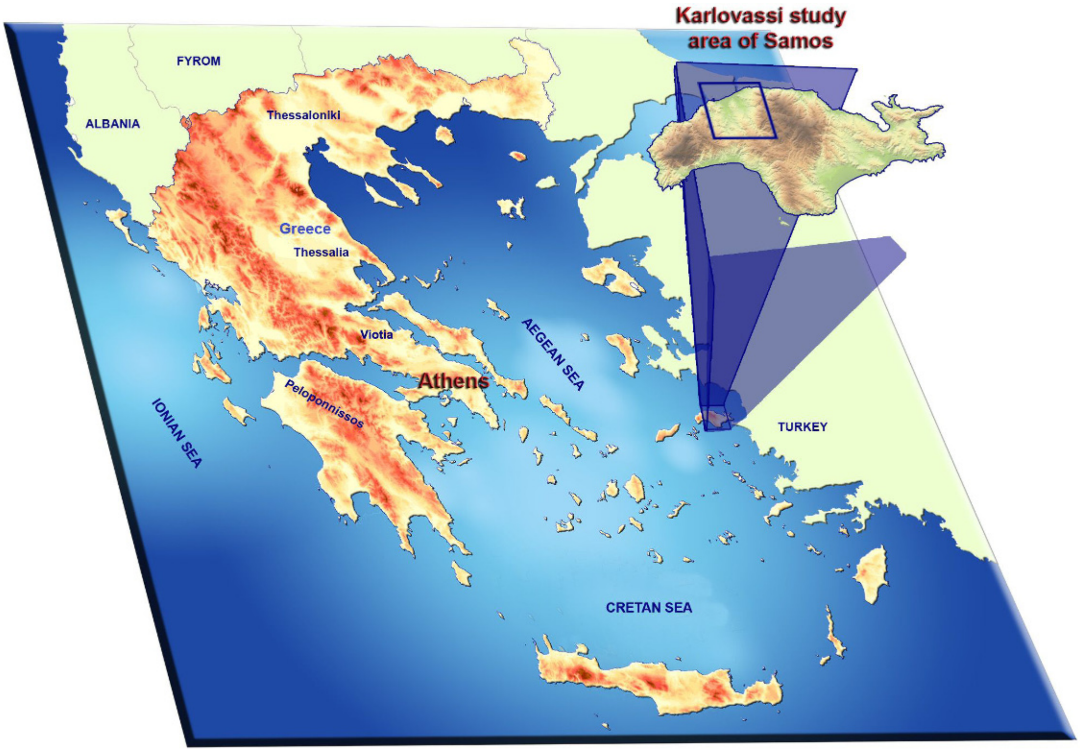

Figure 1. Study area.

Samos Island belongs to a Geotectonical Unit that interpolates between the Attico-Cycladic complex and the Menderes Massif, Western Anatolia, Turkey. The geological structure can be distinguished in Mesozoic and Upper Neogene rocks that are partially covered by Quarternary deposits. The Mesozoic substrate of the island consists of marbles, dolostones, quartzites, schists and phyllites, basic to ultrabasic metamorphic rocks, and an overthrusted younger nape of diabases, peridotites, cherts and limestones [28, 29]. At the margins of the Karlovassi Basin there are occurrences of Neogene volcanic rocks ranging in composition between rhyolite, dacite, trachyte, and basalt [29].

During Upper Miocene, two main sedimentary basins of lacustrine origin were developed on the Mesozoic substrate of the island, namely Mytilinii Basin in the east and Karlovassi Basin in the west (Figure 2).

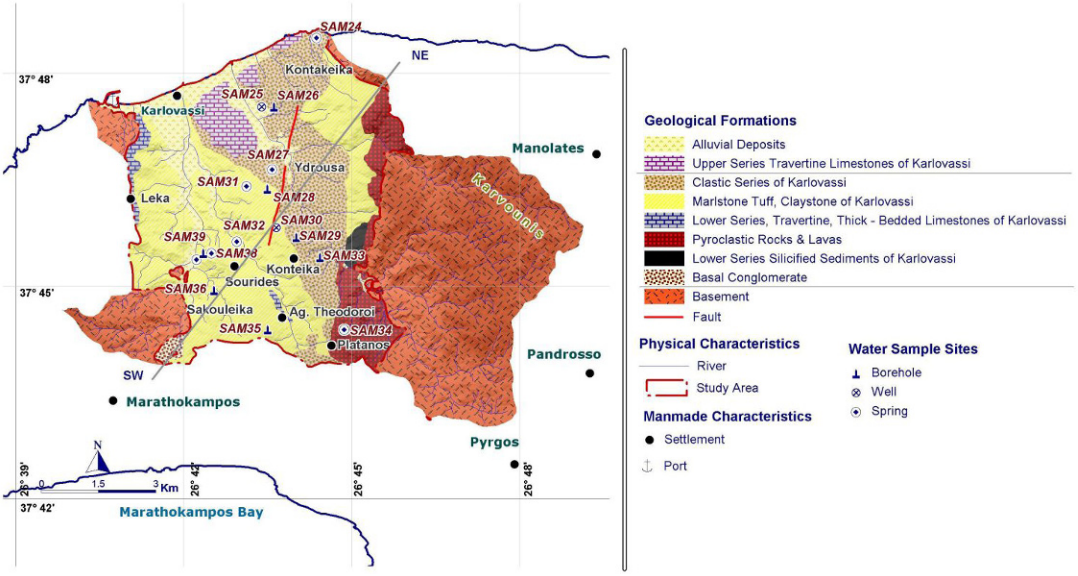

Figure 2. Geological map of Karlovassi Basin.

The major geological characteristics of the basins are: the diatomaceous beds and their diagenetic derivatives (opal-CT-rich rocks) in Mytilinii Basin, and the zeolitized ash tuffs and continental evaporites in Karlovassi Basin [7, 30–35]. The Upper Miocene deposits of both basins were covered by terrestrial sediments of the same age [29, 36]. Pliocene travertine limestone overlies the Upper Miocene rocks [29]. Finally, alluvial deposits locally cover the oldest rocks.

Focusing on the Karlovassi Basin, the Upper Miocene lacustrine deposits have a maximum thickness of 400 m and are subdivided into five well-recognized successions that were unconformably deposited on the Mesozoic substrate. The lithologic sequences embraces from bottom to top (Figure 3): (l) basal clayey sandstone and conglomerate, (2) sandy to marly limestone, (3) zeolitized tuffaceous rocks and dolomitic marlstone with local occurrences of continental evaporites, (4) claystone, and (5) siliceous limestone and porcelanite [30, 31]. The zoning of the authigenic silicates detected in the tuffaceous rocks of the basin are characteristic for the existence of a saline-alkaline lake during Upper Miocene [30, 31]. The continental evaporites of the Karlovassi basin are comprised by the borates colemanite ($Ca_2B_8O_{11}{\cdot}5H_2O$) and ulexite ($NaCaB_5O_9{\cdot}8H_2O$), and also celestite ($SrSO_4$), gypsum ($CaSO_4{\cdot}2H_2O$) and thenardite ($Na_2SO_4$) [7, 27]. The evaporites of the Karlovassi Basin are included in the Samos-Western Anatolian Borate District [37].

Partially preserved borate lenses of small thickness (<2m, see Figure mm-the partially preserved borate lens in Sourides) as well as totally dissolved evaporite lenses have been located in various parts of the basin. The two major borate outcrops occur near Sourides and near Kondeika villages (Figure 5). The presence of carbonate min-

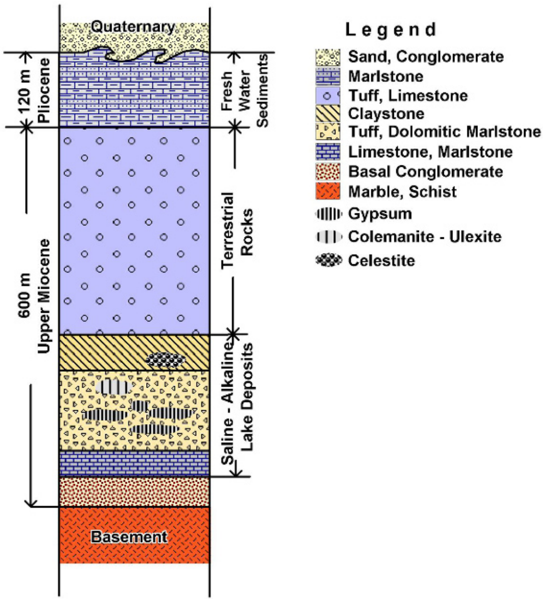

Figure 3. Stratigraphic column of Karlovassi Basin.

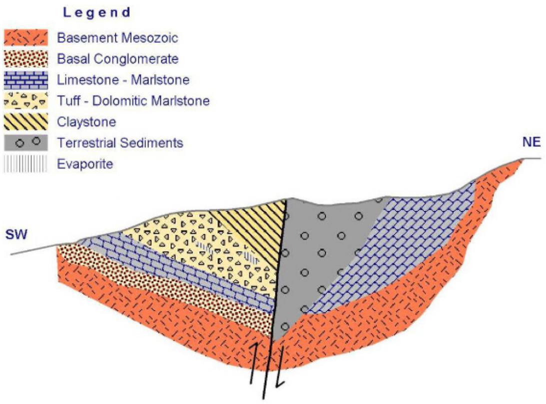

Figure 4. Schematic cross section of SW-NE direction (see Figure 2) in the Karlovassi Basin.

Figure 5. The outcrop of the partially altered borate lens in Sourides area.

Figure 6. Dissolution phenomena in the borate lens of Sourides. Note the vugs formed by the colemanite-ulexite dissolution and the deposition of brownish carbonate pseudomorphs.

erals pseudomorphs in asymmetric lenses with spongy texture in several parts of the basin is indicative of a complete weathering of several evaporite bodies (Figure 6).

The main mineral in the borate lenses is colemanite which occurs as subhedral to anhedral crystals, sometimes forming radiating aggregates. Due to dissolution-replacement phenomena, colemanite is often brecciated and cemented by secondary calcite [27]. Ulexite was also detected with the form of acicular crystals scattered in the colemanite ground mass. Celestite veinlets occur as fissure fillings within massive colemanite and also as individual celestite lenses that stratigraphically overlie the borate lenses (Figure 3). Celestite forms massive fine-grained aggregates, with numerous vugs filled with late stage formed euhedral prismatic celestite crystals. Spongy calcareous earthy material replaces the early formed borates near the surface [27]

The presence of carbonate minerals as a weathering product developed on surface-exposed bodies of colemanite is a quite common phenomenon in borate deposits [38, 39]. This conversion of colemanite to carbonate minerals is caused by intense weathering due to groundwater flow and carbonates often show pseudomorphism after colemanite [38].

The hydrogeological setting of Karlovassi Basin is controlled by the existence of a thick sandy limestone formation that occupies the lowermost part of the Upper Miocene succession. It is characterized by karstic phenomena, mainly in fault-controlled areas. These features create favorable conditions for the development of groundwater, which discharge to karstic springs, or transfuse underground in the alluvial deposits and lateral taluses.

The main aquifer of Karlovassi Basin is developed within the thick Upper Miocene rocks (Figure 3 and 4), as boreholes located in the study area have not reached the Mesozoic substrate. Boreholes up to 400 m deep performed in the central part of the basin in the 1980's (by the Greek Institute of Geology and Mineral Exploration) for the detection of borate beds were stopped within the Upper Miocene tuffs.

The Upper Miocene aquifer is relatively heterogeneous, consisting of sandy limestone, tuffs and dolomitic marls with frequent intercalations of clayey marls and claystone (Figure 3 and 4). Locally, where the unsaturated zone consists of clayey marls, claystone and alluvial deposits, the aquifer is under pressure. The piezometric level is variable, ranging from a few to some tens of meters and the general water flow is heading to the north. The heterogeneity of the aquifer is expressed through the vertical and horizontal differentiations in hydraulic conductivity and permeability. The surface exposed evaporite lenses are stratigraphically located between tuffs and claystones that represent the uppermost part of the aquifer. (Figure 3 and 4). Buried evaporite lenses, similar to those identified in the surface, may have influenced the groundwater chemistry.

Apart from the main aquifer, two others of minor importance are developed, either in the Upper Miocene porcelanous limestone that overlie the clayey sequence, or in the overlying Pliocene travertine limestone [30]. The above aquifers have limited water flow because of their small thickness and extent in the basin, and show no connection with the main Miocene aquifer, hence they act as independent hydrogeological units of minor significance and development.

3. Methodology

Groundwater samples were collected in 1-L polyethylene bottles from 16 different sites of Karlovassi Basin, including spring discharges, boreholes and wells. Sampling was carried out during the July of 2005 and the collected samples were immediately analysed for pH and electrical conductivity (EC), with the use of a glass electrode (pH) and a commercially available conductivity meter (EC). Samples were acidified to a final concentration of about 1% HNO_3 and stored in cool conditions. Before chemical analysis, samples were vacuum filtered through a 0.45 μm pore size membrane.

A total of 17 parameters were determined, including major ions (Ca, Mg, K, Na, Cl, SO_4 and HCO_3) trace elements (As, B, Br, Fe, Li, Mn, Mo and Sr) and general physicochemical parameters (pH and EC). The analyses were performed at the Laboratory of Economic Geology & Geochemistry (Faculty of Geology & Geoenvironment-University of Athens) and at the ACME analytical Laboratories Ltd, Canada. Sulfates and chlorides were measured photometrically using attach DR/4000 apparatus, while the concentration of HCO_3 was determined with the use of an acid/base titrator. Finally, major and trace elements were determined by ICP-MS. Results are shown in Table 1. Data quality was assured by analyzing duplicates of four samples and through the electrical balance ratios [40].

The analytical data were processed statistically, in order to assess any potential correlations between the examined parameters and to give initial information about groundwater chemistry. The analytical data was standardized in order to eliminate the influence of different units. Correlation analysis was performed in order to investigate the correlation between two single variables, through the creation of linear combinations between the examined parameters. The assessment of correlation was achieved through the values of correlation coefficient (r), which ranges between -1.00 (highest negative correlation) and +1.00 (highest positive correlation). For the purposes of the paper, high strong correlations were considered as those equal or above +0.70, and high negative correlations were considered as those equal or below -0.70. Results are shown in Table 2.

Topographic and geological data were digitized from pre existing topographical and geological maps [29]. All primary geographical, geological and environmental data were inputted into a Geographical Information System (GIS), where a database was structured and updated, especially for the area of interest. The database was updated by data collected through fieldwork. The DEM of the study area was used in order to extract the topographic section used for the creation of the geological section. Spatial interpolation analysis was undertaken for B, Na, Li, Sr and Ca in order to extract data for the area around the sampling sites. Finally, all data was processed, statistically and spatially, and the secondary data was visualized and distributed through a series of thematic maps.

4. Results and discussion

A thorough review of the analytical data, statistical processes, existing literature and field work revealed some crucial assessments about the groundwater chemistry of the Karlovassi Basin. Based on the analytical data of Table 1, calcium shows elevated values (100.5 mg/L to

Table 1. Results of chemical analyses for the collected water samples (S.S.: Sampling Site, B: Boreholes, S: Springs, W: Wells. P.L: Piezometric Level - referred as depth from surface).

	S. S.	P. L.	Ca	Mg	Na	K	Cl	HCO_3	SO_4	As	B	Br	Fe	Li	Mn	Mo	Sr	EC	pH
		(m)	mg/L							µg/L								µS/cm	
S24	S	0	125.7	77	393.3	15	861	580	286	3	255	2564	31	54	1	6	919	2760	8
S25	W	10	98.6	9.6	30.7	1.6	83	229	43.8	17	24	195	0	17	0	2	509	630	7.7
S26	B	26	100.5	38.2	26.3	3.2	46	251	186	1	51	102	46	25	38	4	1921	720	7.3
S27	S	0	117	29.3	36.1	3.1	45	345	125	142	115	133	0	73	1	4	2377	800	7.2
S28	B	100	123.9	29.3	30.8	3.5	40	315	168	150	94	135	0	66	3	13	2573	780	7.3
S29	B	80	62.6	45.7	340.5	26.5	37	570	1590	5	721	91	67	890	55	24	7221	1900	8
S30	W	5	16.3	11.2	334.9	17.3	60	580	247	117	889	134	24	1914	6	122	1728	1350	8.4
S31	S	0	188.2	46.3	44.6	6.3	44	413	347	71	127	136	22	148	7	17	4353	1030	7.3
S32	S	0	171.4	13.4	39.6	1.3	126	377	72	2	88	284	0	26	0	2	775	820	7.5
S33	B	25	91.9	21.4	194.2	9.9	44	415	332	24	242	105	61	369	50	79	987	1140	7.4
S34	S	0	105.5	7.1	19.1	1.3	39	297	22.6	9	11	118	99	1	0	3	259	500	7.5
S35	B	110	80.4	42.3	42.4	9.3	35	220	236	10	223	113	52	115	5	11	8252	710	7.7
S36	B	100	66.4	39.7	426.5	11.1	54	640	1180	9	5502	149	34	1049	24	22	10888	2150	7.7
S37	S	0	211.6	42.7	71.9	3.3	91	373	409	2	356	216	117	115	12	2	5245	1000	7.8
S38	S	0	190	83	81.8	3.2	78	374	550	2	521	153	0	183	0	18	8654	1380	7.2
S39	B	70	18	6	184	1.9	44	153	270	46	499	116	0	73	1	6	518	810	7.7

211.6 mg/L) in samples S24, S26, S27, S28, S31, S32, S34, S37 and S38 (Figure 7).

The above values are elevated compared with the Ca-HCO_3 type of groundwater in limestone-clayey substrates [40] and they should be attributed to the dissolution of evaporite minerals; i.e. the Ca-borates (colemanite), the Ca-Na-borates (ulexite), and the Ca-sulfates (gypsum) minerals that have already been detected in the basin. Some of the calcium could however, be supplied by the calciferous beds of the Upper Miocene rocks. A distinction between these two impacts could be easily assessed, as the correlation of high Ca values with other parameters such as B, Na and SO_4 in most of the samples led us to the conclusion that the high Ca content of the groundwater is mainly caused by the leaching of the evaporite minerals of the basin.

Magnesium shows no specific variation in the samples analyzed, apart from samples S24 (77 mg/L) and S38 (83 mg/L) which appear as slightly elevated values compared with the other samples. The Mg enrichment of sample S24 (Zesto Spring, see Figure 2) is attributed to seawater intrusion in the vicinity of the spring, as it lies only few meters from sea. The influence of seawater in the specific sample is also verified by its elevated values of Na, Cl, SO_4, K and EC. The factor of sea spray enrichment should be excluded, as such a fact would require spatially scattered enrichment and a non-point source one, which is located only in sample S24. The elevated magnesium value of sample S38 is probably related to the dolomitic marls and the Mg-smectite-rich zeolite tuffs that frequently occur in the Upper Miocene succession [30, 31] (Figure 3). Additional Mg-enrichments due to the presence of buried Mg-rich borate minerals such as inderite and kurnakovite that were reported from the Western Anatolian-Samos borate district at Kirka, cannot be excluded [6]. Finally, another possible source of Mg enrichment could be associated with the existence of secondary epsomite ($MgSO_4{\cdot}7H_20$) and hexahydite ($MgSO_4{\cdot}6H_20$) which abundantly occur as white efflorescences on dolomitic claystone exposed in the brick-making quarries of Karlovassi, which are located west of the sampling site S31.

Sodium shows abnormally high values in samples S24, S29, S30, S33, S36 and S39, ranging from 184 mg/L to 426.5 mg/L (Figure 8). Apart from sample S24 which is influenced by seawater, the other samples are probably influenced by the leaching of soluble Na-rich borates in depth. High values of sulfate can be related to the presence of Ca, Mg, Sr, Na-sulfates which have been reported within the basin [7, 27]. The simultaneous enrichment of Na and SO_4 reported in several samples (S29, S30, S33, S36, S37, S38 and S39) are probably related to the influence of sodium sulfates such as thenardite (Na_2SO_4), a mineral that along with celestite [7], has already been detected in newly formed artificial outcrops in the NE part of the tuffaceous-clayey succession of the basin.

Lithium content is high, mainly in samples S30 and S36 (Figure 9) and is also an indicator for evaporite mineral dissolution at depth. High Li values related to B and other evaporites are common and characteristic in saline-alkaline lake deposits [41–43].

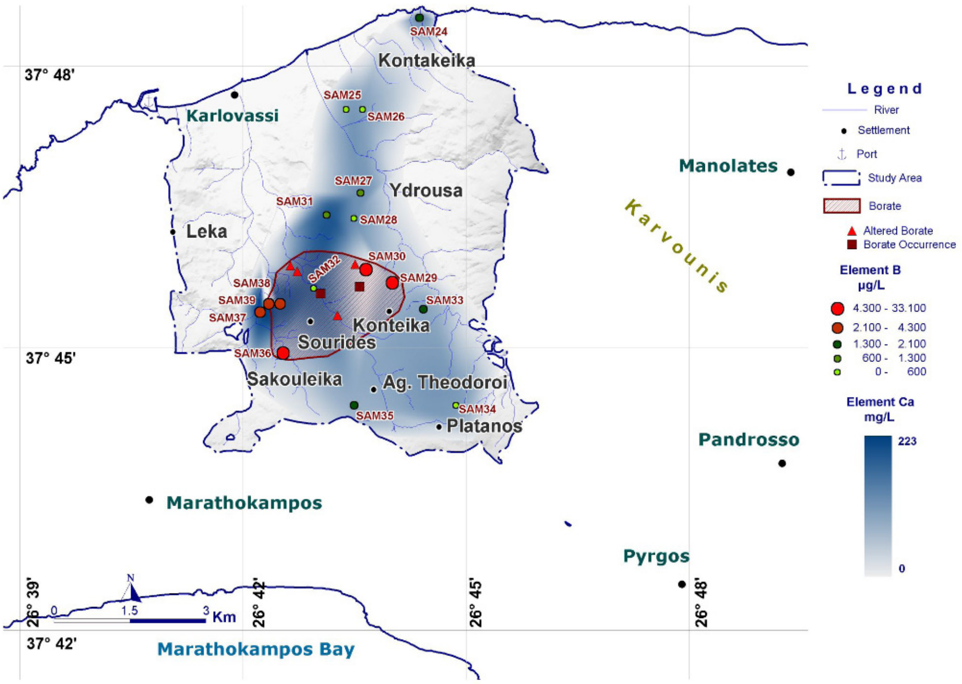

Figure 7. Simulation of Ca concentrations in the groundwater of Karlovassi Basin, with the aid of spatial analysis (natural neighbour method). Values of boron are also shown.

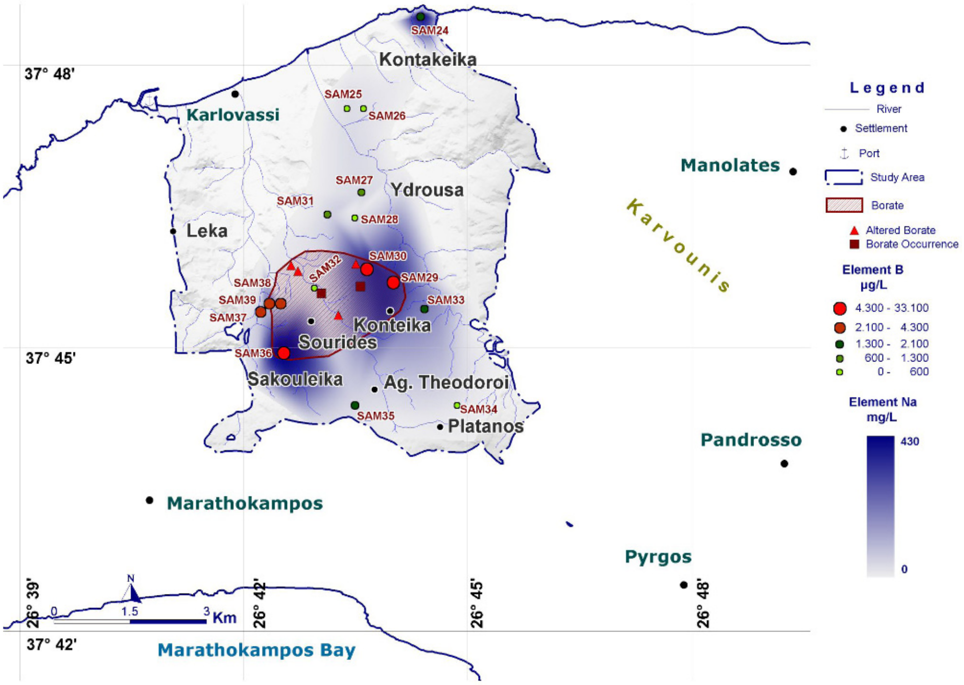

Figure 8. Simulation of Na concentrations in the groundwater of Karlovassi Basin, with the aid of spatial analysis (natural neighbour method). Values of boron are also shown.

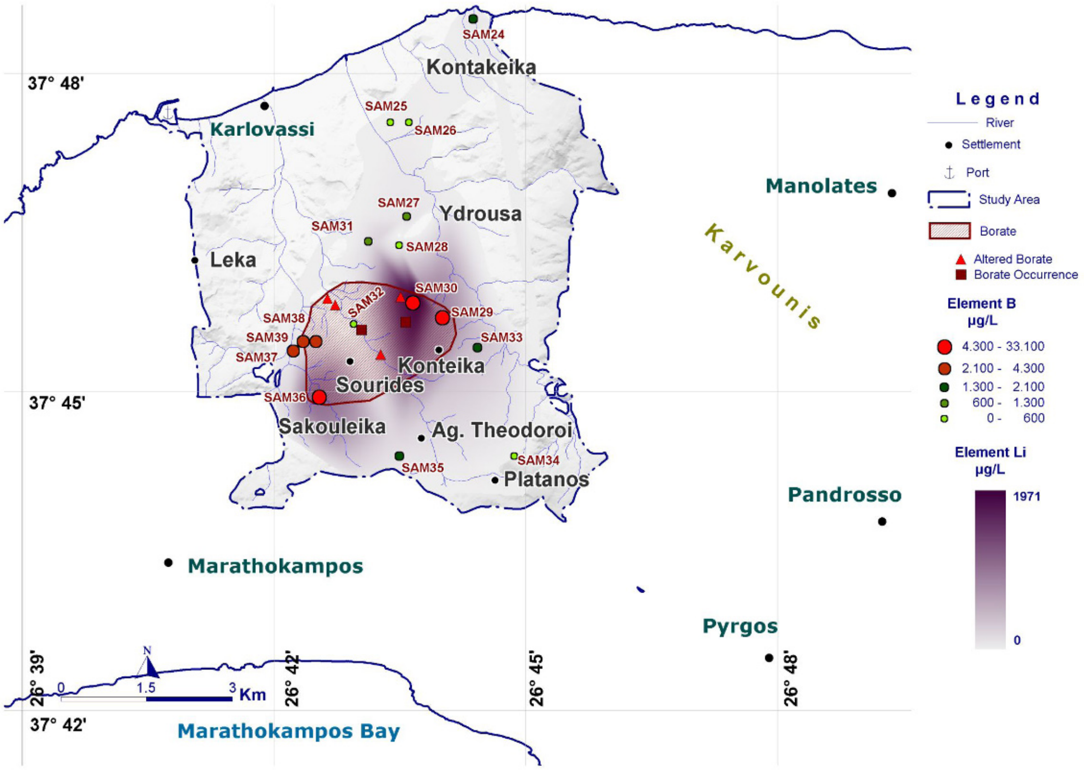

Figure 9. Simulation of Li concentrations in the groundwater of Karlovassi Basin, with the aid of spatial analysis (natural neighbour method). Values of boron are also shown.

Boron shows high values that are uncommon [3]. Apart from sample S24 where the elevated boron content is attributed to the influence of seawater, the samples S36, S30 and secondarily the S38 and S39 are most likely enriched by the leaching of boron-rich minerals. Sample S30 exhibits increased boron values (889 μg/L) which represents water collected from a well, located a few meters from the surface exposed borate lens, NW of Kondeika village (Figure 2). The leaching of Kondeika borate lens is limited due to its emplacement between clayey beds that prevents significant dissolution and boron enrichment in groundwater. The highest boron value measured in groundwater samples is referred to the sample S36 (5502 μg/L) that is located west of Sakouleika village, in tuffaceous formations where there is not any surface indication for the presence of evaporites. In addition, samples S38 and S39, which are spatially associated, show increased boron values. These samples are not associated with any traces of surface exposed evaporites, or their diagenetic derivatives. It is, therefore, concluded that the presence of high boron values in groundwater is not related to the depth of sampling (Table 1), or surface exposed evaporites.

The existence of altered borate lenses in the surface is however indicative of the mechanism of the groundwater enrichment by the continuous dissolving of boron-rich minerals in various depths.

Hence, it is proposed that the hydrogeochemistry of the groundwater is controlled by the leaching of boron-rich minerals that could exist in various depths within the basin, mainly due to the intense tectonism that has influenced the entire basin. Besides the supply of boron by the leaching of evaporites, an additional source of boron in groundwater could be the partial dissolution of the authigenic boron-bearing K-feldspar [2500 mg/kg B] that abundantly occurs in the tuffaceous rocks of the basin [30].

Strontium shows elevated concentrations (1728 μg/L to 10888 μg/L) in almost all samples (Figure 10) and it is strongly related with elevated SO_4 values, denoting an origin mostly from celestite dissolution. Celestite occurs in the top of the evaporite succession and it has significantly influenced the groundwater in the sampling sites S27 and S28. The Sr-rich clinoptilolite tuff (1050-2300 mg/kg Sr) that abundantly occurs in the tuffaceous rocks of the basin can be a supplementary source of strontium in groundwater [30]. Moreover, in samples S29, S30, S33, S36, S37 and S38 the elevated values of strontium relate to a high boron content, so it is concluded that the simultaneous B-Sr enrichment is due to the partial dissolution of the closely associated borates and celestite in the evaporite lenses [27].

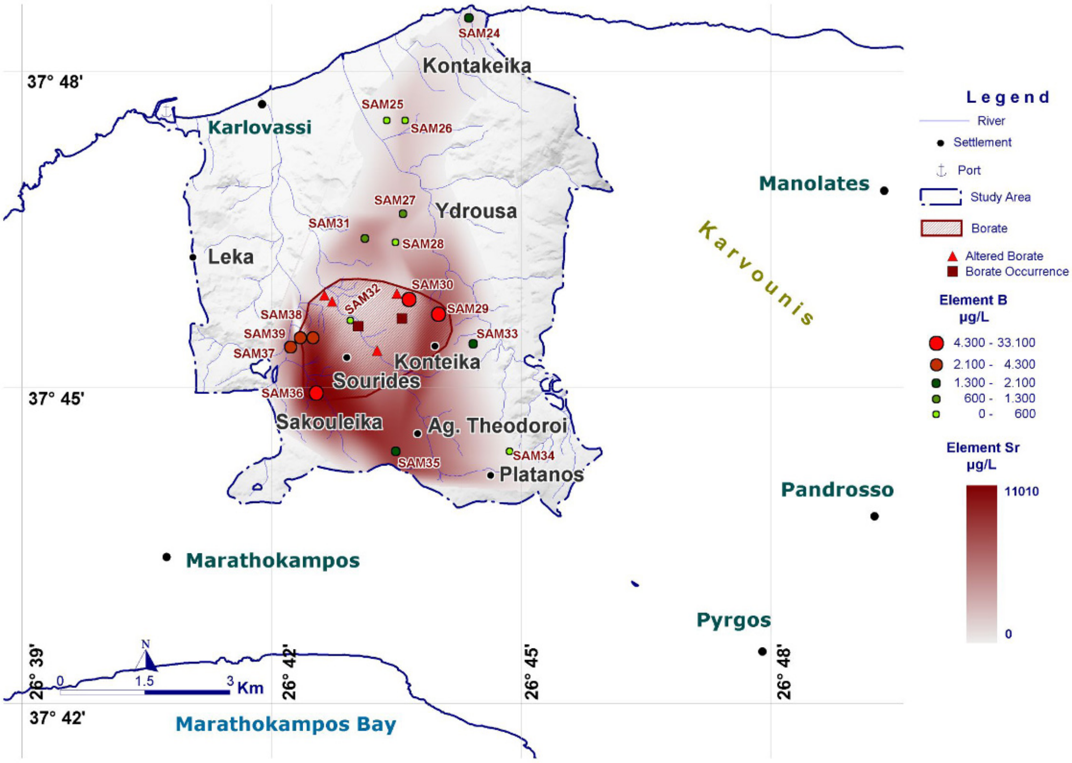

Figure 10. Simulation of Sr concentrations in the groundwater of Karlovassi Basin, with the aid of spatial analysis (natural neighbour method). Values of boron are also shown.

The concentrations of potassium show no significant variation. Minor differences in their values (S29 and S30) could be attributed to the dissolution of K-feldspars and K-clinoptilolite, which are abundant in the tuffaceous rocks of the basin.

Arsenic has been reported in borate deposits in other regions such as Emet (Turkey), Andes (Argentina) and Sonora (Mexico) [9, 39, 44]. It has been determined that As locally accompanies borate deposits in the form of cahnite ($Ca_2B[OH]_4AsO_4$) and teruggite ($Ca_4MgAs_2B_{12}O_{22}[OH]_{12}\cdot 14H_2O$). In Karlovassi Basin, even though arsenic content is relatively high, it is not correlated with high boron values. By contrast, the elevated values of As (S27, S28, S30, S31 and S39), Mo (S30 and S33) and Mn (S29 and S33) are related as a possible weak sulfide mineralization, which occur in Karlovassi Basin [29, 44, 46].

Based on the results of Table 2, some of the above assessments were verified. In detail, the correlation between the examined parameters added some evidence about the potential factors that control groundwater chemistry.

More specifically, the strong positive correlation between B-Li (+0.88), B-Na (+0.83), B-SO_4 (+0.87) and Sr-SO_4 (+0.78) revealed the influence of the groundwater from buried evaporites (sulfates and borates). Even though Br and Cl content of the samples are relatively low indicating negligible seawater influence to the groundwater (with the exception of sample S24), the strong positive correlation of Cl and Br (+0.98) indicate their common origin. As the influence of seawater in the area studied is negligible, the correlation of K-Na (+0.74), K-SO_4(+0.73), Mg-SO_4 (+0.72) and Na-SO_4 (+0.78) can be attributed to the presence of buried soluble sulfates in depth.

Table 2. Correlation matrix for the 17 analyzed parameters.

	As	B	Br	Ca	Cl	Fe	K	Li	Mg	Mn	Mo	Na	SO_4	Sr	HCO_3
As	**1.00**														
B	0.01	**1.00**													
Br	-0.27	0.00	**1.00**												
Ca	-0.41	-0.38	0.26	**1.00**											
Cl	-0.37	0.04	**0.98**	0.25	**1.00**										
Fe	-0.26	0.19	0.01	-0.05	-0.01	**1.00**									
K	0.1	0.65	0.11	-0.29	0.10	0.60	**1.00**								
Li	0.21	**0.88**	-0.15	-0.38	-0.11	0.22	**0.78**	**1.00**							
Mg	-0.36	0.36	0.29	0.53	0.28	0.27	0.50	0.36	**1.00**						
Mn	-0.09	0.48	-0.34	-0.17	-0.32	0.64	0.65	0.62	0.34	**1.00**					
Mo	0.38	0.58	-0.27	-0.44	-0.26	0.31	**0.75**	**0.79**	0.19	0.52	**1.00**				
Na	0.01	**0.83**	0.27	-0.50	0.31	0.31	**0.75**	**0.75**	0.20	0.42	0.60	**1.00**			
SO_4	-0.12	**0.87**	-0.06	-0.13	-0.03	0.31	**0.73**	**0.84**	0.63	0.68	0.57	**0.72**	**1.00**		
Sr	-0.13	0.64	-0.21	0.20	-0.21	0.22	0.52	0.66	**0.76**	0.50	0.37	0.24	**0.78**	**1.00**	
HCO_3	-0.06	0.51	0.32	0.10	0.34	0.42	0.68	0.57	0.46	0.33	0.49	0.60	0.50	0.38	**1.00**

5. Conclusions

The Karlovassi Basin of Samos Island hosts Upper Miocene sedimentary and volcanic rocks that have been deposited in an evaporitic environment. The evaporite minerals were formed in a continental environment and contain borates such as colemanite and ulexite, and sulfates such as gypsum, celestite and thenardite. The evaporites are hosted between tuffs and claystones and are partially or totally leached because of surface runoff and groundwater flow.

The compilation of the analytical results of groundwater samples and the evaluation of the literature data, determined the specific hydrogeochemical conditions of Karlovassi Basin.

Seawater has not influenced the groundwater chemistry (with the exception of sample S24), as determined by the low levels of chlorine content.

Most of the dissolved ions in groundwater are derived from the partial or total leaching of evaporites located either close to the surface, or most likely buried in various depths within the basin.

Boron shows locally high values compared with normal fresh water, most likely as a result of the leaching of boron-rich minerals. The leaching of Kondeika borate lens is limited due to its emplacement between clayey beds, which prevents significant boron enrichment in groundwater. On the contrary, the western borate lens in Sourides appears as a more intense dissolving phenomena as it is hosted in permeable fracture tuff beds.

Both the highest boron value and the increased boron values were measured in groundwater samples located in the western part of the basin, in a wide area where no surface indications for the presence of evaporates have been observed. It is therefore assumed that the presence of buried evaporite beds is of unknown importance.

The elevated values of sodium, strontium and sulfates are also due to the presence of buried evaporites with multiple compositions, in accordance with the already detected evaporites in the surface layer.

The arsenic content in groundwater is not associated with boron and its local enrichments can be attributed to the weak sulfide mineralization.

Finally, based on the detailed geological fieldwork that has been carried out in the Karlovassi Basin since the 1980's and the current hydrogeochemical research, it is proposed that it is possible the existence of buried evaporites in Karlovassi Basin, especially in the western part of the Upper Miocene basin (Aghios Georgios Monastery-Sourides-Sakouleika areas).

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