A natron source at Pikrolimni Lake in Greece? Geochemical evidence

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1. Introduction

During the last decades, the origin of natron (Na₂CO₃) has been a major issue among the researchers of ancient glassmaking. Natron was used during the Greek-Roman period as a source of soda, which is one of the three basic components of glass. Its use was located in Eastern Mediterranean, Egypt and Phoenicia, from the Bronze Age until the medieval time. In Mesopotamian glassmaking, the main source of soda was halophyte ash. The glasses made of plant ash have different composition in relation to those made of natron, so it is practically possible to distinguish the West Asian glass products from those from Mediterranean areas. Glasses from Archaic, Classical and Hellenistic times which have been found in Greece are all made of natron (Ignatiadou, 2002).

Natural natron deposits, created by evaporation and desiccation processes in isolated lakes, exist in Wadi Natrun (De Cosson, 1936; Coulson and Leonard, 1979; Henderson, 1985), northwest of Cairo, Egypt. This source was used in antiquity but also until today and it is considered the main or even the only source of natron for glassmaking.

Natron deposits also existed in Greece, in the region of Macedonia. This source was used in antiquity but also until today and it is considered the main or even the only source of natron for glassmaking.

Nitron forms there when the Dog Star rises for nine days, comes to the surface again and then ceases. Nitron as Chalastraion nitron, named after Chalastra, the lake in Macedonia where natron was being burned (Testimonium 3) or Natron as Chalastraion nitron, named after Chalastra, the lake in Macedonia where natron was being burned (Testimonium 2). Others mention Chalastra as a city or lake in Macedonia where natron was being burned (Testimonium 3) or natron as Chalastraion nitron, named after Chalastra, the lake in Macedonia (Testimonium 4).

A relatively unknown quotation in international studies about ancient glass is that of Pliny, the Elder, which includes the most thorough and enlightening reference to Chalastraion nitron, referring that it abounds in the Macedonian city of Citiae (Testimonium 5). In this quotation, the following are mentioned:

“At Citiae in Macedonia it is found in abundance the best, called soda of Chalestra...” The ion-specific interaction model based on Pitzer’s equations showed that the lake brine samples are saturated versus carbonate-bicarbonate sodium and sodium-chloride-sulfate minerals. The results of individual X-Ray Diffraction (XRD) analyses on the evaporative deposits showed that the salts consist mostly of trona, burkeite, thenardite and halite confirming Pliny’s description.
Lake Pikrolimni is located 20 km to the NW of the town of Thessaloniki, in the region of Macedonia, in Northern Greece, where a spa and installations for mud baths exist.

In order to confirm Pliny's description, we investigated the geochemical data of the area and the evaporative conditions, which are responsible for the formation of "Chalastraion nitron".

2. Natron use

Evaporitic rocks have been used since the dawn of human history. Salt and brines have been used in all cultures, i.e. Knossos Palace is built on Crete Island with big blocks, some of which were pure massive gypsum. Also in more "modern" civilisations, the salt was used for payments. The Romans paid a "salarium" in NaCl and therefore the actual word "salary" came up for wages, originally meaning salt money.

Ancient use of sodium carbonate is known since 5500–4000 BC. However, findings of the material are rare. In general, the main use of natron was as a purifier in mumification. Herodotus provides the best description of the use of natron in mumification.

Natron seems to have been used in glassmaking in Egypt since the Badarian Period (early 4th millennium BC), indicated by the very low potash contents of glasses (Shortland et al., 2006). The use of natron becomes apparent since the 1st millennium BC. Reported glass from the tomb of Nesikhons in Egypt with low content in potash, magnesia and lime indicates that the soda was derived from natron (Schlick-Nolte and Werthmann, 2003). Other evidence of natron use in the same period is the blue glasses from 8–9th century BC Nimrud, Iraq (Reade et al., 2005).

The Roman glassmaking industry seems to have been based on natron, indicated by the low-magnesia content. Until the 9th century AD, natron continued to be the basic material in glassmaking in Levant, the Mediterranean and Europe. The use of natron as the flux in glass production declines in Near East and in Europe in the 9th century AD, when soda-rich plant ash replaced it (Shortland et al., 2006). However, at al-Barnuj in the Western Delta, Egypt, natron was collected during periods that waters were dried up until the 18th century AD (Martin and Sauneron, 1982). From the 1920s and onwards natron was collected at the same area by the Egypt Salt and Soda Company (Evelyn-White and Hauser, 1926–1933).

In ancient Greece natron was mentioned for the first time by Plato in the 5th century in Republic (Testimonium 1).

Today, sodium carbonate is formed in the subtropical region of Lake Natron in Tanzania and Lake Magadi in Kenya (Magadi means bitter, exactly as the name of Lake Pikrolimni, which means bitter-lake). In Table 2, the mineral sequence that precipitates during marine water evaporation and lacustrine water evaporation appears (Lake Natron, Lake Magadi, Deep Springs Lake and Wadi Natrun).

3. Meteorological and geological setting

Lake Pikrolimni is located in the basin of Kilkis plain, near Thessaloniki (23 km), in northern Greece. It is a small shallow lake which usually dries out during summer. It has an average depth of about 0.5–0.7 m and covers an area about 4.5 km² when it is flooded. The mean annual precipitation in meteorological station of Thessaloniki (during 1959–1997, Hellenic National Meteorological service) is 448 mm, while the temperature ranges from 1.3 to 32 °C for the same period. Mean temperature during July and August is 26.3 °C and mean precipitation is 22 mm (1959–1997, Hellenic National Meteorological service). The annual real evapotranspiration for Thessaloniki area (Themis) in 2005 was estimated 482.01 mm, with precipitation 481.8 mm and mean temperature 15.4 °C (Anatoliki AE, 2006). During summer months, July and August (2005), mean temperature was 22.3 °C and 25.5 °C respectively, mean precipitation was 95 and 48 mm respectively while real evapotranspiration was 95 and 48 mm for the same months (Anatoliki AE, 2006). Also Dalezos et al. (2002) report that the maximum values of reference evapotranspiration rates are observed mainly over the northern region and particularly over the plains surrounding the stations of Thessaloniki and Kilkis in the majority of months. This could be merely due to the fact that mainly in summer months strong winds prevail over Greece, which along with the lack of precipitation cause a great deal of aridity variability among different sites. In particular, the observed maximum values of reference evapotranspiration rates in the summer months over the Thessaloniki plain could be due to a strong and dry N–NW wind pattern named Vartharis.

Sediments of Neogene and Quaternary age are prevalent in the region of Lake Pikrolimni (Fig. 1). The Quaternary deposits are Holocene river and lake sediments, alluvial weathering material composed mainly of schists and carbonate sandy clays, sands and gravels of lower terrace system (carbonates). Pleistocene deposits contain gravels, red clays and sands with calcareous concretions and a big amount of mica. The prevalent Neogene formation (Mountaktis, 1985) is the sandstone–marl series, including Hipparion mediterraneum, Mastodon sp., Gazella cf. deperdita.

The bedrock in the region consists of Mesozoic rocks, mainly by conglomerates from Upper Jurassic, including Nerineae, Cladocoropsis sp. and Pseudocyannina sp. (Mercier, 1966), with quartzite, greywacke (quartz and feldspars), quartz and limestone pebbles, basic rocks (gabbro) from Upper Jurassic with pyroxene, altered into biotite and actinolite, hornblende, plagioclase feldspar and epidote and limestone from Middle–Upper Triassic. In a distance less than 10 km from Lake Pikrolimni, the Paleozoic basement is uncovered consisting of mafic rocks (amphibolite with amphibole as hornblende) and plagioclase feldspars.

4. Sampling and analysis

Lake Pikrolimni is not fed by any major river and the hydrography of the area shows that no perennial streams enter the lake directly. In the past, the major source of water to the lake was ground water (Pliny: Many public testimonies vouch that there were a lot of springs in the middle of the lake, but after the big earthquake of 1981 these springs have disappeared). Specifically, there were springs very close to the lake and within the lake itself. These percolating groundwaters probably brought the necessary ionic charge into the lake. So during the summer, according to Pliny, the precipitation of the salt was taking place. Actually, the main input of fresh water to Pikrolimni is the rain. Also, a number of wells and two springs are located in the lake area (one spring is located in the south perimeter of the lake, nr. 21 in Table 1 and one spring emerges in the Pikrolimni Village). The spring water (nr. 21 in Table 1), ranges in temperature from 28 to 30 °C and does not vary in discharge and concentration. It emerges in the ancient basin of the lake and feeds the lagoon which is perennially wet marginal lake areas. During the winter, when temperature is low, the inflow of water (mainly rain water) into Lake Pikrolimni exceeds the evaporation and the lake fills with water. During the summer, when the temperature and evaporation increase, the level of the lake begins to fall, the concentration of the ions increases and evaporite minerals begin to precipitate out of the solution. During some summers, when the lake water is exposed to very intense evaporative concentration, the brines cover all the bottom of the lake. This brine body vanishes during the dry seasons exposing salt deposit, as shown in Fig. 1. In the next year, during the rainy seasons, the lake refills with meteoric water and this water dissolves the salts and the shallow brine body covering the main lake surface. This sequence of filling/ depletion of the lake was observed during the five years of this study. Therefore, evaporative concentrations dominate the chemical composition of the lake water and it is the driving force for the evolution of Pikrolimni brines, although only one segment is observed directly: the lake brines. The spring is postulated as sub-surface flow.

Samples were collected, in different times, from the borehole in the thermal spa of Pikrolimni (which is located at the banks of Lake Pikrolimni), from spring water and samples of brine and salts from the lake itself. We also sampled fresh water of the region. The depth of the...
perforation of the borehole in the thermal spa is approximately 250 m. This water is naturally sparkling, with a metallic aftertaste and a slight organic smell. Stratigraphic data are absent for the area, however reports of the borehole at the thermal spa mention that across the totality of the borehole’s depth, only lake sediments were drilled.

The samples were taken twice during the year: in summer and in winter (2002, 2003, 2004, 2005, 2006 and 2007). The samples were taken in different seasons. Samples with codes PL-8/2002 and PL-9/2006 regard residual brines on the lake bottom. The lake was totally dried out once, on 2002, and never again until 2006. The samples from 2003 to 2005 concern mixing between the residual brines and meteoric water. The analytical scheme includes field measurements of temperature, conductivity and pH. Samples were also subjected to chemical analysis. Filtered (0.45 µm), acidified (with HNO₃ 1:1) water samples were collected for determination of cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺). Untreated samples were collected for analyses of anions (Cl⁻, SO₄²⁻, CO₃²⁻ and HCO₃⁻). The major chemical constituents were analyzed with standard methods described in Apha (1989). The anions and cations of the water samples were analyzed with ion chromatography and atomic absorption.
<table>
<thead>
<tr>
<th>a/a</th>
<th>Sample name</th>
<th>Sample description</th>
<th>Date</th>
<th>T (°C)</th>
<th>pH</th>
<th>Cl(^{-}) (mmol/L)</th>
<th>SO(_4)(^{2-}) (mmol/L)</th>
<th>CO(_3)(^{2-}) (mmol/L)</th>
<th>HCO(_3)(^{-}) (mmol/L)</th>
<th>Ca(^{2+}) (mmol/L)</th>
<th>Mg(^{2+}) (mmol/L)</th>
<th>Na(^{+}) (mmol/L)</th>
<th>K(^{+}) (mmol/L)</th>
<th>NO(_3)(^{-}) (mmol/L)</th>
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<td>1</td>
<td>S/1/2002</td>
<td>Spring–Pikrolimni Vil.</td>
<td>1/2002</td>
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<td>3.81</td>
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<td>3.20</td>
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<td>0.08</td>
<td>0.12</td>
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<td>0.08</td>
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<td>1.69</td>
<td>0.18</td>
<td>0.47</td>
<td>3.43</td>
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<td>0.70</td>
<td>4.35</td>
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<td>0.59</td>
<td>0.38</td>
<td>0.87</td>
<td>10.61</td>
<td>0.48</td>
<td>1.03</td>
<td>9.78</td>
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<td>0.55</td>
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<td>Mg–HCO(_3)</td>
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<td>0.11</td>
<td>0.80</td>
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<td>Water tube</td>
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<td>Borehole</td>
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<td>1.93</td>
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<td>0.03</td>
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<td>3.19</td>
<td>0.23</td>
<td>0.87</td>
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<td>1.05</td>
<td>1.93</td>
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<td>0.03</td>
<td>Mg–HCO(_3)</td>
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</tr>
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a Unpublished data, sources in text.
5. Chemical results

5.1. Solute acquisition

Four chemically different water types (Table 1) are recognized in the Pikrolimni area for diluted water and one type for the lake water. The four recognized groundwater types, based on both chemical and TDS, are: Mg–HCO₃, Na–HCO₃, Ca–HCO₃, and Na–Cl type (only one sample). The two first types represent fresh water that has flown from boreholes and spring in the old bottom of Lake Pikrolimni. The municipality water of Pikrolimni village is also Na–HCO₃ type although municipality water which waters the spa is Na–Cl type. The Ca–HCO₃ represents the aquifer of local groundwater system in Philadelphia area. The lake waters are Na–Cl, however when the lake began to evaporate until the evaporating conditions were such that lake water is nearly totally evaporated, then the residual water is Na–Cl(CO₃–SO₄) type. Fig. 2 presents the Pikrolimni area water, groundwater and Pikrolimni brine, in terms of the major ions. The groundwaters are predominantly HCO₃, whereas the cations are mixtures of Na, Ca and Mg. In contrast, the cations of the brines are dominated by Na and the anions are a mixture. This data is in agreement with the model proposed by Hardie and Eugster (1970).

The Pikrolimni saline alkaline lake is enriched in dissolved minerals that have accumulated in the brines following evaporation. Such brines indicate a very considerable range in ionic composition and concentration. The total salinity ranges from saline water to brine: total dissolved solid (TDS) concentrations ranging from 7.5 to 426 g/L. The pH ranges from 8.8 to 10.5 and increases as salinity increases. The surface water temperature is between 22 and 31 °C. All the saline lake waters are Na–Cl type, with Na⁺ and Cl⁻ representing about 95% and 70% respectively of the total cations and anions. Concentrations of Ca²⁺ and Mg²⁺ are very low in the brines of 8/2002 and 9/2006.

The two types of groundwater of Pikrolimni area, Na–HCO₃, Mg–HCO₃ types, are tepid (temperature ranging from 18 to 30 °C), near-neutral to alkaline (pH ranging from 6.3 to 9.8) and have total salinities that range from fresh to brackish water: total dissolved solid (TDS) concentrations ranging from 0.50 to 4.5 g/L. This variability of TDS is due to the HCO₃⁻ concentrations.

The dominant ionic species in the Na–HCO₃ (soda) groundwater are Na⁺ and HCO₃⁻–CO₃²⁻ with these two ions comprising 70–80% of all ions in solution. The concentration of other major ions is low, with Mg²⁺ and Ca²⁺ contents less than 2 mmol/L. The Cl⁻, K⁺ and SO₄²⁻ concentrations are also low.

In the Mg–HCO₃ type water the dominant ionic species are Mg²⁺ and HCO₃⁻–CO₃²⁻ with these two ions comprising 70–80% of all ions in solution.

The Na–HCO₃ waters were found in the Pikrolimni/Keratea area, approximately 2 km away from Lake Pikrolimni, and these waters end up in the basin of Lake Pikrolimni. Sample Keratea (IGME, unpublished data) belongs in this category, which was measured with SiO₂ = 31 mg/L and CO₂ = 668 mg/L. The Mg–HCO₃ groundwater was found within the Holocene lacustrine sediments of Pikrolimni. Sample Pikrolimni-mud of 2000 (Manasis Mitra, unpublished data) belongs in this water type, which was measured SiO₂ = 47 mg/L and CO₂ = 1650 mg/L. These waters, of meteoric origin, flow through the clay minerals, rich in mica, alternating with carbonate rocks. The Mesozoic and Paleozoic basement in the area consist of basic–mafic rocks. When the aquifer matrix is composed of alluvial fill, silicate hydrolysis is the typically invoked explanation for the formation of Mg–HCO₃ groundwater and Na–HCO₃ groundwater. So it is tempting to assume that this process is controlling the water chemistry. However, many other weathering reactions contribute to the solute load of inflow waters. Thus, reconsidering the facts and data, it could be said that generally rain water and weathering reactions are the principal solute sources. Rain water contributes to all principal solutes of dilute waters, excepting silica, but the most significant contribution will be to Na⁺, Cl⁻, SO₄²⁻ and HCO₃⁻. The amounts of these solutes vary with the distance from seawater and pollution. Regarding the weathering reactions, one of the most important is the congruent dissolution of soluble minerals, e.g. gypsum or halite that can load the solution with very high concentration — this is a very important mechanism for recycling evaporites — and the silicate hydrolysis. The alteration of feldspar to clay minerals charges the waters with Na⁺, HCO₃⁻ and silica. Other silicates provide the additional cations Ca²⁺, Mg²⁺ and K⁺ but such waters are always dominated by bicarbonate derived by atmosphere or from soil processes. The increase in Ca²⁺, Na⁺, Mg²⁺ versus HCO₃⁻ from the Pikrolimni/Keratea area (nr. 1,2,3,19) to boreholes (nr. 4 to 16) near Lake Pikrolimni seems to support silicate hydrolysis as the weathering reactions that contribute to the solute load of inflow water. However silicate hydrolysis cannot be the only control on the water chemistry. Moreover, the critical control on the precipitation of trona, in Lake Pikrolimni waters, is the relative amount of Ca²⁺ and CO₃²⁻ and CO₃²⁻ and H₂CO₃, where bracketed symbols refer to concentration) in the water to be evaporated. According to the conceptual model of Hardie–Eugster of evaporites formation (Hardie and Eugster, 1970), the first mineral

Fig. 2. Ternary diagrams of water samples from Pikrolimni area. White diamonds: Mg–HCO₃ groundwaters; white circles: Na–HCO₃ groundwaters; white squares: Ca–HCO₃ groundwaters; black diamonds: Pikrolimni Lake brines.
to form from evaporating water is calcite, and calcite precipitation continues until either Ca$^{2+}$ or CO$_3^{−}$ is exhausted. Waters with a low proportion of CO$_3^{2−}$/TOT relative to Ca$^{2+}$ will be carbonate depleted after calcite formation, and will thus not yield Na-carbonate minerals upon further evaporation. So the elevated alkalinity/[2Ca$^{2+}$] ratio is a main requirement, according to Hardie and Eugster (1970), for the formation of significant quantities of Na-carbonate minerals. Also, according to Hardie and Eugster (1970) the appearance of sepiolite and gypsum determines the evaporative sequence. So, after the sepiolite precipitation the water can become carbonate-enriched and alkaline earth-poor or vice versa. If alkalinity is higher than [2Ca$^{2+}$ + Mg$^{2+}$] then the sepiolite precipitation is not capable to modify the evolution of the solution along the path of alkaline facies (Risacher, 1992). The significantly high proportion of CO$_3^{2−}$/TOT relative to [2Ca$^{2+}$ + Mg$^{2+}$] in Pikrolimni area waters causes them to move along the path, in the Hardie-Eugster model, of alkaline faces, forming Na–CO$_3$ minerals.

However, because the ratio of alkalinity to Ca$^{2+}$ and Mg$^{2+}$ controls the types of evaporite minerals formed, and specially the deposition of trona mineral, it is very important to determine the potential processes that affected the HCO$_3^{−}$ contents in these waters.

### 5.2. Potential processes affected the concentration of HCO$_3^{−}$

There are a number of processes that can affect the HCO$_3^{−}$ contents in groundwater [these waters are rich in HCO$_3^{−}$ (about 1.50–3 g/L)], Eugster (1980) described in detail processes that can affect the concentration of alkalinity in groundwater: dissolution or precipitation of carbonate minerals, chemical weathering of silicates, redox reactions, especially the reduction of NO$_3^{−}$ to NH$_4^{+}$ and SO$_4^{2−}$ to HS$^{−}$, microbial respiration or anaerobic decay and the conversion of CO$_2$ of deep origin to HCO$_3^{−}$ in the aquifer. The dissolution/precipitation of carbonate mineral is a common control of HCO$_3^{−}$ contents in groundwater. These waters show an important over-saturation with respect to calcite (Parkhurst and Appelo, 1999). In Fig. 3a the relationship Ca$^{2+}$ versus alkalinity (HCO$_3^{−}$ + 2CO$_2^{−}$) is shown. For the Mg–HCO$_3$-type waters it is observed that, from Pikrolimni village (Na–HCO$_3$) to boreholes near Pikrolimni Lake (Mg–HCO$_3$), increase of HCO$_3$ contents takes place: the Mg–HCO$_3$ groundwater that was sampled within the Holocene lacustrine sediments of Pikrolimnios has HCO$_3^{−}$ contents higher than 33 mmol/L. It is also observed that the HCO$_3^{−}$ increases with relatively slight change in Ca$^{2+}$, suggesting that carbonate mineral dissolution/precipitation reactions are not an important control on HCO$_3^{−}$. Also the absence of chlorine in the soda and Mg–HCO$_3$ type waters suggest that the dissolution of marine carbonates is not the only source of the carbon. Furthermore, these waters are plotted to the right of the 2(Ca$^{2+}$) = (HCO$_3^{−}$) equilibrium line (Fig. 3a). If the dissolution of the calcite was the dominant process producing CO$_2$ in the system then these waters would plot along the 2(Ca$^{2+}$) = (HCO$_3^{−}$) equilibrium line.

Chemical weathering of silicates is another major influence on groundwater. The Na/HCO$_3$ ratio of dilute Na–HCO$_3$ inflow is very close to unity. When accompanied by the absence of Ca–HCO$_3$ groundwater, this shows that these Na–HCO$_3$ waters do not evolve from Ca–HCO$_3$ groundwater that undergoes normal ion exchange. Therefore the ratio Na/HCO$_3$ very close to unity, suggests that the chemistry of soda water is controlled by simple weathering reactions like Na-feldspars:

\[
\text{Na-AlSi}_3\text{O}_8 + \text{H}_2\text{CO}_3 + 4.5\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{HCO}_3^{−} + 2\text{H}_2\text{SiO}_3 + 1/2\text{Al}_2\text{Si}_5\text{O}_{10}(\text{OH})_2
\]

The hydrolysis of silicate minerals takes place rapidly producing bicarbonate rich water with high silica content (sample Keratea, nr. 21a). Probably this fresh water is from the deep cell of the local groundwater system and probably circulates in the bedrock. On the contrary, the Na/HCO$_3$ ratio of dilute Mg–Na–HCO$_3$ inflow (Fig. 3b) indicates that not only silicate alteration but also more processes are involved in the chemistry of these waters. The correlation between HCO$_3^{−}$ and Mg$^{2+}$ indicates that basic rocks become a major target of weathering reactions in the Mg–HCO$_3$ waters. In summary, as referred by Eugster (1980), the composition of inflow water depends largely on the minerals present in the watershed: basic and ultrabasic rocks are probable to give Mg–HCO$_3$ waters.

Redox reactions are an additional possible control on HCO$_3^{−}$ in particular the reduction of NO$_3^{−}$ to NH$_4^{+}$ and SO$_4^{2−}$ to HS$^{−}$, both of which produce CO$_2$. So, concerning the reduction reactions as a possible control of HCO$_3^{−}$, although Eh was not measured, the high SO$_4^{2−}$ and NO$_3^{−}$ contents in these waters suggest that these reactions are not likely to be occurring.

Also the microbial respiration or anaerobic decay process (potential sources of CO$_2$ that could be converted to HCO$_3^{−}$) appears unlikely to apply significant control on the ground water chemistry because the material that would indicate large accumulation of organic matter in the borehole logs is absent.

The final major reaction that could influence the HCO$_3^{−}$ contents in the deep aquifer is the addition in the system of CO$_2$ of deep origin. The pCO$_2$ values of the most Mg–Na–HCO$_3$ type waters (10$^{−0.5−1}$) are higher than the atmospheric value (10$^{−3.5}$) and the value of the soil (10$^{−2.5−10^{−1.5}}$), suggesting that input of atmospheric/soil is not a major source and evidencing that gas is being added to the aquifer from the deep. The highest values are observed for the Mg–HCO$_3$ type waters emerging in the Holocene lacustrine sediments of Lake Pikrolimni. These waters present also the highest Na$^{+}$, Mg$^{2+}$ and HCO$_3^{−}$ contents, from Pikrolimni area (Pikrolimni Village) to Lake Pikrolimni (borehole near Pikrolimni), suggesting probably that basic mineral hydrolysis driven by injection of deep (mantle or metamorphism source?) CO$_2$ is acting to control the concentration of HCO$_3^{−}$ in the lacustrine basin.
5.3. Brine evolution

The plot of Na⁺, SO₄²⁻, CO₃²⁻, HCO₃⁻ versus Cl⁻ contents of the borehole sample in the thermal spa of Lake Pikrolimni and the domain of brine from Lake Pikrolimni are illustrated in Fig. 4. In these diagrams we also put published data for Lake Natron in Tanzania (Gueddari, 1984) and Lake Magadi in Kenya (Gueddari, 1984), where the natron actually precipitates and for Wadi Natrun which was the natron source in antiquity (Taher, 1999). According to all diagrams, it is concluded that the chemical composition of Lake Pikrolimni’s water is similar to that of the lakes that precipitate natron today. Such solute concentrations support that the evaporative concentration is the dominant process in the chemical evolution of these lake waters. The Na–Cl relation (Fig. 4a) illustrates in general the stability of Na/Cl ratio in the lake brine. The Na/Cl ratio of Lake Natron and Lake Magadi, as well as of Wadi Natrun which was natron source in antiquity, remains stable between diluted waters and concentrated brines. Comparatively to the waters of Lake Natron (Na/Cl ratio = 3.3) and Magadi (Na/Cl ratio = 2), the water of Lake Pikrolimni presents a lower Na/Cl ratio (Na/Cl ratio from 1.2 to 1.7), almost two times. The Na/Cl ratios of Lake Pikrolimni samples, Lake Magadi and Wadi Natrun tend to unity, close to Pikrolimni brines, only in the most concentrate brines (Gueddari, 1984) showing a very small deviation from the evaporative trend (from diluted to brine waters), until within the concentration range appropriate for trona saturation. Once trona precipitates, the Na⁺ extraction from the solution enriches the brine in chloride and thus, Na/Cl ratio decreases. In fact in the diagram log Na/Cl versus Cl (Fig. 4b) the values of diluted waters and brines from Lake Magadi are given as well as the corresponding data from Lake Pikrolimni. As precisely referred by Eugster and Jones (1979), “from groundwaters to all but the most concentrates brines Na/Cl remains constant, because no fractionation occur. The most concentrated brines are saturated with respect to trona and precipitation clearly leads to a decrease in Na/Cl”. In Lake Pikrolimi the most concentrated brine (8/2002) shows a decrease in Na/Cl in relation to the most groundwaters that are related to trona precipitation. Between groundwater and lake brines, a decrease of Ca/Cl, Mg/Cl and HCO₃/Cl ratios is observed (Table 1). Carbonate species are subject to removal from solution by different mechanisms. In Fig. 4c, the greater than 1:1 slope of the regression line for Cl⁻ versus CO₃²⁻ + HCO₃⁻ contents illustrates the gradual loss of carbonate species, accompanying evaporative concentration of Lake Magadi (Jones et al., 1977). The same is observed for the waters from Pikrolimni area. This loss is attributed to equilibration with the atmosphere [2HCO₃⁻ (aq) → CO₃²⁻ (aq) + CO₂ (gas) + H₂O], calcite precipitation from diluted waters [Ca²⁺ (aq) + HCO₃⁻ (aq) → CaCO₃ (sol) + H⁺] and trona precipitation from saturated brine [3Na⁺ (aq) + HCO₃⁻ (aq) + CO₃²⁻ (aq) + 2H₂O → Na₂CO₃, NaHCO₃, 2H₂O (sol)]. In most diluted lake waters, the carbonate loss is probably related to both degassing and carbonate precipitation. Loss to atmosphere is expected for pCO₂ greater than 10⁻³.5 atm (Jones et al., 1977). In fact, in these diluted waters the pCO₂ is lower than 10⁻¹². In the lake brines, the
carbonate loss is probably related to calcium and sodium carbonate precipitation. An additional mechanism is also associated with efflorescent crust (Eugster, 1966). These crusts are the products of complete desiccation of lake water and consist predominantly of soluble salts. When rain or dilute runoff comes in contact with these crusts only the most soluble salts, such chlorides, carbonates and sulfates are resolved into solution and increasing the solute load, while the less soluble phases like the alkaline earth carbonates and silica remain in the crust. The dissolution of these crusts leads to high alkaline water with a specifically lower HCO₃⁻/CO₃²⁻ ratio. The high pH (9.6) of some waters of Lake Pikrolimni (like PL-1/2003) can be attributed to recycling of residual brines (PL-8/2002) from the fresh water. The finding of abundant calcite precipitation in lake beds that are covered by crusts, consisting of trona, burkeite, thenardite and halite minerals, as shown by the XRD analysis (Table 2) of Pikrolimni crusts, shows that the above play a competitive role in the geochemistry processes of Pikrolimni brines. In fact, salt analyses from different parts of the lake showed that they consist of carbonates (calcite, dolomite), trona, burkeite and halite. Salts from Wadi Natrun show similar mineral composition (Shortland et al., 2006).

Indeed, the brines of PL-8/2002 and PL-9/2006 are saturated in halite, thenardite and mirabilite minerals, as shown by the XRD analysis (Table 2) of Pikrolimni crusts, shows that the above play a competitive role in the geochemistry processes of Pikrolimni brines. In fact, salt analyses from different parts of the lake showed that they consist of carbonates (calcite, dolomite), trona, burkeite and halite. Salts from Wadi Natrun show similar mineral composition (Shortland et al., 2006).

In the graph of SO₄²⁻ versus Cl⁻ (Fig. 4d), the molar SO₄²⁻/Cl⁻ ratio indicates generally neither loss nor gain of SO₄²⁻ between diluted and brine waters. The relations SO₄²⁻ versus Cl⁻ suggest a possible incipient precipitation of a sulphate mineral only for PL-8/2002. All the other lake waters indicate an excellent conservative behaviour of sulphate relative to chloride. This also suggests that sulfate reduction is not a major process at Lake Pikrolimni.

6. Geochmical model

6.1. Thermodynamic model for groundwaters and lake water

An ion-specific interaction model based on Pitzer’s equations has been used (EQL/EVP by Risacher and Clement, 2001) to calculate the saturation index versus different solid phases, of the Pikrolimni waters and brines.

The lake brine samples are put in ionic strength diagram versus the saturation index (Fig. 5a, b, c) and in Table 3 the minerals that are supersaturated in the lakes Pikrolimni, Magadi, Natron and Deep Springs are given. The calculation of saturation index versus different carbonate and/or bicarbonate sodium minerals shows that the borehole waters are saturated in calcium minerals. The lake waters are saturated in Na_Ca carbonate minerals and only the lake brines are saturated also in Na–carbonate and bicarbonate, Na–sulfate and Na–chloride minerals.

Table 3 shows that the brines with I>6 are saturated in halite (NaCl), thenardite (Na₂SO₄) and mirabilite (Na₂SO₄·10H₂O) confirming that in such lakes, the Ca–Na–HCO₃ salts precipitate first and the SO₄–HCO₃ salts follow. The results of measurement of Na⁺ and Cl⁻ show indeed that only the saturation in halite, thenardite and mirabilite is achieved.

6.2. Simulation of evaporation of groundwaters

Using geochemical program (EQL/EVP by Risacher and Clement, 2001), it is possible to investigate the mineralogical composition of the minerals that precipitate from the water, with different initial chemical compositions, as they evaporate. All sampled waters from boreholes and the spring were evaporated in order to check if sodium carbonates could precipitate by evaporation of these waters theoretically. As shown in Table 4, most waters can give nahcolite (NaHCO₃) and thenardite (Na₂SO₄) precipitates in the last phase of evaporation. In Table 4, the evaporated samples that can give trona and natron precipitates are shown. In the same table, a diluted water from Lake Pikrolimni (PL-5/2003) is also shown. It is observed that three samples, S/1/2002; b/2/2002; PL-5/2003, give Na–carbonate–bicarbonate minerals [gaylussite Na₂Ca⁺((CO₃)₂⁺5H₂O; pirssonite Na₂2Ca⁺((CO₃)₂⁺2H₂O; trona Na₂CO₃⁺NaHCO₃⁺2H₂O and natron Na₂CO₃⁺10H₂O]. Na–sulfate minerals (burkeite Na₂CO₃⁺2Na₂SO₄; thenardite Na₂SO₄ and Na–chloride minerals [halite NaCl]. Water samples S/1/2002, b/2/2002 and PL-5/2003 give similar minerals with those found by XRD analysis in collected salt samples but also similar minerals referred in literature (Shortland et al., 2006; Taher, 1999; Gueddari, 1984). However, only the water sample coded S/1/2002 and b/2/2002, Na–HCO₃ type, could give natron and trona.

Fig. 6 shows the results of S/1/2002 sample when the initial chemical composition of this water was modeled. As it can be seen, as the water is concentrated about 250 times of the initial chemical composition, the first Na–carbonate mineral, gaylussite, deigns to precipitate. After a concentration of 395 times of the initial chemical composition, natron, pirssonite, and mirabilite precipitate. The gaylussite and the pirssonite are among the first salts that precipitate and their formation is related to calcite. The gaylussite [Na₂Ca⁺((CO₃)₂⁺5H₂O] generally forms by the reaction of primary calcite (CaCO₃) and the sodic carbonate solution, according to the reaction

\[
\text{CaCO}_3 + 2\text{Na} + \text{CO}_3^- + 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{Ca}⁺((\text{CO}_3)₂⁺5\text{H}_2\text{O})
\]

The pirssonite is usually found in the presence of gaylussite or of calcite crystals. The direct precipitation of pirssonite takes place according to the reaction

\[
\text{Na}_2\text{Ca}⁺((\text{CO}_3)₂⁺2\text{H}_2\text{O}) + 2\text{Na} + \text{Ca} + 2\text{CO}_3^- + 2\text{H}_2\text{O}
\]

Secondarily, pirssonite forms either by the dehydration of gaylussite or by the reaction of Ca–Na solutions with calcite according to the following equations

\[
\text{Na}_2\text{Ca}⁺((\text{CO}_3)₂⁺5\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{Ca}⁺((\text{CO}_3)₂⁺2\text{H}_2\text{O} + 3\text{H}_2\text{O}
\]

Table 2

<table>
<thead>
<tr>
<th>Lake Pikrolimni 2002</th>
<th>Wadi Natrun</th>
<th>Lake Natron, Tanzania</th>
<th>Lake Magadi, Kenya</th>
<th>The Deep Springs Lake, California</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (CaCO₃)</td>
<td>Dolomite (Ca,Mg)CO₃</td>
<td>Dolomite</td>
<td>Calcite (CaCO₃)</td>
<td>Calcite (CaCO₃)</td>
</tr>
<tr>
<td>Trona (Na2CO₃⁺NaHCO₃⁺2H₂O)</td>
<td>Trona (Na2CO₃⁺NaHCO₃⁺2H₂O)</td>
<td>Pirssonite Na₂Ca⁺((CO₃)₂⁺2H₂O</td>
<td>Pirssonite Na₂Ca⁺((CO₃)₂⁺2H₂O</td>
<td>Trona (Na2CO₃⁺NaHCO₃⁺2H₂O)</td>
</tr>
<tr>
<td>Burkeite (Na₂CO₃⁺2Na₂SO₄)</td>
<td>Burkeite (Na₂CO₃⁺2Na₂SO₄)</td>
<td>Burkeite (Na₂CO₃⁺2Na₂SO₄)</td>
<td>Burkeite (Na₂CO₃⁺2Na₂SO₄)</td>
<td>Burkeite (Na₂CO₃⁺2Na₂SO₄)</td>
</tr>
<tr>
<td>Thenardite (Na₂SO₄) not detected in 2006 salt</td>
<td>Thenardite (Na₂SO₄)</td>
<td>Thenardite (Na₂SO₄)</td>
<td>Thenardite (Na₂SO₄)</td>
<td>Thenardite (Na₂SO₄)</td>
</tr>
<tr>
<td>Halite (NaCl)</td>
<td>Halite (NaCl)</td>
<td>Halite (NaCl)</td>
<td>Halite (NaCl)</td>
<td>Halite (NaCl)</td>
</tr>
</tbody>
</table>


The precipitates than halite: trona (50%) and natron (14%) represent.

Trona are the more abundant precipitates. Trona is more abundant in

1200, halite begins to precipitate. When the models stop, halite and

ates. Much later, when the water is concentrated by about a factor of

initial chemical composition, burkeite and trona precipitation initi-

–

triangles: nahcolite; x: gaylussite; •: pirssonite; white diamonds: natron; black

⁎

ionic strength (logarithmic). White

versus

ð

CO3

2

2H2O

↔

Na2Ca

⁎

aversions as the dominant process in the chemical evolution of these lake

waters that have high proportions of Na⁺ and HCO₃⁻. The derived high

Na⁺ and HCO₃⁻ contents are due to silicate hydrolysis. The computing

program has shown that the dilute spring inflow was concentrated (by

the assumption of Cl⁻ conservation in solution throughout evaporation)

about 12000 times to obtain the most saline residual actual lake water,

The Na/Cl ratio in Lake Pikrolimni supports evaporative concentra-

tions every year, a fact that is due to the weather (temperature, humidity, precipitation). Therefore, the collection would have been
taking place only during particularly hot and dry summers.

7. Conceptual model

The Na/Cl ratio in Lake Pikrolimni supports evaporative concentra-
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about 12000 times to obtain the most saline residual actual lake water,
the way of increasing the solute load of the groundwater. Precipitation and re-solution inevitably lead to strong segregation of the initial solutes. Therefore, sorption ion exchange and reduction reaction on mineral surface may also remove certain solute.

### 8. Conclusions

Lake Pikrolimni is a saline lake that is characterized by alkaline brine, poor in Ca\(^{2+}\) and Mg\(^{2+}\). The dilute HCO\(_3\) spring fresh water (<0.2 g/L dissolved solid) evolves into alkaline Na–Cl (CO\(_3\)\(^{2-}\) SO\(_4\)\(^{2-}\)) brine (>350 g/L dissolved solid). Such brines show a considerable range in ionic composition and concentration. High solute concentration due to solar evaporation of water, mineral precipitation, fractional dissolution and solute recycling are the main processes responsible for these brines formation. In particular, these evaporating conditions were such that incurred a hydrogeochemical environment that was responsible for the lake to provide, in dry periods, “nitrum chalestricum” (trona). Besides, the progressive concentration of brines in alkaline lakes leads to a preferential precipitation of sodium carbonate followed by sulfates and chlorides. This conclusion comes in agreement with the results. Also, the mineralogical analysis (X-Ray Diffraction of salts), the evaporation simulation and the thermodynamic model showed that salts of trona, burkeite and halite, deposit from these brines. So, the conditions that are responsible for the formation of soda seem to be present in the basin and confirm Pliny’s description.

#### Table 3
Thermodynamic calculation model: sequence of minerals precipitation.

<table>
<thead>
<tr>
<th></th>
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<td>Calcite (CaCO(_3))</td>
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<td>Calcite (CaCO(_3))</td>
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<td>Dolomite [Ca(Mg)CO(_3)]</td>
<td>Dolomite [Ca(Mg)CO(_3)]</td>
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<td></td>
<td>Calcite–Mg [Ca(Mg)CO(_3)] Dolomite (MgCO(_3))</td>
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<td>Gaylussite [Na(_2)Ca(^{+})]</td>
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<td></td>
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<tr>
<td>(CO(_3)(^{2-}) 5H(_2)O)</td>
<td>(CO(_3)(^{2-}) 5H(_2)O)</td>
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<td></td>
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<tr>
<td>Pirsonite [Na(_2)Ca(^{+})]</td>
<td>Pirsonite [Na(_2)Ca(^{+})]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(CO(_3)(^{2-}) 2H(_2)O)</td>
<td>(CO(_3)(^{2-}) 2H(_2)O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nacolite [Na(_2)HCO(_3)]</td>
<td>Nacolite [Na(_2)HCO(_3)]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Trona (Na(_2)CO(_3) NaHCO(_3) 2H(_2)O)</td>
<td>Trona (Na(_2)CO(_3) NaHCO(_3) 2H(_2)O)</td>
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</tr>
<tr>
<td>Gypsum (CaSO(_4) 2H(_2)O)</td>
<td>Gypsum (CaSO(_4) 2H(_2)O)</td>
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<tr>
<td>Mirabilite (Na(_2)SO(_4) 10H(_2)O)</td>
<td>Mirabilite (Na(_2)SO(_4) 10H(_2)O)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Thenardite (Na(_2)SO(_4))</td>
<td>Thenardite (Na(_2)SO(_4))</td>
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</tr>
<tr>
<td>Halite (NaCl)</td>
<td>Halite (NaCl)</td>
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</tbody>
</table>


#### Table 4
Simulation of evaporation of groundwater.

<table>
<thead>
<tr>
<th>Label</th>
<th>Minerals</th>
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</thead>
<tbody>
<tr>
<td>S/1/2002</td>
<td>BURKEITE_CALCITE_GAYLUSSITE_GLASERITE_HALITE_MAGNESITE_MIRABILITE_NATRON_PIRSONITE_TRONA</td>
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<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Fi/5/2003</td>
<td>HALITE_PIRSONITE_THENARDITE_TRONA</td>
</tr>
</tbody>
</table>

In each line, the list of minerals corresponds to the whole sequence of precipitated minerals during concentrative evaporation.

Fig. 6. Minerals molarity versus concentration factor.
Table 5
Chemical composition (mmol/L) of the residual water, after evaporation, when the models stop.

<table>
<thead>
<tr>
<th>Label</th>
<th>CF</th>
<th>alk</th>
<th>Cl</th>
<th>SO₄</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>TDS</th>
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<tr>
<td>S/1/2002 chemical composition</td>
<td>1230</td>
<td>1913</td>
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<td>0</td>
<td>0.02</td>
<td>455,699</td>
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<tr>
<td>b/2/2002 chemical composition</td>
<td>6850</td>
<td>1057</td>
<td>4510</td>
<td>780</td>
<td>6320</td>
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Testimonia

Testimonium 3. Etymologicum Magnum, Halastri.

Acknowledgements

The authors would like to express their gratitude to Mr. Aggelakis for his help during sampling sessions as well as to Dr. Risacher F. and Dr. Fritz B. for their contribution of the geochemical program EQL/EVP. Finally, special thanks go to the two unknown reviewers for their ready contributory remarks and suggestions of the manuscript and to the editor of this journal for his helpful guidance.

References