Δελτίο Ελληνικής Γεωλογικής Εταιρείας τομ. XXV/4, 173-182, 1991
Πρακτικά 5ου Επιστημονικού Συνεδρίου, Θεσσαλονίκη, Μάϊος 1990

Bulletin of the Geological Society of Greece vol. XXV/4, 173-182, 1991
Proceedings of the 5th Congress, Thessaloniki, May 1990

ENVIRONMENTAL ISOTOPE STUDIES ON KARST GROUNDWATER IN THE HELICON MOUNTAINS (BEOTIA/GREECE)

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ABSTRACT

The compositions of stable oxygen isotopes in karstic water and carbon isotopes in dissolved inorganic carbon (DIC) have been investigated from springs, wells and open drainage channels in the Helicon Mountains and the Copais depression. Main drainage directions of shallow and deep karstic systems have been determined by ^{18}O distributions of the groundwaters. The $\delta^{13}C_{DIC}$ ratios refer less to atmospheric CO_2 than to soil-CO_2, which is the main carbon source. Characteristic δ-values for open and closed systems as well as geothermic water have been outlined for this region.

INTRODUCTION

Stable isotope ratios have become a powerful tool for solving problems in hydrology in the last years (MOSER & RAUERT 1980).

In the Helicon Mountains, which recently were analysed stratigraphically and structurally (JUX et al. 1987, KONERTZ 1987, SIMON 1987, STEUBER 1989) the groundwater system has been studied by investigation of $^{18}O/^{16}O$ ratios of the water and $^{13}C/^{12}C$ ratios of dissolved inorganic carbon (DIC).

^{18}O can be used as an environmental tracer for determining recharge areas and drainage directions of subsurface waters, because its content in local precipitation is known to decrease with altitude (DANSGAARD 1964).

The investigated area is located in the southeast of the greek mainland in the province of Beotia (Fig. 1). The prominent peaks of the Helicon-massiv are the Paleovouna (1748 m) and the Diacopi (1525 m), whereas the adjacent Copais lowlands form a plain 100 m above sea level.

Major structural elements of the mountain range consist of Triassic to Cretaceous limestones. The sequences include a variety of rocks, such as late Jurassic ophioliths and radiolarites, transgressed by sandy, clay rich

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*University of Cologne, Dept. of Geology, Zülpicher Str. 49, D-5000 Köln 1, Germany beds of Aptian to Cenomanian age (JUX et al. 1987, KONERTZ 1987, SIMON 1987, STEUBER 1989).

Intensively karstified limestones dominate the scenery and control subsurface runoff of meteoric waters. Therefore open flow-systems are rare and periodical.

Most springs with moderate, but rather constant discharge are found at the lithological boundaries between limestones and less permeable beds such as ophioliths and radiolarites.

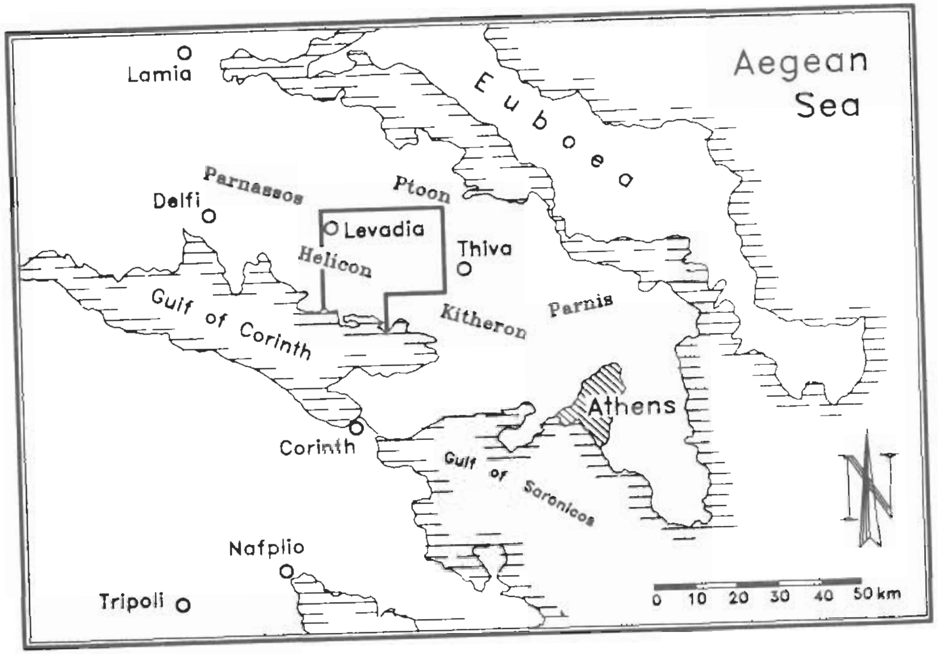

Fig. 1. Location of the investigated area.

METHODS

Temperature, pH, the amounts of dissolved bicarbonates and dissolved CO_2 of the water samples were directly determined in the field. The bicarbonate content was measured by titriating with 0.01 mol/l HCl down to pH 4.3 and dissolved CO_2 by titriating with 0.01 mol/l NaOH up to pH 8.2. The total amount of DIC (HCO_3^- + CO_3^{2-} + CO_2) was fixed to $BaCO_3$ at the sampling site. This was done by pouring 50 ml of a saturated alkaline $Ba(OH)_2$-solution to 1 l of sample-water. Another sample was taken for both the ^{18}O analysis and the measurement of ionic concentrations (Ca^{2+}, Mg^{2+}).

50 - 100 mg of the dried $BaCO_3$ was acidified by 100 % orthophosphoric acid in a vacuum-system. Stable carbon isotope ratios were measured with a Finnigan MAT 250 mass-spectrometer: δ-values are referred to PDB standard. The ^{18}O-concentrations of the waters have been determined by applying the CO_2-equilibration method (GAT & GONFIANTINI 1981); results are given relativ to SMOW.

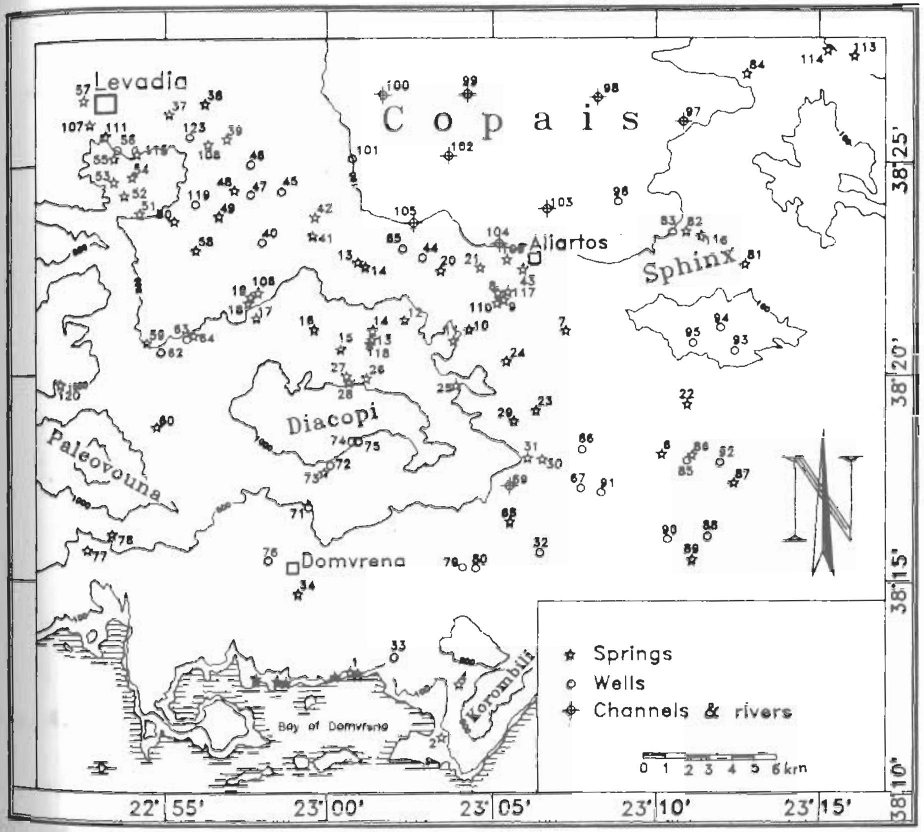

Fig. 2. Map of the investigated area with marked sample sites.

OXYGEN ISOTOPIC COMPOSITION

The fractionation of ^{18}O in natural meteoric water mainly depends on the continental and the altitudinal effect (DANSGAARD 1964).

KALLERGIS et al. (1983) determined the altitudinal effect of meteoric waters in the Parnis Mountains, 40 km east of this studying area. It is at about -0.21‰ per 100 m of orographic altitude. STICHLER et al. (1989) investigated

$\delta^{18}O$-ratios in rain water at different altitudes in the eastern Peloponnisos during a period of 16 months. He determined ^{18}O-depletion of -0.18‰ for each 100 m of orographic altitude (Fig. 3).

It seems to be problematic to transfer this results to the Helicon region. The average $\delta^{18}O$-ratios of different springs, sampled at a certain altitude are not uniform and depend on local meteorological and topographical situation. In this area no long time record of $\delta^{18}O$ in precipitation is available, but linear depletion of maximum ^{18}O contents per altitude on spring waters indicate an altitudinal effekt of about -0.33 ‰ per 100 m.

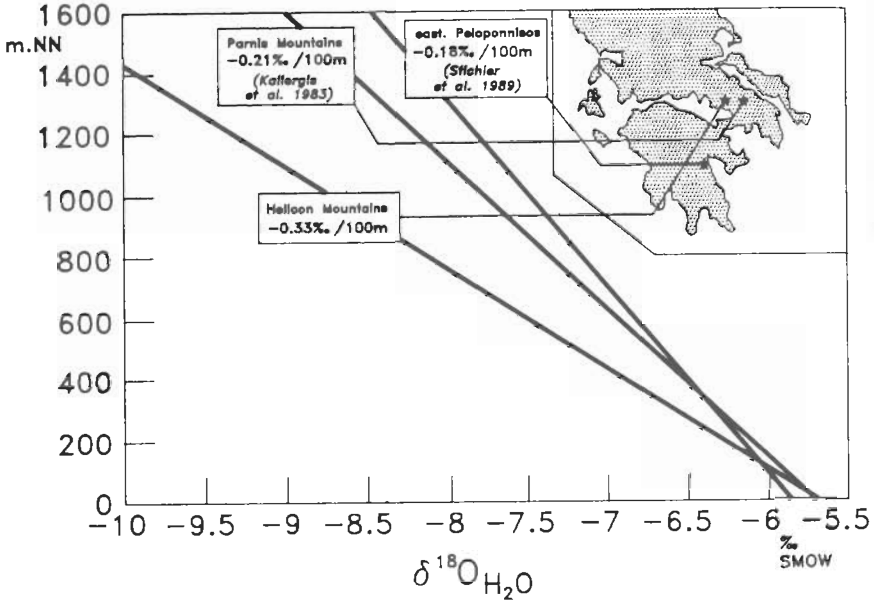

Fig. 3. Altitudinal effects in different regions of Greece.

Due to $\delta^{18}O$ values shallow and deep karstic water can be distinguished. Deep karst reservoir refers to extended and topographical high recharge areas. This is indicated by "light" isotopic composition and high flow rates (more than 300 l/min) of certain spring waters. An example is the Oracle Spring (No. 107, -8.8 ‰ $\delta^{18}O$), from which the whole city of Levadia is supplied with water.

Many springs are located along the Bay of Domvrena at sea level (Fig. 2). Some submarine springs, flowing out as much as 5 m below sea level, indicate a karst system, which was established during eustatic changes in the Mediterranean Sea. It is difficult to determine the recharge areas of these brackish coastal springs by means of the ^{18}O contents (-7.0 ‰ $\delta^{18}O$) because of the mixing effects with isotopically "heavy" sea water (0 ‰ $\delta^{18}O$). But the corrected δ-values which are at about -8.5 ‰ and the amount of water discharge point to an extended recharge area, obviously the southern Diacopi Range.

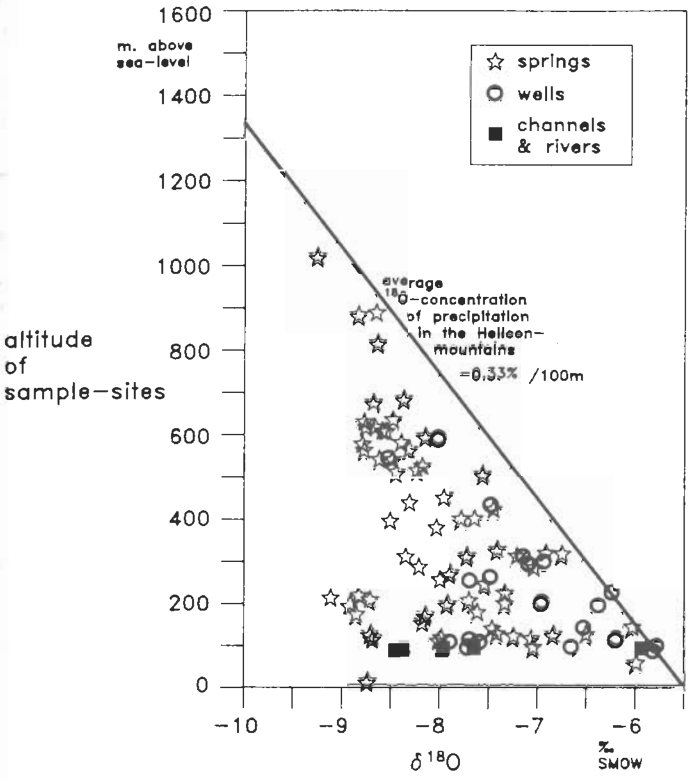

Fig. 4. Altitude versus ^{18}O-content of the groundwater in the Helicon-Mountains.

A geothermal area with water temperatures ranging from 25 to 30 °C has been discerned southeast of Levadia (No. 49, 108, 119, 123). $\delta^{18}O$-values (-8.6 to -8.8 ‰) indicate recharges from the Paleovouna massiv, because there is a subsurface watershed between the Paleovouna and the Diacopi Mountains. The ^{18}O content of spring water from this zone is almost in accordance to the altitude of the sample sites. The subsurface discharge of deep karst systems of the Paleovouna massiv is directed to the north. Many isotopically "light" springs south of Levadia support this assumption (Fig. 5).

Karstic water from the northern Diacopi Mountain is mainly drained in shallow karst systems to northern and eastern directions (Fig. 5). The highly deformed sequences of the Cretaceous age presented a structural pattern, which favoured small reservoirs and springs with mean flow-rates. There, karst springs from deep seated reservoirs do not occur.

"Light" isotopic ratios of the Copais drainage channels can be traced back to the Melas Spring. The discharge amount (ca. 5000 l/sec) and the isotopical "light" composition (-8.7 ‰ $\delta^{18}O$) of its water, which supply most irrigation systems in the Copais depression point to a hydraulic connection with the Parnassos Massiv, 40 km NW.

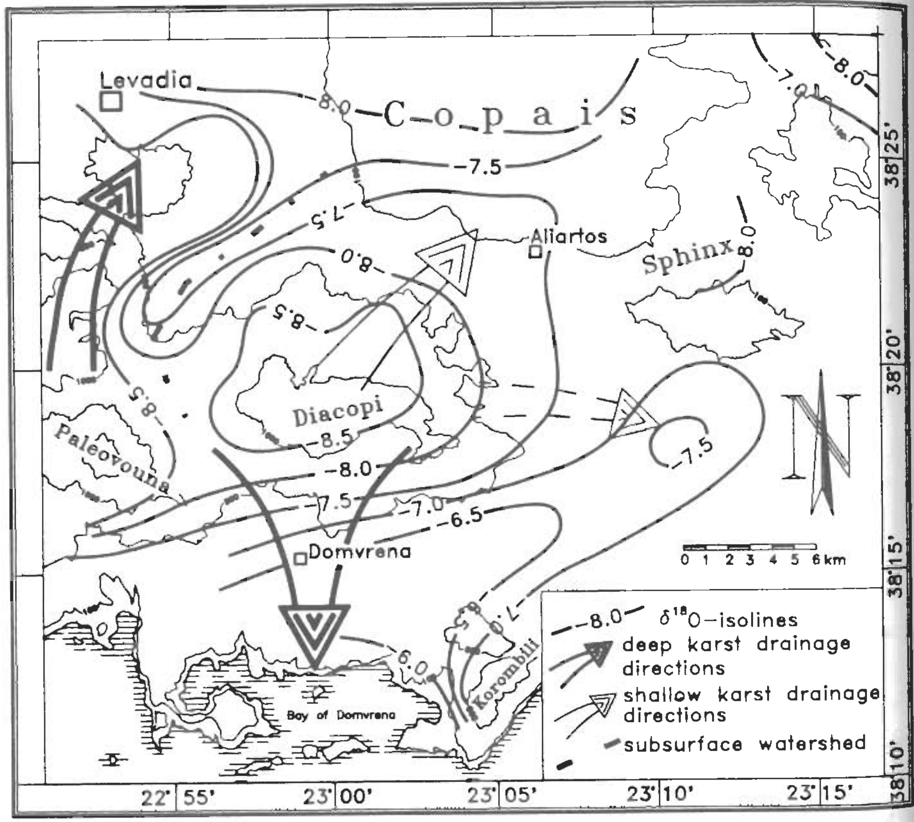

Fig. 5. $\delta^{18}O$ isoline map with main drainage directions of shallow and deep karstic waters.

ISOTOPIC COMPOSITION OF DIC

Dissolved inorganic carbon (DIC) in natural groundwater systems can be derived from atmospheric CO_2, endogenic sources, soil-microbiological activities and interaction with solid carbonates.

Freshwater bicarbonates trace back either to soil-CO_2 or carbonates of the aquifer (MOOK 1968). $\delta^{13}C$-fractionations (ϵ) are differnt at transition of atmospheric CO_2 to the bicarbonates and carbonates. As different CO_2 sources vary in their isotopic composition, $\delta^{13}C_{DIC}$ in freshwater bicarbonates ranges between 0 and -16 ‰ PDB (Fig. 6).

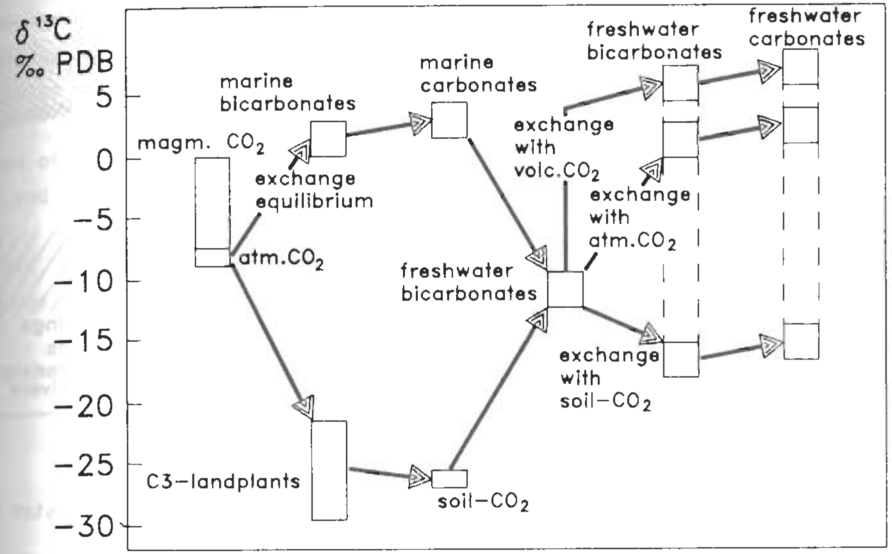

Fig. 6. Carbon isotope fractionation in natural waters (after MOOK 1968).

The interpretation of $\delta^{13}C_{DIC}$ creates difficulties, because total fixed DIC consists of carbon from gaseous and dissolved CO_2 as well as bicarbonate- and carbonate-ions with different ϵ for each of them.

In natural waters the fractional amount of these components varies in pH dependence, which allows to interpret $\delta^{13}C_{DIC}$ ratios in the equilibrated CO_2 - H_2O - $CaCO_3$ - system. Up to pH 4.3 only gaseous and dissolved CO_2 are able to exist. Between pH 4.3 and pH 8.2 DIC consists of CO_2 and HCO_3^-. Above pH 8.2 no CO_2 remains in solution, but CO_3^{2-} contributes than to DIC.

Most of the investigated waters range between pH 6.8 and pH 8.2, so that DIC mainly exists as HCO_3^-. ϵ between CO_2 and HCO_3^- amounts -temperature depended- about 10 ‰ (MOOK 1968).

In the equilibrated system $\delta^{13}C_{DIC}$ ratios increase with rising pH; this is because HCO_3^- increases in comparison to CO_2 (Fig. 7).

Most carbon of the waters investigated originated from CO_2 of soils. Shifts towards "heavier" isotopic composition indicates that exchange atmospheric CO_2 took place. Intensive karstification with thin soil above, especially in higher regions of the massiv, favour fast percolation of meteoric water into the groundwater. There, enrichment of the groundwater with "light" carbon from the soil is rather diminished.

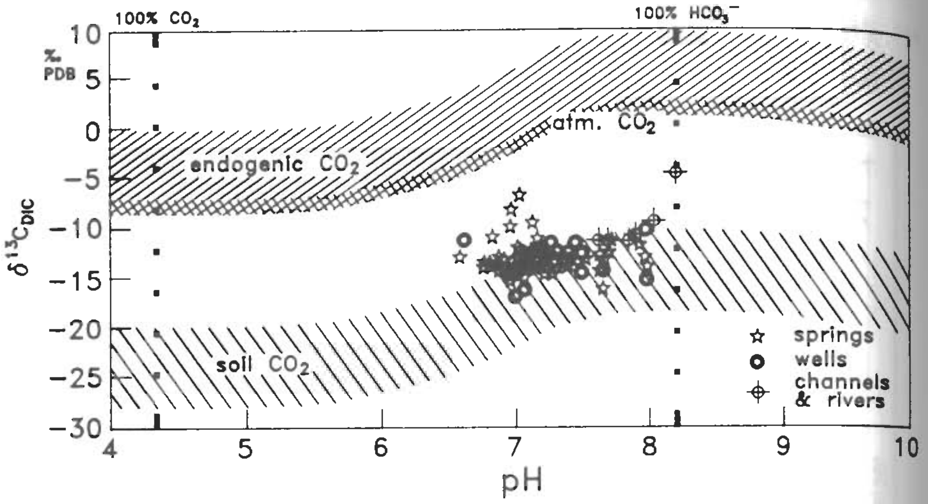

Fig. 7. Diagram for interpretation $\delta^{13}C_{DIC}$ ratios in the equilibrated system CO_2 - H_2O - $CaCO_3$.

Highest $^{13}C_{DIC}$ contents of subsurface water have been traced in waterbodies of springs and wells within the geothermic area SE of Levadia (-7.4 to -8.6 ‰ $\delta^{13}C_{DIC}$). Influx of magmatic CO_2 is possible, as generally $\delta^{13}C_{DIC}$ of karstic water ranges between -10 and -14 ‰ (Tab. 1). A greater input of atmospheric CO_2 seems to be improbable, because the equilibration of DIC in surface waters with atmospheric CO_2 takes time, nearly 30 days (MOOK 1968).

The inorganic carbon of waters from the irrigation and drainage channels of the Copais is mainly derived from biogenic sources. It reveals only little equilibration with atmospheric CO_2 (-8.5 to 10.5 ‰, Tab. 1). On the other hand water from the river Kiffisos, which flowed for a rather long distance indicates the exchange of carbon with atmospheric CO_2 (-3.7 ‰).

The content of most of the investigated well waters is highly variable when soil-CO_2 interacts. There, exchange with atmospheric CO_2 is restricted by a limited reaction surface in contrast to the water amount within the well. Frequent pumping of irrigation plants additionally limites normal exchange.

CONCLUSIONS

The combinated study of $\delta^{13}C_{DIC}$ and $\delta^{18}O$ ratios reveals characteristic isotopic values for different natural waters in Beotia (Tab. 1).

The nearly constant isotopic values of deep karstic waters are due to the extension of their recharge areas and the volume of their reservoirs. In case that such waters are isotopically heavy, the $\delta^{13}C_{DIC}$ values point to carbon exchange with atmospheric CO_2. In this respect mountainous regions with reduced coverage of soil yield fast supplies to the groundwater. Mean altitudes of the recharge areas, which can be estimated from ^{18}O data, underline these facts.

The restricted sizes and the altitudinal variations of the recharge areas of shallow bodies of karstic waters are reflected in varying δ-values of DIC and ^{18}O.

Recharge areas of geothermic waters are similar to those of deep karst waters. They are to be distinguished on account of isotopical "heavy" DIC content and due to endogenic carbon sources.

The varying δ-values in waters of open systems are generally related to exchanges with atmospheric carbon and ^{18}O enrichment due to evaporation.

type	$\delta^{13}C_{DIC}$ (‰ PDB)	$\delta^{18}O$ (‰ SMOW)
deep rooted karstic water	-10.3 to -11.2	-8.6 to -8.8
shallow rooted karstic water	-11.5 to -14.5	-6.0 to -9.2
geothermic water	-7.4 to -8.6	-8.6 to -8.8
well water	-4.5 to -15.9	-0.9 to -8.5
drainage channels in the Copais	-8.5 to -10.5	-7.6 to -8.4
water from Kiffisos river	-3.7	-5.9

Tab. 1: Ranges of δ-values from different water sources

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