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C. R. Geoscience 336 (2004) 367–374



Tectonics

## Fluid geochemistry along the Eliki and Aigion seismogenic segments (Gulf of Corinth, Greece)

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Received 9 November 2003; accepted after revision 17 November 2003

Written on invitation of the Editorial Board

### Abstract

Three geochemical surveys in ground waters were carried out in the Selianitika–Trapeza area, Gulf of Corinth, with the main purposes: (1) to define the geochemical patterns of the circulating ground waters; (2) to discriminate the role of active fault systems in affecting the ground water chemistry and hydrogeology, exploiting geochemical techniques tested in other areas; (3) to select sites for the continuous geochemical surveillance of the tectonic activity of the area. A total of 50 sites have been sampled, and numerous chemical and stable isotope analyses have been performed. We identify three geochemical active fault zones: (i) the Eliki–Nikolaïkea area; (ii) the Selianitika–Rododafni–Nerazes area, and (iii) the Trapeza sector. The Nerazes well site and the Selianitika spa have been selected for exploiting a geochemical-hydrological monitoring surveillance of the tectonic activity. *To cite this article: L. Pizzino et al., C. R. Geoscience 336 (2004).*

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### Résumé

**Géochimie des fluides le long des segments sismogéniques d'Eliki et Aigion (golfe de Corinthe, Grèce).** Trois campagnes géochimiques sur les eaux souterraines ont été entreprises dans le golfe de Corinthe, avec comme principaux objectifs : (1) de déterminer les configurations géochimiques des eaux souterraines en circulation ; (2) de mettre en évidence le rôle des systèmes de failles actives sur la chimie et l'hydrogéologie des eaux souterraines ; (3) de sélectionner des sites pour la surveillance géochimique en continu de l'activité tectonique de la région. Un total de 50 sites a été échantillonné et analysé du point de vue de la chimie des eaux et de leurs compositions isotopiques. Le puits de Nerazes et les thermes de Selianitika ont été choisis comme sites de surveillance. *Pour citer cet article : L. Pizzino et al., C. R. Geoscience 336 (2004).*

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*Keywords:* Corinth Gulf; Aigion Fault; Fluid geochemistry; Water circulation in fault zones

*Mots-clés :* Golfe de Corinthe ; Faille d'Aigion ; Géochimie des fluides ; Circulation aquifère en zone de faille

### Version française abrégée

Dans le cadre des projets de l'UE 3F-Corinth et Corseis, faisant partie du « Corinth Rift Laboratory », trois campagnes géochimiques en eaux souterraines

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ont été menées en octobre 2000, septembre 2001 et juillet 2002 dans la zone orientée NW–SE comprise entre Selianitika (NW) et Trapeza (SE), à travers les secteurs d’Aigion, Temeni, Eliko et Diakofto. Les principaux objectifs de cette étude étaient : (i) la compréhension du comportement géochimique des eaux souterraines circulantes ; (ii) la détermination de l’influence des systèmes de failles actives sur la géochimie et l’hydrologie des eaux souterraines, l’exploitation de techniques géochimiques testées dans d’autres régions ; (iii) la sélection de sites appropriés pour l’installation de prototypes de stations géochimiques GMS II destinées à la surveillance géochimique de l’activité tectonique de la région.

Nous avons échantillonné 50 sites (42 puits et 8 sources). Nous avons fait des analyses géochimiques complètes sur tous les échantillons, et aussi l’analyse des isotopes stables (C, H et O) sur une sélection de 19 d’entre eux.

Nous avons identifié trois zones de failles avec des anomalies géochimiques : (i) la région d’Eliko–Nikolaïkea, qui se situe à l’intersection de deux segments en échelon de la faille d’Eliko ; (ii) à proximité des bordures nord–ouest et sud–est de la zone d’investigation, qui s’appelle la zone de Selianitika–Rododafni–Nerazes ; (iii) le secteur de Trapeza. Dans les deux derniers secteurs, un aquifère Na–HCO<sub>3</sub> artésien jaillit, caractérisé par (1) une teneur anormale en CO<sub>2</sub>, F, NH<sub>4</sub> et en éléments traces et (2) par une composition isotopique en C, H et O complètement différente. De plus, ces données isotopiques suggèrent que les eaux échantillonnées ont une origine météorique, excluant toute origine volcanique, juvénile ou magmatique.

En ce qui concerne les gaz dissous dans les eaux souterraines, nous pouvons dire que cette région n’est pas particulièrement affectée par un dégazage profond de la croûte/manteau, comme l’on aurait pu s’y attendre, en raison de la présence de failles actives/sismogéniques régionales. Nous considérons cette géochimie des fluides comme source de données de base pré-requises pour comprendre les éventuelles variations futures enregistrées dans le cadre de mesures géochimiques discrètes ou en continu.

En considérant l’ensemble de ces données, le puits de Nerazes et les thermes de Selianitika ont été sélectionnés en vue de l’exploitation d’une surveillance

géochimique et hydrologique multivariées continue de l’activité tectonique.

## 1. Introduction

In the frame of the EU projects 3F-Corinth and CORSEIS, being part of the ‘Corinth Rift Laboratory’, in October 2000, September 2001 and July 2002 three geochemical surveys in ground waters were carried out in a NW–SE trending belt from Selianitika (NW) to Trapeza (SE), throughout the sectors of Aigion, Temeni, Eliko and Diakofto (see Fig. 1, also showing the map of the total CO<sub>2</sub> content in ground waters). The main purposes of this study were:

- (i) to define the geochemical patterns of the circulating ground waters;
- (ii) to discriminate the role of active fault systems in affecting the ground water chemistry and hydrogeology, exploiting geochemical techniques already tested in other areas [2,3,6,9–12];
- (iii) to select optimum sites in order to install the GMS II geochemical station [10] for continuous geochemical surveillance of the tectonic activity of the area.

A total of 41 wells and 9 springs have been sampled. In addition, chemical analyses of AG-10 deep-well groundwater samples, collected at different depths during July 2002, have been performed; these data are presented and discussed by Giurgea et al. (this issue).

## 2. Fluid geochemistry survey: results and discussion

### 2.1. Methodology

In the field, physicochemical parameters such as temperature, pH,  $E_h$ , electrical conductivity, alkalinity (by titration with HCl 0.05 N), H<sub>2</sub>S and NH<sub>4</sub> (by colorimetric methods) and total dissolved CO<sub>2</sub> content (with an ORION ion-selective electrode) have been determined. All samples have been analysed for <sup>222</sup>Rn by the ACC- $\gamma$ -spectrometry method [6]. Water samples were filtered through cellulose filters

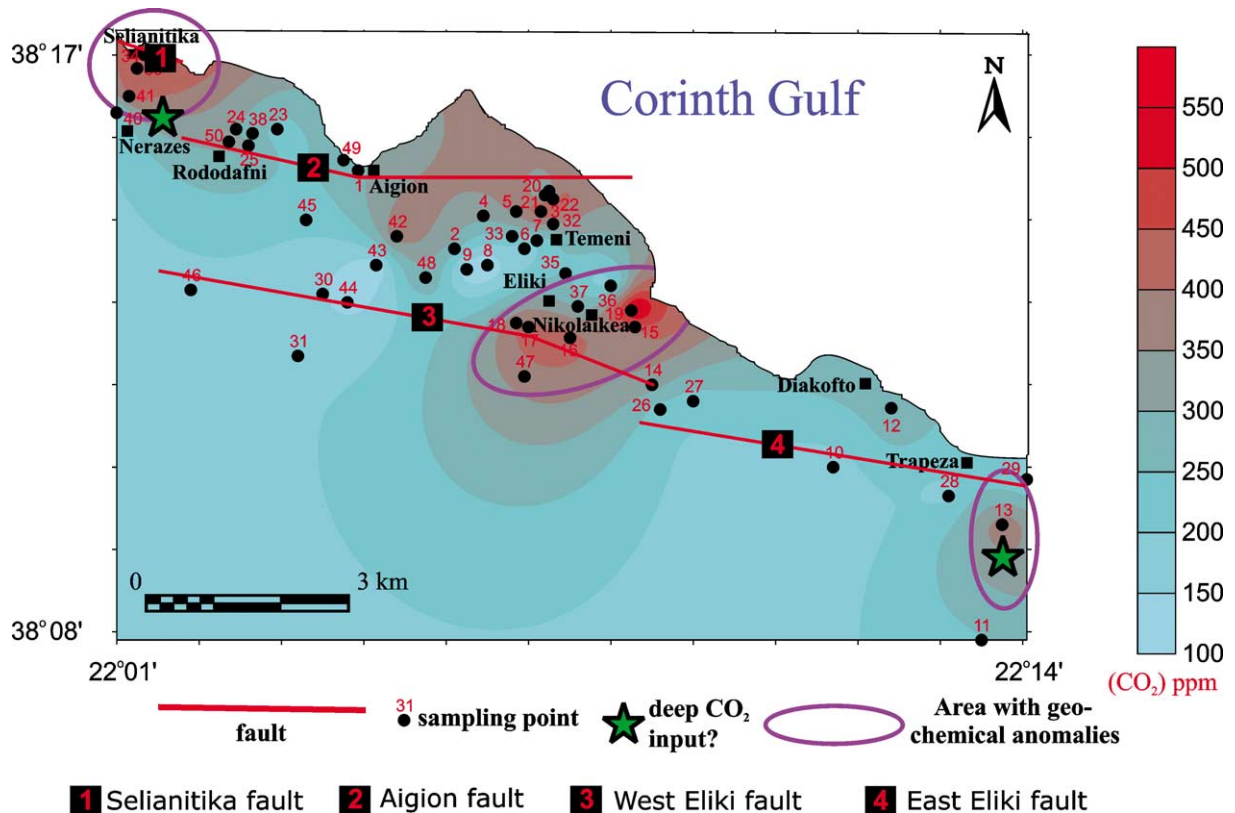


Fig. 1. Geographical distribution of the sampled sites (springs and wells). Main faults and distribution of the total CO<sub>2</sub> content in ground waters are also reported.

Fig. 1. Distribution géographique des sites échantillonnés (sources et puits). Les failles principales et la distribution du CO<sub>2</sub> total contenu dans les eaux souterraines sont aussi représentées.

(0.45 μm) and acidified (for cations analysis) with HCl 6 M. In laboratory, major and some minor constituents have been determined on all samples by DIONEX ion chromatography. On 17 selected samples, analyses of minor and trace elements (Li, B, Si, Fe, Mn, As, Br, Sr, Sb, Hg, U) have been performed by an ICP-mass spectrometry (ELAN 6100). On 19 samples,  $\delta^{13}\text{C}_{(\text{TDIC})}$ ,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of waters have been measured.  $^{13}\text{C}/^{12}\text{C}$  analysis followed certified methods [7] and are expressed as  $\delta^{13}\text{C}\%$  vs PDB standard. D/H isotopic analyses were performed using the Kendall and Coplen technique [4].  $^{18}\text{O}/^{16}\text{O}$  analyses were carried out by the CO<sub>2</sub>–water equilibration technique [1]. Results are reported in  $\delta\text{D}$  and  $\delta^{18}\text{O}\%$  vs V-SMOW standards.

## 2.2. Groundwater chemistry

The chemical composition of the 50 water samples is presented in terms of relative Ca, Mg and Na + K concentrations (Fig. 2a) and relative Cl, SO<sub>4</sub> and HCO<sub>3</sub> contents (Fig. 2b). Inspecting these triangular plots, the types of water may be classified as follows:

### 2.2.1. Ca–HCO<sub>3</sub> waters

They represent the bulk of our samples, and their chemistry indicates a very fast and shallow interaction with conglomerates and limestones cropping out in the studied area. The waters are cold (< 18 °C), neutral or slightly alkaline, not mineralised (Total Dissolved Solids-TDS, < 0.7 g l<sup>-1</sup>), and show positive

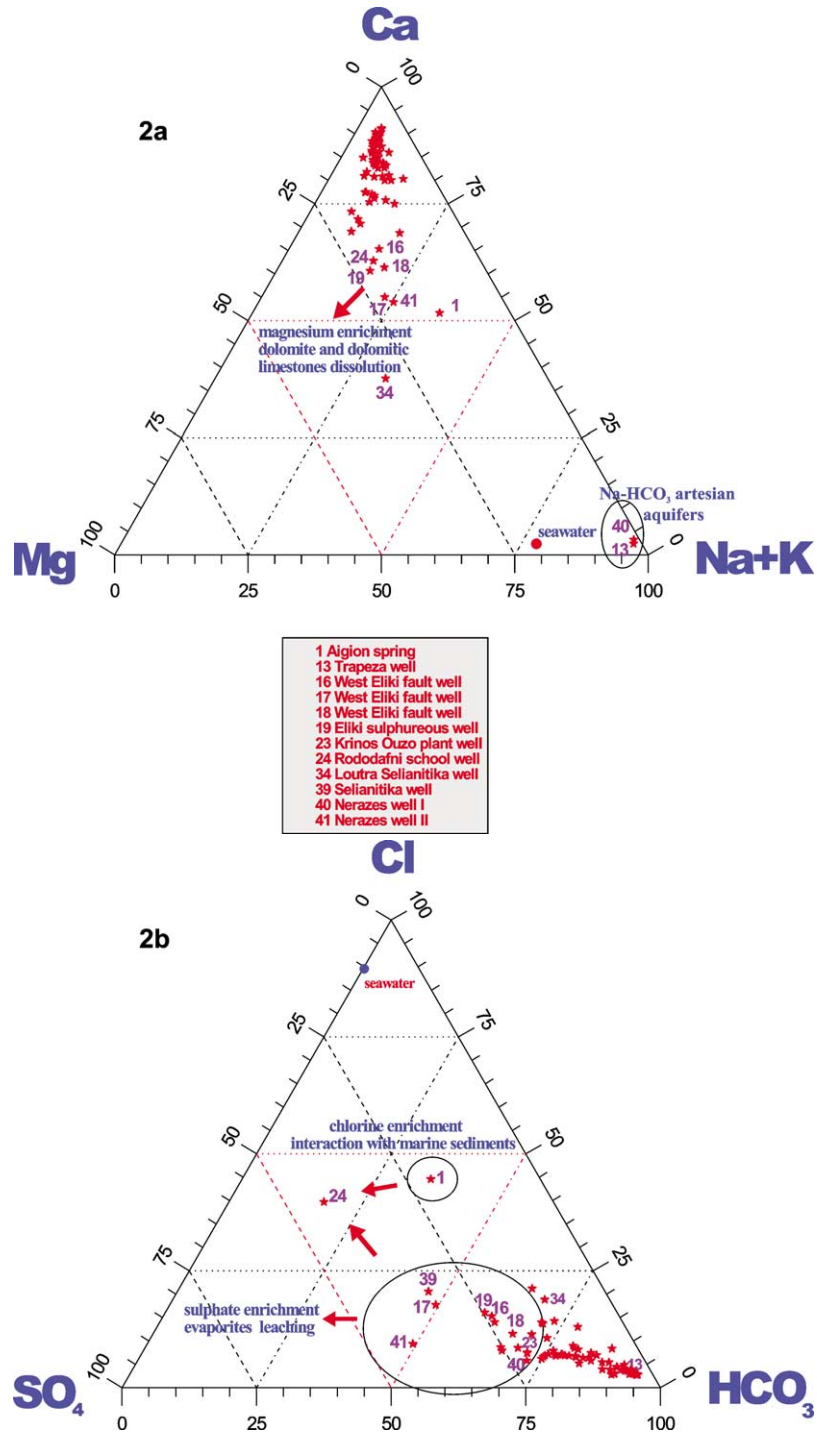


Fig. 2. (a) Triangular plot Ca–Mg–Na + K; (b) triangular plot Cl–SO<sub>4</sub>–HCO<sub>3</sub>.  
 Fig. 2. (a) Représentation triangulaire Ca–Mg–Na + K; (b) représentation triangulaire Cl–SO<sub>4</sub>–HCO<sub>3</sub>.

$E_h$  values (typical of shallow oxidising fluids, with no  $H_2S$  content). The main geochemical characteristics indicate shallow hydrologic circuits along the regional tectonic structures.

#### 2.2.2. Ca (Na–Mg)– $HCO_3$ (Cl– $SO_4$ ) waters

These waters are slightly enriched in chlorine, sulphate, sodium and magnesium and are regarded as geochemically evolved calcium-bicarbonate waters. Their temperatures are  $>18^\circ C$  (up to  $21^\circ C$ , Loutra Selianitika spa, sample 34) and the salinities (TDS  $> 1\text{ g l}^{-1}$ ) were the highest found in the investigated area. Redox potential values ( $E_h$ ) are lower, even though still positive, for samples located in the Eliki area and for the artesian wells of the Nerazes and Trapeza areas. The only clear occurrence of  $H_2S$  ( $E_h = -150\text{ mV}$ ) was found at site 34. Very likely the  $H_2S$  (up to 0.5 ppm) has an organic origin, being produced by the reduction of  $SO_4$  due to bacterial activity in anaerobic environment. In the 70 m-deep well feeding the thermal bath, a continuous monitoring station was installed in September 2001, which is, presently, on line.

Two different water–rock interaction processes are emphasised to account for their sulphate and magnesium enrichment:

- (i) interaction with marine sediments (containing NaCl-rich pore fluids relatively concentrated in  $SO_4$  and Mg) and/or with a brackish sequence of silty sands, marls, clays and diatomitic shales, observed in the Aigion spring and Rododafni School well area [5,8] (samples 1 and 24, respectively);
- (ii) dissolution of dolomite and dolomitic limestones (with the presence of evaporitic strata) for samples 16, 17, 18 (located on the West Eliki fault), sample 19 (located in the plain between the village of Nikolaikea and the coast), as well as for samples 34, 39 and 41 (located in the Selianitika–Nerazes area).

#### 2.2.3. Na– $HCO_3$ waters

This peculiar chemistry pertains only to samples 13 and 40, located in the village of Nerazes and close to the town of Trapeza, respectively. They are the most pronounced artesian wells in the area, representing the existence of deeper  $CO_2$ -rich aquifers interacting

with clayey strata. The salinity of these waters (TDS  $> 1\text{ g l}^{-1}$ ), together with their relatively high and even temperatures (about  $20\text{--}21^\circ C$  all the year round) testify both, deep hydrological circuits and longer lasting water–rock interaction processes with respect to the other shallow aquifers discharging throughout the entire area. The Nerazes well is an optimum site to monitor continuously the relationships between seismic events and hydrodynamic as well as geochemical variations. Because of the promising hydrological characteristics and the easy logistics, a geochemical continuous monitoring station (GMS II) [10] was installed at the Nerazes well in September 2001.

#### 2.3. Stable isotope compositions

In the diagram  $\delta^{18}O\text{--}\delta D$  (Fig. 3) all the waters investigated in the study area plot close to the worldwide meteoric water line, indicating their meteoric origin. The observed small differences in the isotopic composition are mainly due to climatic effects, controlling the final isotopic composition of rain and ground waters. Magmatic, juvenile, volcanic and other particular origins that can lead to anomalous isotopic fluid compositions can be excluded.

Any enrichment in  $^{18}O$  in the investigated fluids, with respect to the meteoric water line, was detected. A shift toward less negative  $\delta^{18}O$  values is generally observed for thermal ground waters, indicating isotopic exchange between hot fluids and carbonates. The lack of any thermal signature in the discharging waters fully supports the outlined features. A trend of increasing  $\delta^{18}O$  and  $\delta D$  from southeast to northwest is observed ('heaviest' waters towards the southeast, 'lightest' waters towards the northwest). This observation reflects different altitudes of the recharge areas for each group of shallow aquifers. The Trapeza artesian well (sample 13) is characterised by an unusually light isotopic composition, suggesting a higher altitude of the recharge area with respect to the other analysed waters. This area is far from the well about 5–10 km southward. Therefore, the artesian circulation is necessarily longer with respect to the other shallow aquifers, having a local recharge. This interpretation, based on isotopic data, fits very well with other characteristics of the Trapeza water, such as the peculiar Na– $HCO_3$  chemistry and the salinity, one of the highest measured in the investigated area.

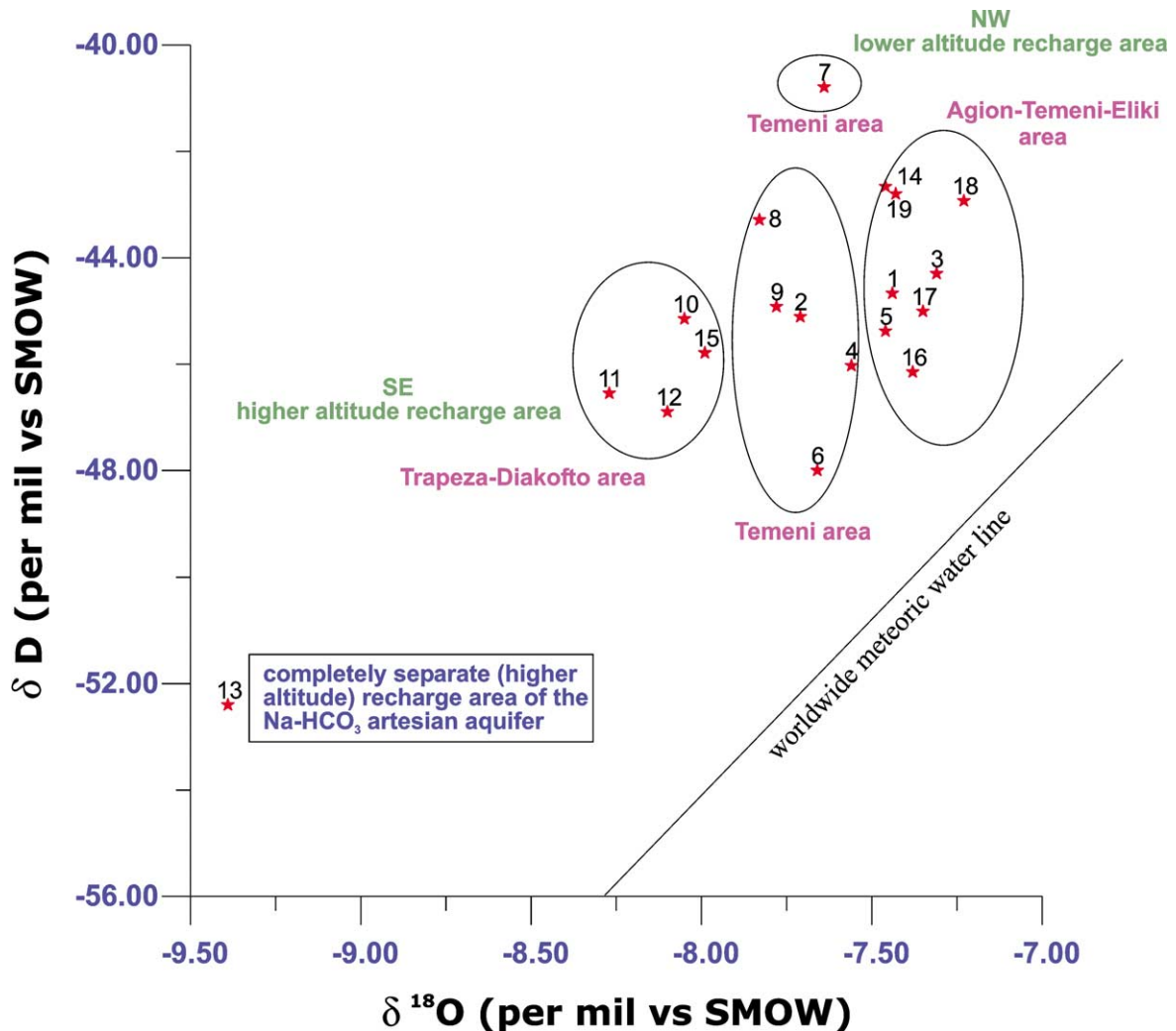


Fig. 3.  $\delta^{18}\text{O}$  vs  $\delta\text{D}$  diagram, showing the isotopic composition of water samples in the study area. The worldwide meteoric water line is also shown.

Fig. 3. Diagramme  $\delta^{18}\text{O}$  en fonction de  $\delta\text{D}$ , montrant la composition isotopique des échantillons d'eau dans la région d'étude. La ligne de l'eau météorique mondiale est aussi représentée.

#### 2.4. Dissolved gases

$^{222}\text{Rn}$  content in the sampled ground waters is quite low, ranging between 1 and 10  $\text{Bq l}^{-1}$ . The values reflect:

- (i) the interaction of the circulating waters with the carbonatic lithologies cropping out in the investigated area, notoriously depleted in uranium (precursor of  $^{222}\text{Rn}$ )-bearing minerals;

- (ii) the lack of convection of fluids from great depth, being the  $^{222}\text{Rn}$  a typical pathfinder of this peculiar fluid-transport process [11,12];
- (iii) the lack of an uprising gaseous components acting as carrier for radon, like deep  $\text{CO}_2$  [9].

The map of the dissolved  $\text{CO}_2$  distribution (Fig. 1) shows four areas characterised by high contents (>350 ppm) compared to a low general background level: Selianitika–Nerazes–Rododafni, Aigion–Temeni,

southeastern sector of the Eliki Fault–Nikolaïkea and Trapeza. For all investigated waters, carbon isotope values ( $-15.12 < \delta^{13}\text{C} < -6.91$ ) indicate an atmospheric and/or a biogenic origin of carbon dioxide. Any deep origin (mantle and/or thermal decomposition of the carbonates) can be inferred. Only for the Trapeza artesian aquifer the measured carbon isotope value ( $\delta^{13}\text{C} = -5.26$ ) indicates a partial equilibrium with the marine carbonates.

### 3. Conclusions

Despite the investigated area is crossed by very active and seismogenetic fault segments (Eliki and Aigion ones), elsewhere normally associated with upraise of deep fluids [2,3,6,9–12], our fluid geochemistry study did not show characteristics of deep circulation fluids. Low salinity, low temperature, neutral-alkaline pH, positive  $E_h$ , low  $^{222}\text{Rn}$ , low concentration of deep seated fluid tracers such as Li, B,  $\text{SiO}_2$ , As, Hg, etc.) as well as O, H, C isotopic ratios denote slight water–rock interaction processes and the lack of convection of fluids from great depth. However, deep fluid signatures may be masked by a mixing of huge amounts of meteoric waters. Moreover, the O and D isotope data suggest that sampled waters are predominantly of meteoric origin.

Some weak hints such as low Eh values, high  $\text{CO}_2$  and slightly enriched  $\text{H}_2\text{S}$ ,  $\text{SO}_4$ ,  $\text{NH}_4$ , B contents indicate the presence of ‘Geochemically Active Fault Zones’ (GAFZ definition [12]) mainly (i) within the Eliki–Nikolaïkea area, which is located at the intersection-en-echelon sector between the two Eliki fault segments and (ii) in proximity to the northwestern and southeastern edges of the investigated area, namely the Selianitika–Rododafni–Nerazes and the Trapeza sectors. In these last areas, an artesian  $\text{Na–HCO}_3$  aquifer is up-welling, characterised by anomalous contents of  $\text{CO}_2$ , F,  $\text{NH}_4$  and other trace elements and by completely different C, O, H isotopic signatures.

The studied area is affected mainly by two ground-water circuits:

- (i) deep artesian and alkaline aquifers discharging mainly in the Nerazes and Trapeza sectors;
- (ii) a fast and shallow circulation in conglomerate and carbonates characterised by  $\text{Ca–HCO}_3$  waters, locally interacting with deeper dolomitic strata (containing evaporitic lenses) along the Eliki fault and in the Nerazes–Selianitika sector and with marine sediments in the Rododafni and Aigion areas. These processes caused enrichments in  $\text{SO}_4$ , Cl, and Mg as well as B, Br, Li, and Sr.

Regarding amount and nature of the dissolved gases in ground waters, we may assess that the area is not particularly affected by crustal/mantle degassing, which is normally expected as a consequence of the presence of regional active/seismogenetic faults.

However, we assessed the regional fluid geochemistry background as pre-requisite to understand possible future variations to be investigated by discrete or continuous geochemical monitoring.

Considering the gathered data as a whole, the Nerazes well site and the Selianitika spa have been selected for exploiting a multivariable geochemical-hydrological continuous monitoring surveillance of the tectonic activity. The choice to perform continuous geochemical observations is strongly encouraged considering the geologic and tectonic framework in which these sites are situated.

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