Chemical and isotopic characterization of the thermal fluids emerging along the North–Northeastern Greece

E. Dotsika1,2, P. Dalampakis3, E. Spyridonos4, G. Diamantopoulos1, P. Karalis1, M. Tassi1, B. Raco2, A. Arvanitis5, N. Kolios6 & J. L. Michelot7

Hydrochemical and isotopic characteristics of fluids from major geothermal fields of middle/low temperature in N/NE Greece are examined (basins: Strymon River (SR), Nestos River Delta (ND), Xanthi–Komotini (XK), Loutros–Feres–Soufli (LFS) and Rhodope Massif). The geodynamic context is reflected to isotopic/chemical composition of fluids, heat flow values and elevated CO2 concentrations in emitted fluids. B and Li are derived from leaching of the geothermal systems hosting rocks. δ18O H2O, δ18O SO4, δ13C CO2 values and chemical compositions of Cl, B and Li of geothermal discharges suggest two distinct source fluids. Fluids in SR exhibit high B/Cl and Li/Cl ratios, suggesting these constituents are derived from associated magmas of intermediate composition (andesitic rocks). Geothermal discharges in LFS exhibit low B/Cl and Li/Cl ratios, implying acid (rhyolitic) magmatism. δ13C CO2 and CO2/(CO2 + 105He) ratios in the west part, suggest fluids affected by addition of volatiles released from subducted marine sediments. For the eastern systems, these ratios suggest gas encountered in systems issued from mixing of crustal and mantle-derived volatiles. Isotopic geothermometers reflect, for the same direction, equilibrium processes more (LFS, XK) or less (SR) pronounced and discriminate the geothermal field from low to middle [SR, ND (Erasmio)] and middle to high enthalpy [ND (Eratino), LFS, XK].

Isotope geochemistry, has greatly contributed in understanding geothermal systems since chemical and isotopic composition of geothermal fluids provides information on their origin, recharge areas, flow patterns, water–rock interaction processes and geothermal reservoir’s deep temperature1,2.

Geothermal systems with low to high enthalpy are present in North and Northeastern Greece. The wider region (Fig. 1) is extending between the Strymon River in the West and the Evros River in the East (Greek–Turkish borders). The hydrothermal area include Traianoupolis, Fylakto–Tycher (Loutros–Feres–Soufli basin, [LSB]), Nea kessani [Xanthi–Komotini basin (XK)], Erasmio and Eratino [Nestos Delta basin (ND)] and Nigrita–Therma, Sidiokastro, Iraklia, Agistro, Achinos–Iriva and Akropotamos [Strymon River basin (SR)] thermal springs. These thermal waters have been well-known since antiquity. Today, they are mainly used for green-house heating and hydrotherapy. The temperature of these water springs, which present low to high-salinity, ranges from 30° to 80 °C. Please refer to Supplemental material for more information of the study areas.

The thermal exploration of the area began in the 1970’s with an investigation carried out by I.G.M.E. (Institute of Geology and Mineral Exploration). During this stage, the well of Fylakto–Tyche [Loutros–Feres–Soufli basin, (LSB)], Nea kessani [Xanthi–Komotini basin (XK)], Erasmio and Eratino [Nestos Delta basin (ND)] and Nigrita–Therma, Sidiokastro, Iraklia, Agistro, Achinos–Iriva and Akropotamos [Strymon River basin (SR)] thermal springs. These thermal waters have been well-known since antiquity. Today, they are mainly used for green-house heating and hydrotherapy. The temperature of these water springs, which present low to high-salinity, ranges from 30° to 80 °C. Please refer to Supplemental material for more information of the study areas.

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1Stable Isotope Unit, N.C.S.R. "Demokritos", 15310 Ag. Paraskevi, Attikis, Greece. 2Institute of Geosciences and Earth Resources, C.N.R., Via G. Moruzzi 1, 56124 Pisa, Italy. 3Hellenic Agricultural Organization - Demeter, Soil and Water Resources Institute, Sindos, Greece. 4PPC Renewables S.A, 15343 Ag. Paraskevi, Attikis, Greece. 5Hellenic Survey of Geology and Mineral Exploration GR, Acharnes, Greece. 6Institute of Geology and Mineral Exploration (IGME), Thessaloniki, Greece. 7CNRS, Géosciences Paris Saclay (GEOPS), Université Paris Saclay, Orsay, France.

*email: e.dotsika@inn.demokritos.gr
relatively elevated heat flow regime and the subsequent presence of geothermal aquifers with low water temperatures ranging between 30 and 45 °C at depths 400–500 m. On the contrary, on the western margin of the basin and most precisely in the area of Nea Kessani–Xanthi, the main hot reservoir is found at shallow depths (150–400 m) with water temperatures ranging from 75 to 82 °C. In Nestos Delta basin the maximum depth of the 22 exploration boreholes drilled by I.G.M.E. reaches 500 m. The values of the geothermal gradient are very high (up to 25 °C/100 m). The water temperatures range from 40 to 72 °C. The geothermal gradient for the Strymon basin has been estimated to fluctuate from 25 to 36 °C/km at depths over than 2000 m.

The geochemical characteristics of these thermal waters have already been investigated in few studies. Especially, the chemistry of thermal springs has been investigated in various studies and are focused on in the N. Kessani–Evros area. Dotsika et al. elucidated also the isotopic characteristics of thermal water discharges in the Northern and Northern Eastern Greece. The comprehensive investigation by Dotsika et al. provided also, except from chemical and isotopic data (δ2H and δ18O of H2O, δ34S) the application of isotopic geothermometers for these thermal waters.

Therefore, until now, no systematic chemistry and isotopic research has been undertaken on these geothermal waters, low to high enthalpy, which emerge from coastal to volcanic rocks, in order to define the geothermal model of this region. In high enthalpy geothermal systems, the dominated theory for the origin of water was that the thermal fluids were of magmatic and/or juvenile origin and not of meteoric origin. However, through the measurements of the stable isotopes of water and steam of well-known geothermal fields, was proven (Craig, 1963) that the origin of thermal waters could be of meteoric origin. The positive shift of δ18O of thermal water of meteoric origin is attributed to exchange between the water and the reservoir rocks, showing the high temperature of this thermal environment. However, for many water types in Greece, a shift not only in δ18O but also in δD is observed, indicating mixing of local groundwater with marine or magmatic or metamorphic water. The high mobile constituent chloride, which are typically found in most deep aquifers, especially in Na-Cl type waters, are generally attributed to direct seawater intrusion, particularly near the coastal zones and modified seawater.

Additionally, the correlations among δ18O, δD, δ34C and mobile specie are particularly important tools used in geochemical investigations, both to detect processes of liquid–vapor separation, absorption of magmatic gases in groundwater, mixing processes and to provide information on water origins. Especially, the δ18O–δD–δ34C isotope composition of cold ground waters is mainly affected by recharge altitude and mixing of different fluids, while in deep aquifers, isotopic values are governed by the water–rock interaction, mixing and boiling (vapor separation). The δ18O and δ34S values of dissolved inorganic carbon and sulphate in thermal and cold waters are used to identify the provenance of CO2, sulphate participation of marine origin, mixing of sulfates of different origin (marine sulfate, sulfates resulting from sulfur oxidation and from dissolution of sulfur of deep rocks).

In this study the stable isotopes of water (δD, δ18O), carbonate (δ13C), sulfate (δ34S, δ18O) values with the chemical solutes, major and minor (Br, Li, B) ions, are used in order to identify the possible origin of thermal
water as well as the possible procedures responsible (ex. water–rock interaction processes) for the alteration of the initial composition of these waters and to allows one to reconstruct the conceptual geochemical model of the investigated area. The use of isotopic and chemical geothermometers will provide also an estimation of the temperature of the deep geothermal fluids.

**Geological framework.** The geological evolution of North Eastern Greece is related to the Late Cretaceous closure of the Vardar Ocean when subduction related magmatism developed in the Eastern European margin causing the consumption of different portions of Tethys Ocean (e.g., Stampfli and Borel 2004)\textsuperscript{12}. It belongs mainly to the crystalline mass of the Rhodope Massif. Parts of this area belong to the Circum-Rhodope belt (southern and northeastern Evros area) and to the Serbomacedonian massif (western part of the Strymon basin)\textsuperscript{4}.

**Results and discussion**

**Hydrochemistry.** Chemical data and isotopic values are reported in Supplemental Table S1. Water samples have been analyzed for the major elements, lithium, boron and silica (Table S1 of the supplemental material). On the basis of the Cl contents, they may be categorized as follows:

- **Low Chloride waters: < 200 mg/l** This group includes the thermal waters of SR (NIG, SID, AGS, ACH and IRA), ND (ERA) and LFS (FYL) basins. Their temperature ranges from 18 to 62 °C. The relatively low concentration of Cl\textsuperscript{−} excludes the marine participation (Fig. 1).

- **High Chloride waters: > 200 mg/l** This group includes the thermal waters of SR (AKR and ELF), XK (KES, POT), LFS (ARS, TRA, FYL), ND (ERA, MYR, ERC) basins. Their temperature ranges from 51 to 92 °C. The relative ratios between Cl–HCO\textsubscript{3}–SO\textsubscript{4} and the main cations Na–Ca–Mg are displayed in the ternary plots (Fig. 2) for all water samples (thermal, cold and seawater). In general, the two ternary plots show that the thermal waters have Na–Cl composition and are situated in the Cl–Na corner while the fresh waters are plotted close to the HCO\textsubscript{3} corner.

Based on Cl\textsuperscript{−} contents it appears that the marine participation for the analyzed samples varies considerably. In order to identify the origin of chloride in this geothermal system, Cl\textsuperscript{−} and Br\textsuperscript{−}\textsuperscript{1,2,11,13–15}. The Cl/Br ratio of some high chloride samples, plotted on the seawater dissolution line, displays values ranging between 259 and 303, which are quite close to that of seawater 320. This correlation, Cl\textsuperscript{−} versus Br\textsuperscript{−}, was used in order to determine the marine contribution in samples, assuming that this contribution originates from a marine component. The marine contribution calculated from O–H–Cl and Br in the deep geothermal systems varies considerably between the samples, showing that the boron concentration of these waters originates from both marine and water interaction in high temperature environments (Table S3 of the Supplemental material).

In the diagram Cl\textsuperscript{−} versus B (Fig. 3a), the correlations between B and Cl\textsuperscript{−} suggest a different origin for both elements. The ideal mixing line between seawater and fresh water (seawater dilution line, SWDL) suggests that Cl\textsuperscript{−} and B derive from seawater, as both Cl\textsuperscript{−} and Br\textsuperscript{−} contents showed, which is more or less diluted by fresh water and subsequently the supply of these ions by rock leaching is negligible. The majority of the other analyzed thermal waters show very variable concentrations of B (B = 0.05–11 mg/l), which is probably related to the high temperature leading to enhanced water–rock interaction and leaching of boron. Two distinct groups are observed: the thermal waters of the first group, area A, show boron concentrations between 0.05 and 7 mg/l. They exhibit high temperature (T = 30–62 °C) and Cl\textsuperscript{−} concentration less than 250 mg/l. The samples of this group are come from the SR basin [Nigrita (NIG), Sidirokastro (SID) and Iraklia (IRA)]. Moreover, the B/Cl and Li/Cl ratios (and Br/Cl, Cation/Cl) of most of these waters are different from those of the seawater (the B/Cl ratio of sea water sample is 2 × 10\textsuperscript{−4}) suggesting a non-marine origin of the B and Li.

The thermal waters of the second group show similarly very variable concentrations of B (B = 1–11 mg/l), which is related to the very high temperature (T = 50–92 °C). The high B/Cl ratio, (area B, Fig. 3), for these thermal waters, SR basin [Akropotamos (AKR)], ND basin [Eratino (ERC)], XK basin [Nea Kessani (KES) and LFS basin [Traianoupolis (TRA), Aristino (ARS)] show a variability, about 3 times more than that of seawater,
indicating that the excess of B can probably be of marine sedimentary origin. Apart from boron, these waters (second group plus the AKR thermal water) are also rich in Li+ especially the thermal waters of Nea Kessani (KES), Aristino (ARS) (the Li/Cl of ARS is 163 times greater than that of seawater) and Eratino (ERC), suggesting that water–rock interaction adds lithium and boron contents to this these thermal waters.

The condensation of CO₂ geothermal gas enhances the influence of thermal water and thus the water–rock interaction process (the HCO₃⁻/Cl ratios of most of the thermal waters analyzed are higher than those of the seawater, see Fig. 3b). The observed HCO₃⁻ in the thermal spring waters of SR (especially in Nigrita) and XK (Nea Kessani) basins is high compared to the respective fresh waters (Fig. 3b). This suggests that these thermal waters are enriched in HCO₃⁻ (Fig. 5), probably through the absorption of CO₂ bearing gases or by the condensation of CO₂ of geothermal steam. In Fig. 3b we observe a gradual increase of Cl⁻ contents of the other samples. This indicates the participation of the Cl⁻ component in the deep geothermal system. For most of the thermal waters the Mg/Cl ratios are lower compared to the marine ones, a fact that indicates the interaction of the waters housed in deep volcanic formations (under high temperatures and CO₂ pressures). In such environment, the Mg²⁺ is incorporated into secondary alteration minerals by ion exchange reaction¹⁶ stripping the solution of its Mg²⁺ contents. The cation–Cl ratio and the gradual increase of Cl⁻ content indicate that these waters are mixed with a deeper geothermal fluid that probably contains water of marine origin. Furthermore, the Li/Cl and B/Cl ratios of most thermal waters are much higher than those of sea water which indicates major secondary processes during the water circulation in deep hot reservoirs. In addition, the K/Cl, Na/Cl and Ca/Cl, ratios of most thermal waters are higher compared to those of seawater, thus confirming that their salinity is controlled by water–rock interactions.

**Origin of lithium and boron.** The Cl⁻, B and Li⁺ contents in fresh and geothermal waters, areas A and B (Fig. 3a, Cl vs B), as mentioned before, can be attributed to water–rock interaction (mainly for B and Li⁺) and to marine participation into the geothermal field (mainly for Cl⁻). The water of meteoric origin has a Cl⁻/B ratio equivalent to that of seawater because these elements are originating from seawater spray and aerosols. When this water absorbs heat through deep convection, B is dissolved stoichiometrically from the surrounding rocks. The B should be removed from sediments and transferred easily to the submerged fluids; however the transfer of Li from rock requires intense water–rock interaction at high temperatures¹⁷. Li/B ratio of the thermal water shows wide variability from 0.09 to 1.0, which probably reflects the effects of secondary processes such as leaching of Li from terrigenous materials, in high environment temperature.

As a result, the Cl/B and Cl/Li ratios of the water are getting lower than those of seawater because rocks are rich in B and Li. B and secondarily Li⁺ are present in significant amounts in igneous rocks, with their average crustal abundances close to 10⁻⁴₅ ppm and 6⁻¹⁷ ppm, respectively¹⁷–¹⁹. During the evolution of rock dissolution, the aqueous Cl/B and Cl/Li ratios in thermal waters are gradually approaching the rock ones, due to rock weathering. Hence, water–rock interaction adds a significant amount of B and Li to geothermal waters, but only a very limited amount of Cl⁻, since rocks do not contain important quantities of Cl⁻ (except from evaporites). Consequently, all thermal waters exhibit Cl/B and Cl/Li ratios lower than seawater (SW). However, the thermal waters of Eratino (ND) and Aristino (LFS) exhibit Cl/B ratio lower than seawater but higher than the rest of the analyzed thermal waters. The B excess with respect to Cl in these thermal waters, is due to the contribution of seawater (Fig. 4a Cl vs Cl/B). When the contribution of seawater is important, geothermal water similar to that encountered in the Eratino and Aristino fields (80–99 °C with Cl > 200 mg/l) is susceptible to be generated.

In Fig. 4a three members are distinguished: fresh water (sea water dilution line), thermal water of meteoric origin (Cl < 200 mg/l) and thermal water by mixing (either with marine or meteoric water). Thus, the potential source of B in the study area is related mainly to the recharge of meteoric water and to the interaction of water with the aquifer matrix. Marine contribution represents only minor localized contributions of B. The same observations are also valid for Li contributions. Furthermore, the Li/B ratio of thermal waters shows wide variability.

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**Figure 3.** (a) Cl⁻ versus B for the studied areas. Area A (mixing between cold water and deep thermal water of SR), area B (mixing between cold water and deep thermal water of XK, LFS,) and line C (seawater dilution line-SWDL). (b) HCO₃⁻ versus Cl⁻ of the thermal waters for the studied areas. The shaded part of the graph indicates the mixing between fresh water of the area and marine water.
(0.001–1), typical of waters encountered in geothermal systems. The high Li/B ratio of Eratino, Aristino and Nea Kessani fields also exhibits wide variability from 0.4–1 to 0.3–0.67 respectively, typical of waters discharged from volcanic systems. The Li/B ratio of Nigrita (0.06–0.4), Akropotamos (0.08–0.4) and Loutra Elefteron (0.4) thermal waters are also in the range of volcanic systems. The maximum Li/B ratio is observed in Aristino and Nea Kessani geothermal fields. The intensity of the water–rock exchange depends, among other parameters, on the relative proportions of water and rocks, on the surface area and the duration of the contact. This variation observed from Nigrita to Nea Kessani and Aristino fields is consistent with the tensional tectonic regime and the water age that both increase from west to east. Probably the supply of B+ and Li+ ions by rock leaching removal process is compatible with geothermal fluids alteration occurring in the crustal zone during emerging and resurfacing of the waters. In order to evaluate the nature of the hosting rocks all data points and the ratios of Andesitic and Rhyolitic rocks are shown in Fig. 4b.

In Fig. 4b, the distribution of all data points supports the above classification into two distinct groups, based on chloride contents: a high 50*B/(50*B + Cl) (~ 1), Cl-rich thermal water, as represented by Aristino and Nea Kessani, and a low 50*B/(50*B + Cl) (< 0.4), as represented by Nigrita. The other sites occupy intermediate positions. Possible source of both B and Li ions by rock leaching removal process is compatible with geothermal fluids alteration occurring in the crustal zone during emerging and resurfacing of the waters. In order to evaluate the nature of the hosting rocks all data points and the ratios of Andesitic and Rhyolitic rocks are shown in Fig. 4b.

Isotope analysis. Origin of CO₂ gases. To evaluate the CO₂ origin, the δ¹³C of thermal waters was analyzed. The δ¹³C reflects the different origin of CO₂ gas and DIC that can be related to the atmosphere, geological processes, lithology and other exogenous sources.
In shallow carbonate aquifers, the $\delta^{13}C_{\text{DIC}}$ in groundwater ranges between −10 and −22‰ (Please refer to Figure S2 of the Supplemental material), indicating mixing processes between soil—CO$_2$ ($\delta^{13}C$ value around −22‰, C3-temperate climate) and CO$_2$ produced by carbonate water–rock interaction ($\delta^{13}C$ $\delta^{13}C = −2$ to 1‰)$^{20,21}$. In silicate aquifers the chemical reactions that took place during the deep circulation of water in this hydro-geological system produce an insignificant shift in $\delta^{13}C_{\text{DIC}}$ producing water with $\delta^{13}C_{\text{DIC}}$ that ranges between −22 and −8‰.

For groundwater that circulates in deep aquifers with long residence time, the carbon chemistry results from mixing procedures between: (1) deep CO$_2$ with $^{13}C$ value between −8 and 3‰; (2) CO$_2$-gas from atmosphere (3) biogenic CO$_2$ with $^{13}C$ value between −10 and −22‰ and (4) mineral C with $^{13}C$ content at +0‰ (Fig. 4a). In such aquifers, the carbon mass balance is related to the rate of water–rock interactions under high temperature and to fractionation factors. In nature, this is represented with $\delta^{13}C_{\text{DIC}}$ contents around −8‰$^{22}$. The geochemical processes, which can produce large amounts of deep origin CO$_2$, are associated with magmatic-volcanic fluids, thermal or metamorphic decarbonation of carbonate rocks (limestones) and diagenesis of organic sediments. The $\delta^{13}C_{\text{DIC}}$ values of gas originating from earth mantle emanations range between −4 and −8‰$^{23,24}$. The marine limestone, with $^{13}C$ value between −2 and 1‰, metamorphism produces $\delta^{13}C_{\text{CO}_2}$ about 0‰ ± 3‰$^{20,23}$, while the gas originating from the thermal decomposition of crustal carbonate rocks has values between −4 and 0‰$^{25}$. The carbon originating from diagenesis of organic sediments shows $\delta^{13}C_{\text{DIC}}$ around −30‰$^{21}$ (Fig. S2 of the Supplemental material & Fig. 5a).

The $\delta^{13}C_{\text{DIC}}$ values of the collected thermal waters range from 9 to −12‰ (Fig. 5a). In order to assess the system in which the C evolves and to better discuss the carbon origin in conjunction with the relationship of magmatic versus crustal contribution, a calculation of $\delta^{13}C$ of the gaseous phase in equilibrium ($^{13}C_{\text{DIC}}$ eq) with measured DIC has been carried out using adequate equation and the fractionation factors$^{26}$. The calculated $\delta^{13}C_{\text{DIC}}$ contents of the CO$_2$ in equilibrium with the DIC vary between −19.7 and 0‰. Daskalopoulou et al. (2016) $^{27}$ measured the $\delta^{13}C$ of CO$_2$ contents from the Rodope massif with values very similar to those computed.

Considering that the isotopic value of gas of deep origin originating from earth mantle emanations ($\delta^{13}C$ values around −6‰) and the gas originating from "crustal", thermal or metamorphic decarbonation of limestones, ($\delta^{13}C_{\text{DIC}}$ values close to 0‰±3‰) the thermal waters from Sidirokastro (−6.3‰), Potamia (−4.9‰), Aristino (−8.0‰), Erasmeio (−8.0‰) Agistro (−8.0‰) and Therms (−6.5‰) produce results of $\delta^{13}C$ typical of magmatic source. In the case of Nigrita (0.2‰), Loutra Elefteron (−1.0‰) and Nea Kessani (0‰) fields, the carbon source could be associated to "crustal" component, thermal or metamorphic decarbonization of limestone, (Fig. 5b). Conversely, the carbon source of the samples from Erasmeio12 (−19.7‰), Eratino (from −19.4 to −17.6 ‰), and Traianoupolis (−15.6‰) indicate that carbon reflects organic contribution.

**Stable isotopes of water.** The stable isotopic composition ($\delta^2H$ versus $\delta^{18}O$) of all waters is shown in Fig. 6$^{28,29}$. Some waters samples from Nigrita and Sidirokastro geothermal fields are localized in the group of fresh waters along the Local Meteoric Water Line for Greece (LMWL)$^{30}$ (Fig. 6), indicating a meteoric origin without the participation of seawater, as it is concluded by the geochemical analysis. Contrary, the points representative of the SR basin (Akropotamos) and respectively those of ND basin (Eratino, ERC-4 and 8) are slightly shifted to the right of the LMWL and fall to the line that represents an ideal mixing between seawater and local fresh water. This is originated through dilution and addition of local groundwater to a deep, hot geothermal liquid of marine origin. The majority of these samples have been plotted onto the mixing line confirming the ratios of sea water participation as calculated by Cl contents (Table S2 of the Supplemental material). However, the mixing

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**Figure 6.** $\delta^{18}O$ versus $\delta^2H$ of the thermal waters for all studied areas. The black solid line is the Global Meteoric Water Line. The blue dash-dot line is the Local Meteoric Water Line ($\delta^2H = (8.7 \pm 0.44) \delta^{18}O + 19.5 \pm 3.1$) and the red dash line is the Meteoric Water Line of Thrace ($\delta^2H = (7.39 \pm 0.37) \delta^{18}O + 7.9 \pm 3.0$).
between the SR (Akropotamos) and ND (Eratino) basins thermal fluids and seawater is favored by the location of the waters discharge on the shoreline. The occurrence of this process is also confirmed by $^{18}$O and Cl contents (Table S2 of the Supplemental material).

The points representing the thermal water from Nea Kessani fall to the right of a ‘mixing’ point resulting from mixing between fresh and marine water. The deuterium content of these thermal waters is $-50 \pm 1$‰, as expected for waters originating from the mixing of cold ($-53$‰ (samples KES-6; KES-7), at about 95%) and sea water (4‰, at about 5%). Nevertheless, their $^{18}$O value ranges from $-6.2$ to $-6.4$‰, which is significantly different from what is expected [$-8.2$‰ (samples KES-6; KES-7)] from the above mixture percentages. Also, the $^{18}$O content of the Nea Kessani thermal water is below the LMWL indicating significant $^{18}$O enrichment with respect to “mixing” water and suggesting an isotopic exchange with the rocks of the geothermal reservoir. In order to approach the isotopic equilibrium state, between water and rocks, corresponding to the temperature of the geothermal reservoir, we consider that the liquid phase is enriched in oxygen isotope. This process affects only the oxygen, because the Deuterium content of rocks is too low to significantly modify the isotopic composition of thermal fluids. The horizontal line that deviates from the mixing point and plotted in the mixing line between fresh and marine water, to higher $^{18}$O values ($-6.2$% to $-6.4$‰), represents an ‘oxygen shift’ caused by the previously mentioned water–rock interaction process. This positive oxygen shift, at least of 1.5‰, seems to occur in areas of high thermal potential of the geothermal reservoir. A similar oxygen-sift is compatible with water–rock interaction at high temperatures (200 °C). The existence of high temperature in the geothermal reservoir is also supported by the high Li (and B) content, since the Li transfer from reservoir rocks requires intense water–rock interaction at high temperatures. This Li/B variability probably reflects intermediate maturation steps towards the composition of average reservoir rocks. All the used geothermometers show such high temperatures at Nea Kessani area.

This isotopic enrichment is also observed in the thermal waters of LFS and ND (ERA-9), although these waters are the result of a mixture of sea and meteoric water (Table S3 of the Supplemental material). So their representing points would be expected to be on the marine dilution water line and that they would not be shifted to the right (in respect of the dilution water line). Their shift to the right, which isn’t so pronounced in relation to Nea Kessani, is attributed also to water–rock interaction at relatively high temperatures. Their Li and B contents are also in favor of this case.

Stable isotope of sulfate. The $^{34}$S and $^{18}$O contents of the analyzed samples (Table S2 of the Supplemental material) are compared to those of marine sulfate ($^{34}$S = 20.1‰ CD and $^{18}$O = 9.3‰ SMOW)30. In contrast, the isotopic ratios of sulfates in rain-water are dependent on their origin (the isotopic ratios of rain-water show a variability between 5 and 17‰ for $^{18}$O31 and $-2.5$ to $19.5$‰ for $^{34}$S32).

The $^{34}$S and $^{18}$O values of all thermal waters are very different to those of marine sulfate. The water samples from Nigrita, Sidirokastro, Agistro, Thermes, Potamia and Nea Kessani are of meteoric origin, without any significant participation of seawater, while the waters from LFS basin (Aristino and Traianoupolis) show a marine participation lower than 25%. Whatever the origin of water is, the $^{18}$O values (1.5 to 7.5‰) of the thermal waters are very different from those of marine sulfate ($^{18}$O = 9.3‰).

The $^{34}$S, $^{18}$O and $SO_4^{2-}$ values of thermal waters from Sidirokastro and Agistro (Fig. 7a, b) are too low compared to the $SO_4^{2-}$ corresponding values of marine water. This fact indicates that the $SO_4^{2-}$ in the water of these springs results from the mixing of aerosol (marine sulfate) with “light” sulfate that is transported by the meteoric component. This “light” sulfate probably originates from dissolution of sulfur of deep rocks (average value $^{34}$S = 0‰ to $-12$‰)34 or from mixing of sulfates resulting from sulfur oxidation. The contribution of sulfur oxidation is confirmed by the increase of $1/SO_4^{2-}$ ratio (0.25 versus 0.0003 of seawater), as indicated in Fig. 7b.

The sample (ERC-4) has the lowest $SO_4^{2-}$ content measured in ND basins and its $^{34}$S is lower than those of seawater. This low content in $SO_4^{2-}$, suggest that its $SO_4^{2-}$ has been almost totally reduced. These values are so

Figure 7. (a) $^{18}$O versus $^{34}$S, values of the thermal waters for all studied areas. (b) $1/\text{SO}_4^{2-}$ versus $^{34}$S of the thermal waters for all studied areas.
different from marine sulfates that any possibility for marine water participation is excluded. The δ18O of SO4$^{2-}$ is influenced by the intervention of the phenomenon of reduction as well as the interaction of the 18O of water with the 18O of aqueous sulfate. In fact, not only the δ18O value of the SO4$^{2-}$ in this sample but also the reduced values of δ18O in the water of the sample ERC-4 (8.5‰) may also be attributed to isotopic exchange between the oxygen of the water molecules and that of the sulfate ions.

The δ34S value of the rest of the thermal water samples shows that their 34S content (δ34S = 18.4–20.9‰) and respectively their Cl/SO4$^{2-}$ ratios are similar to those of the SO2$^{4-}$ in seawater, indicating the seawater origin of these anions. The reduced δ18O value of the SO2$^{4-}$ in the samples of thermal waters (2.5–8.5‰), comparing to the corresponding SO2$^{4-}$ value of seawater origin (9.3 ± 0.2‰) may be attributed to isotopic exchange, in high temperature, between the oxygen contained in the water molecules and in the sulfate ions [δ18O–(H2O–SO4)]. This oxygen variation seems to reflect an equilibrium process more (Nea Kessani–Aristino samples) or less (Nigrita, Erasmio samples) completed.

### Geothermometry.

For evaluating the reservoir temperatures, the following geothermometers: SiO2$^{33}$, Li–Mg$^{34}$, Na–K$^{35}$, Na–Li$^{36}$ and Na–K–Ca$^{37}$ were applied. In general, the temperatures obtained with the Na–K and Na–K–Ca geothermometers (Table 1) are higher than those obtained with the other geothermometers. Generally, Watek-F thermodynamic model indicates that most of the studied waters are oversaturated (> 0.8) as far as silica is concerned, and therefore the temperatures obtained represent the lowest range attributable to the deep hydrothermal waters. Na–Li and Li–Mg geothermometers also show temperatures close to those obtained by applying the silica geothermometers.

The application of Na–K and Na–K–Ca geothermometers for the samples from the SR and ΧΚ basins indicates temperatures ranging between 45–275 °C and 60–245 °C respectively. These temperatures are overestimated and this is probably due to the precipitation of carbonate minerals during the up flow of water to the surface under high temperatures. In fact, all the studied waters are saturated with calcite. The latter is confirmed by the presence of extended travertine deposits in the area. The application of Na–Li (40–140 °C) and Li–Mg (60–110 °C) geothermometers gives temperatures close to those calculated by the silica geothermometers (50–140 °C) that are the minimum accepted for these fields.

The resulting temperature for ND and LFS basins is different among the various geothermometers applied, which is more evident from sample to sample. The contribution of marine solutions to the deep thermal fluids is one of the main causes of the disturbance of chemical and isotopic geothermometers. Additionally, the SiO2 geothermometer (70–130 °C) that is not affected by the marine contribution does not agree with the maximum temperature of 170 °C and 200 °C estimated by the Na–K and Na–K–Ca geothermometers, respectively. Furthermore, the Na–Li (60–170 °C) and Li–Mg (70–130 °C) geothermometers also exhibit values much lower than those taken by the Na–K–Ca but similar to those of the SiO2 and Na–K geothermometers. In all, the temperature obtained by the use of SiO2 geothermometer is considered to be the lowest one, attributable to the deep hydrothermal waters (ND and LFS basins).

Conclusively, the use of these chemical geothermometers is very ambiguous, except for the SiO2 geothermometer, since they are not representative of water–rock equilibrium. The sulfate–water isotopic geothermometer$^{38,39}$, which is based on the equilibrium exchange of oxygen isotopes between aqueous SO4$^{2-}$ and H2O, was used for the comparison with the chemical geothermometers. The 18O content of aqueous sulfate depends on the contribution of oxygen, which participates in the SO4$^{2-}$ ion, the oxidation fractionation factors, and the equilibrium between 18O of SO4$^{2-}$ and 18O of water.
The calculated temperatures for the wider sampling area, were variable and dependent on the sampling location [NIG (120–130 °C) < KES (180–200 °C); SR basin] and from spring to spring (ex. LFS springs = 150 °C to 200 °C).

The δ18O values of thermal waters from the LFS (Aristino, Traianoupolis), the XK (KES, POT) and the SR basin (NIG-4, NIG-6 to 8, NIG-11) are much diminished in relation to that of seawater. The decrease of δ18O value of the SO4^2− in the water of these springs (from 2.8 to 7.4‰) in comparison with the SO4^2− of sea water origin (9.3 ± 0.2‰) could be attributed to the isotopic equilibration between δ18O(H2O) and δ18O(SO4^2−). This oxygen variation seems to reflect an equilibrium process more (Aristino and Nigrita samples) or less (Potamia) completed. In particular, if the δ18O content of aqueous sulfate of these samples is only controlled by equilibration with water, and if isotopic equilibrium is reached, the δ18O (SO4^2−–H2O) temperature will better express the deep geothermal temperature. In fact, the calculated temperatures are 120 °C and 200 °C respectively. The advanced equilibration process of KES-2 and KES-5 (δ18O = 2.8–3.6‰) is followed by TRA-2 (δ18O = 3.1‰) and ARS-4 (δ18O = 6.0‰), NIG-4,6,8,11 (δ18O = 6.3–6.8‰) and POT (δ18O = 7.4‰). The equilibration between δ18O (SO4^2−–H2O) in NIG-4 (6.8‰) and POT (δ18O = 7.4‰) water isn't so pronounced in relation to the other deep geothermal fields and this appears in the calculated temperature. The temperature obtained for NIG-4 and POT is significantly reduced (120–140 °C) in relation to LFS and XK geothermal fields. The δ18O content of the SID-6, 7, AGS-1,2, MYR and THE water samples was the result of mixing between sulfate of marine origin and sulfate resulted from sulfur oxidation and consequently the temperatures obtained by the use of this isotopic geothermometer, ranging between 130 and 190 °C, are questionable. The calculated temperatures, by the isotopic geothermometer, for the Eratino (ERC-4) are questionable because partial reduction of aqueous sulfate has been detected and as a result the suggested temperatures are underestimates. In fact, since it is not possible to quantify the reduction processes, the estimated temperature is considered to be the lowest acceptable for the sample reservoir. If isotopic equilibrium was achieved, then the temperature of deep thermal water would be greater than 200 °C.

Thus, the isotopic geothermometer suggests a probable existence of a deep geothermal field of low to middle enthalpy (120–130 °C) for SR (NIG samples) and ND (ERA samples) basins and of middle to high enthalpy (150–200 °C) for Eratino (ERC-4), LFS (ARS, TRA samples) and XK (KES samples) basins.

Conclusions

The enrichment in δ18O, δ2H and the Cl− content, are significant parameters to assess the participation of marine water in geothermal systems. These isotope-chloride relations suggest the contribution of marine water, and if isotopic equilibrium is reached, the δ18O (SO4^2−–H2O) temperature will better express the deep geothermal temperature. In fact, the calculated temperatures are 120 °C and 200 °C respectively. The advanced equilibration process of KES-2 and KES-5 (δ18O = 2.8–3.6‰) is followed by TRA-2 (δ18O = 3.1‰) and ARS-4 (δ18O = 6.0‰), NIG-4,6,8,11 (δ18O = 6.3–6.8‰) and POT (δ18O = 7.4‰). The equilibration between δ18O (SO4^2−–H2O) in NIG-4 (6.8‰) and POT (δ18O = 7.4‰) water isn't so pronounced in relation to the other deep geothermal fields and this appears in the calculated temperature. The temperature obtained for NIG-4 and POT is significantly reduced (120–140 °C) in relation to LFS and XK geothermal fields. The δ18O content of the SID-6, 7, AGS-1,2, MYR and THE water samples was the result of mixing between sulfate of marine origin and sulfate resulted from sulfur oxidation and consequently the temperatures obtained by the use of this isotopic geothermometer, ranging between 130 and 190 °C, are questionable. The calculated temperatures, by the isotopic geothermometer, for the Eratino (ERC-4) are questionable because partial reduction of aqueous sulfate has been detected and as a result the suggested temperatures are underestimates. In fact, since it is not possible to quantify the reduction processes, the estimated temperature is considered to be the lowest acceptable for the sample reservoir. If isotopic equilibrium was achieved, then the temperature of deep thermal water would be greater than 200 °C.

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Sampling and analytical methods

Thermal waters (springs and wells) and sea water were sampled in geothermal areas of North and Northeastern Greece (Table S2 of the Supplemental material). Temperature, pH, conductivity and alkalinity were measured directly in the field.

For the chemical analysis, water samples were collected in polyethylene containers of 700 ml. Two samples of waters were taken, one acidized (HNO3 1:1) for cation analysis and one not-acidized for anion analysis. Samples were analyzed at the Institute of Geosciences and Earth Resource, C.N.R., Pisa and I.G.M.E. Moreover, for the isotopic analyses of water (δ18O, δ2H), carbonates (13C) and sulfates (δ18O(SO4^2−), δ34S), samples were taken separately in two-glass bottles (50 ml and 1 l) at every sampling point.
The analysis of major chemical constituents was carried out according to the standard methods described in Alpha (1989). SiO₂ contents were determined by atomic absorption. Anions were analyzed by ion chromatography. The B content was determined photometrically using the curcumin method. The samples were acidified and evaporated to dryness (at 55 °C) in the presence of curcumin. The precipitate is red in color and can be dissolved in ethyl alcohol. The red alcholic mixture was photometrically determined at 540nm. The chemical analysis took place at the Institute of Geosciences and Earth Resource, C.N.R.-Pisa. Minor element (Li) was measured using inductively coupled plasma optical emission spectrometry with a precision of better than ± 2%. Silica contents were determined by atomic absorption with a precision of ± 2%, (404A Method of Standard Methods for the Examination of Water and Wastewater, APHA-AWWA WPCF, 19th edition, 1995). The isotopic composition of oxygen (δ¹⁸O), hydrogen (δ²H), carbon (δ¹³C), and sulfate (δ³⁴S), was measured at the Stable Isotope laboratory of the Institute of Nanoscience and Nanotechnology of the National Center for Scientific Research “Demokritos” (Athens, Greece) by a Thermo DELTA V plus IRMS (Isotope Ratio Mass Spectrometer) coupled with Gas Bench II and Flash Elemental Analyzer (Thermo Electron Corporation, Bremen, Germany). δ¹⁸O and δ²H were determined in water samples using the CO₂–H₂–water equilibration method. The dissolved inorganic carbon

Figure 8. Schematic diagram summarizing the relevant characteristics of geothermal fields in North and Northeastern Greece. *See Shimizu et al. (2005).
in the water, for the analysis of $^{13}$C, was collected as BaCO$_3$ precipitate. Carbon and oxygen isotope analyses of samples were carried out using the conventional phosphoric acid procedure and the continuous flow technique$^{48}$. The dissolved SO$_2$ in the water samples was precipitated as BaSO$_4$ for the analysis of S isotopic compositions$^{48}$. The isotope composition of $^2$H, $^{18}$O, $^{13}$C and $^{34}$S is indicated in delta notation, versus VSMOW, VPDB and CDT standards, respectively, as:

$$\delta = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000$$

where $R_{\text{sample}}$ and $R_{\text{standard}}$ refer to $^{2}H/^{1}H$ or $^{18}O/^{16}O$ or $^{13}C/^{12}C$ or $^{34}S/^{32}S$ ratios of samples and standard respectively. Determination of the different isotope ratios has the following precisions: ± 1‰ for $\delta^{2}H$ and $\delta^{18}O$; ± 0.2‰ for $\delta^{13}C$; and ± 0.1‰ for $\delta^{34}S$ of water and $^{13}$C.

**Data availability**

Data are available from the corresponding author upon request.

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Author contributions
E.D. wrote the main manuscript text. N.K. prepared figure 1. E.D., G.D., M.T. and P.K. prepared figures 2 to 8 and performed isotopic analysis. R.B. performed chemical analysis. P.D., A.A., N.K. and E.S. wrote the geology section and performed part of the chemical analysis. J.L.M. performed the sulfur isotopes analysis. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to E.D.

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