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Groundwater origins and mixing pattern in the multilayer aquifer system of the Gafsa-south mining district: a chemical and isotopic approach

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Riadh Ahmadi · Khalid Mehdi · Hamed Ben Dhia

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Abstract Major ion geochemistry and environmental isotopes were used to identify the origins and the mineralisation processes of groundwater flowing within the three aquifer levels of the multilayer system of the Gafsa-south mining district (Southwestern Tunisia). It has been demonstrated that groundwaters are characterised by a Ca–Mg–SO₄ water type. Geochemical pattern is mainly controlled by the dissolution of halite, gypsum and/or anhydrite as well as by the incongruent dissolution of dolomite. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are much lower than the isotopic signature of regional precipitation and fall close to the meteoric water lines, indicating that groundwaters have not been significantly affected by evaporation or mineral–water

reactions. The distribution of stable and radiogenic isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$ and ^{14}C) within the aquifer levels suggests that the deep confined aquifer receives a significant modern recharge at higher altitudes, while, the shallow unconfined aquifer has been mainly recharged under cooler paleoclimatic condition, likely during Late Pleistocene and Early Holocene humid periods. However, waters from the intermediate confined/unconfined aquifer have composite isotopic signatures, highlighting that they are derived from a mixture of the two first end-members.

Keywords Major ion geochemistry · Environmental isotopes · Multilayer aquifer system · Tunisia

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Introduction

The Gafsa-south mining district in Southwestern Tunisia is one of the most important producers of phosphate in the world. The exploitation of this district started at the beginning of the twentieth century a few years after the first discovery of this valuable resource in 1885 by the French amateur geologist, Philippe Thomas (1893). Since 1896, date of the foundation of the French phosphate company “la Compagnie de Phosphate et de Chemin de Fer de Gafsa”, the first excavation took place with a total production of 200,000 metric tons/a (CPG-GCT 2009). Currently, the merchant rock output rises to more than 8 million metric tons/a, placing Tunisia fifth in the world for phosphate production (CPG-GCT 2009). This production is ensured by the Tunisian phosphate company, “la Compagnie des Phosphates de Gafsa-CPG”, which operates seven open-pit quarries and one underground mine scattering within ca. 1,250 km² area around the of Moularès and Redeyef cities (Boujlel et al. 2008). In order to

meet the international standards of quality, the Tunisian phosphate undergoes several refining and enrichment procedures, such as mechanical separation (grinding, sieving, etc.), washing and floatation, which increase the P_2O_5 concentration in phosphate rocks from 12 to 29.5% (Naeili et al. 2008). The latter two procedures basically depend on groundwater resources pumped totally from the Gafsa-south multilayer aquifer system. On the basis of available statistics, the global consumption of the phosphate mining sector is currently put at some 25 Mm^3/a , and if this figure is compared to the current total exploitation, provisionally put at ca. 39 Mm^3/a (DGRE 2009), the proportion corresponding to the CPG utilisation represents 65%. This percentage is, however, two times more agricultural and urban water supplies.

Despite uncertainties about the exact volume of groundwater reserve within this multilayer aquifer system, it is certain that more water is being removed from its resources than is replenished by recharge. In fact, within the last two decades, water tables have display some signs of over-exploitation due to the long-term withdraw. These are water-level declines in boreholes, drying of several springs due to the acute decrease of artesian head, and significant increase of groundwater salinity.

Although the importance of this aquifer system in the regional and national economy, fundamental hydrogeologic patterns, such as groundwater hydrodynamics, hydrochemical characteristics, origins and migration pathways of water masses remain poorly defined. It is within this framework that the present study is undertaken, which aims to provide baseline information about (1) the hydrochemical characteristics of groundwater, (2) the main groundwater

mineralisation processes and (3) the sources of different groundwater bodies and their migration pathways.

Physiographic settings

The study area, which extends over about 1,250 km^2 , belongs to the foreland Gafsa basin located in the North African Oriental Atlas (Fig. 1). It constitutes the eastern part of an important endoreic basin shared between Tunisia and Algeria. It is boarded to the northeast by the major northwest–southeast Gafsa fault and to the south by the east–west Chott trough. Ground elevation in the Gafsa-south mining district ranges from 524 m a.m.s.l. near Sbeitla outlet to 1,150 m a.m.s.l. in the Bouramli Mountain, in the northeastern limit of the basin (Ahmadi 2006). The climate is semi-arid with a long-term mean annual rainfall ranging from about 200 mm at the highest elevations to less than 130 mm in the lower portion of the basin (Hamed 2008). The potential evapotranspiration exceeds 1,600 mm. The mean annual temperature is 22°C with maximum temperatures of up to 43°C in summer (Hamed 2008). Regionally, the surface drainage is toward the south reflecting regional topographic gradients. The principal drainage network is constituted by several ephemeral wadis, which collect surface runoff from the surrounding hills and from the Algerian territories toward the endoreic salt lake depressions (locally known as Sebkhah or Chott) of Chott El Gharsa and Garet Douza (Fig. 1). At the foothills, pediments are generally overlaying thick conglomerate alluvial fans. Below 500 m a.m.s.l., the topography flattens, relatively thin sandy and clayey soils are present

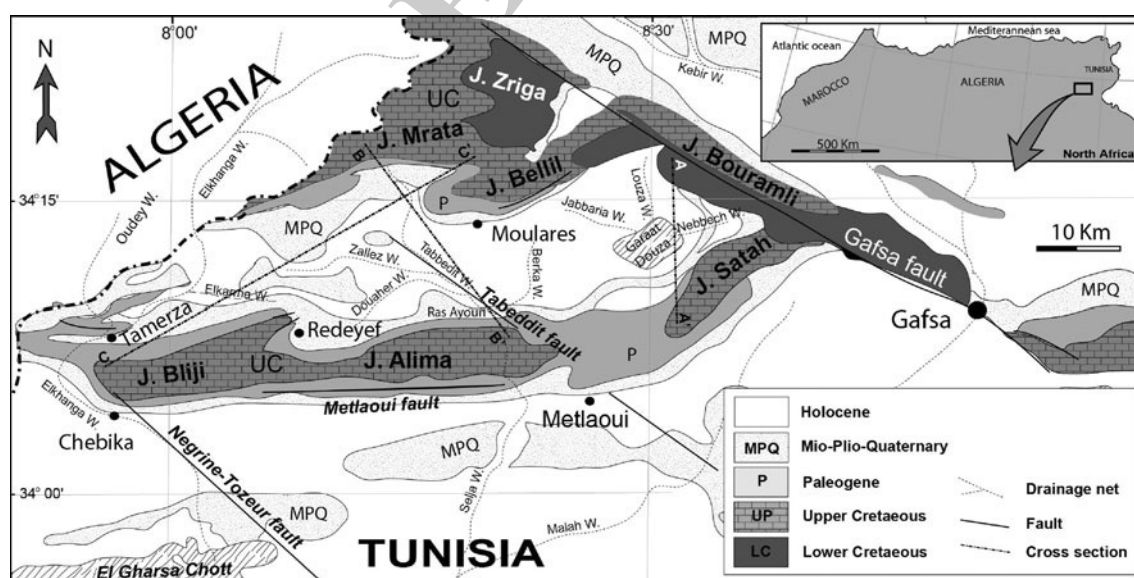


Fig. 1 Location and geologic map of the study area

(Ahmadi 2006). The eastern portion of the basin, in the vicinity of Garet Douza endoreic depression, evaporite deposits are abundant. The dominant tree type changes from a mix of semi-arid climate trees such as *Olea europea* L., *Pistacia vera* L., *Ficus carica* L. and *Phoenix dactylifera* L. in the floodplain and near the wadis, to sparsely distributed halophytes such as *Zygophyllum album* L., *Halocenem strobilaceum* L. near Garet Douza salt lake depression, and finally to annual terrestrial xerophytes such as *Artemisia herba alba* L., *Astragalus armatus* L., *Artemisia campestris* L., *Moricandia suffruticosa* L., *Lygeum Spartum* L., on the mountain slopes and seldom at the highest elevations (Chaieb and Boukhriss 1998).

Geology

The sedimentary series in the study area range from the Triassic sandstone and evaporite to Quaternary siliceous deposits. Considering the aim of this work, only the upper stratigraphic column extending from the Upper Cretaceous to the Actual will be presented in detail (Fig. 1). The Upper Cretaceous series begin with a thick Cenomanian–Turonian dolomite and claystone unit, locally interbedded with gypsum levels, belonging to the Zebbag Formation. This unit is overlaid by the Aleg Formation deposits constituted of thick Late Turonian–Early Campanian marly and calcareous claystone, locally intercalated with fossiliferous thin limestone layers that increase in thickness and frequency to the top (Burolet 1956). On the Aleg Formation reposes the Early Campanian–Late Maestrichtian limestone and dolomitic limestone of the Abiod Formation, which represents the end of the Upper Cretaceous series. The lower and the middle parts of this formation are dominated by clayey and marly thin layers, while, the upper part is distinguished by a fissured feature (Ahmadi 2006). Above the Abiod Formation reposes the Late Campanian–Paleogene claystone of the El Haria Formation, which represents the Cretaceous–Tertiary transition. This formation is overlaid by shallow marine to shore-face Paleocene–Early Eocene series belonging to the Metlaoui Group. This latter consists of thin gypsum, clay and highly fossiliferous dolomitic intercalations belonging to the Selja Formation, which is overlaid by the phosphatic carbonates and claystone series of the Chouabine Formation and the massive limestone layer of the Kef Eddour Formation. On these formations reposes the Late Eocene thick gypsum-rich dolomite of the Seugdal Formation that constitutes the last marine facies. The oldest continental Neogene Formation is represented by the Sehib clayey and silty conglomerate, which is overlaid by the Middle–Late Miocene sandstone of the Beglia Formation. This latter is made up of loose to locally friable well-sorted sands (Burolet

1956). The uppermost deposits in the study area belong to the Segui Formation of Late Miocene–Pleistocene age. It is a heterogeneous Formation represented by silty and gypsiferous claystone in the bottom; sandstone, siltstone, thin claystone intercalations and paleosol with pedogenic calcite nodules in the middle, and finally by sands, gypsiferous and argillaceous silts with thick sandy conglomerates layers in the top (Ahmadi 2006).

From the tectonic point of view, the sedimentary series of the oriental Atlas, particularly in the study area, have been controlled by extensive tectonics during the Mesozoic age leading to the setting up of normal east–west and northwest–southeast fault networks (Zargouni 1985; Zouari 1995). During the Cenozoic age, the Gafsa foreland basin was affected by compressive deformation events producing fault-related fold belts in relation with a thin-skinned mechanism (Ouattani et al. 1995; Ahmadi et al. 2006). These compressive tectonic events, mainly acting during the Quaternary age (Dlala and Hfaiedh 1993; Ahmadi 2006) and controlled by inherited fault directions, created east–west fold belts such as Mratta-Bellil and Satah-Alima-Bliji.

Hydrogeology

A three-level multilayered aquifer system exists within the Gafsa-south mining district (Fig. 2). The shallowest aquifer occurs within the Plio-Quaternary detrital deposits and ranges typically from 50 to 250 m in thickness (Hamed 2008). It is unconfined throughout the study area and consists of varying proportions of carbonate conglomerates, gravel, sand, silt, clay, reworked phosphate grains, evaporites and abundant pedogenic calcite nodules. This surficial level is not usually a large producer of water, likely due to its low hydraulic conductivity. However, in the eastern part of the study area, numerous privately owned wells tap this aquifer due to the presence of relatively high permeable conglomerate lenses. The clayey bedrock in the lower parts of the Plio-Quaternary deposits separates this shallow groundwater reservoir from the intermediate aquifer. Groundwater circulation in the shallow unconfined aquifer is somewhat complicated. Water flowing from a height from the potentiometric surface generally follows the topography. In the central part of the basin, precisely in the Zeller and Mazreg Chems elevated areas, groundwater divides, likely in relation with tectonic substratum uplifts, determine three flow pattern compartments. In the eastern compartment, groundwater converges radially from the surrounding highlands toward the salt lake depression of Garet Douza. In the central compartment, between the two divides, groundwater discharges into the Berka Wadi following two northwest–southeast

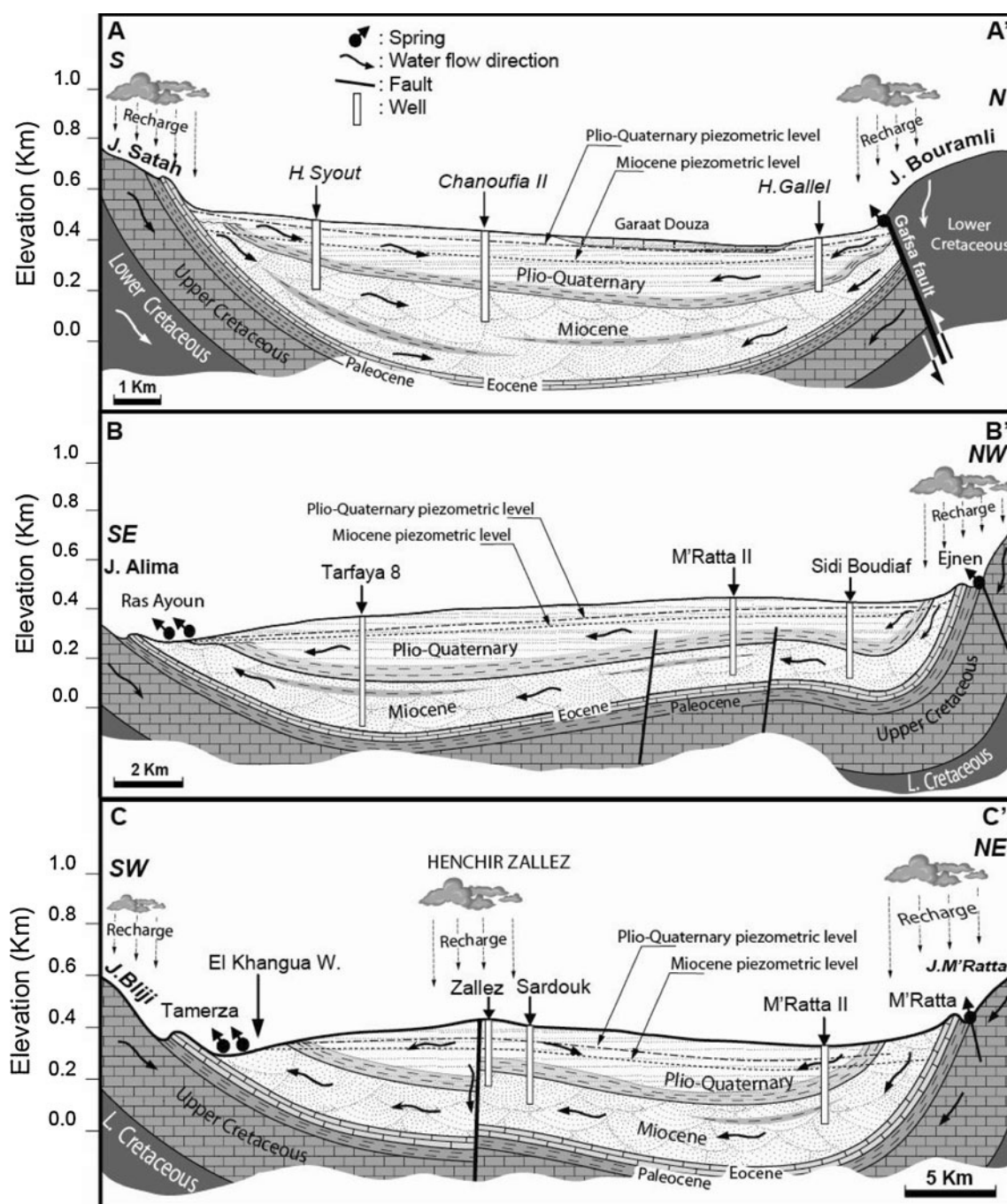


Fig. 2 Hydrogeological cross-sections of the studied multilayer aquifer system

215 and northeast–southwest flow directions. Finally, in the
216 western compartment, groundwater flows east–west and
217 northeast–southwest and discharges in the El Khanga Wadi
218 near the Tamerza outlet zone.

219 The intermediate aquifer, with an average thickness of
220 ca. 225 m, is hosted in the Miocene deposits. It is made up
221 of loose to locally friable well-sorted sand, which gives an
222 excellent intergranular porosity and high permeability
223 (Hamed et al. 2008). This aquifer is confined in major part

of the study area, except in the foothills and the discharge
224 areas, where the overlying Plio-Quaternary deposits are
225 completely eroded. In these zones, the intermediate aquifer
226 is drained by several perennial springs. Elsewhere, this
227 aquifer is tapped by hundreds of private dug wells and state
228 deep boreholes with depths ranging from ca. 10 to 500 m.
229 From a production potential point of view, the Miocene
230 confined/unconfined aquifer represents the main ground-
231 water reservoir due to its relatively important thickness and
232

the presence of several highly permeable zones, separated by clays and finer grained clastics deposits. The degree of connection between these permeable zones and their areal extent is not well understood because of the bad distribution of boreholes tapping this aquifer (Hamed et al. 2008). Groundwater flow pattern in the Miocene aquifer is relatively simple. Surface runoff infiltrates in the foot of the surrounding mountains and converges to the central part of the basin. There, a general flow from east to west carries the groundwater to the Tamerza and Ras El Ayoun outlet areas, where the water discharges via several overflow springs.

The Upper Cretaceous deep aquifer is constituted of vertically continuous carbonate sequences with generally high permeability that are hydraulically connected in varying degrees (Hamed 2008). It typically consists of ca. 300 m-thick fissured limestone and dolomitic limestone with fracture density ranging from 5 to 20 m/m² (Ahmadi et al. 2006). This aquifer is confined far and wide the study area and yields a great artesian pressure, especially in the central part of the hydrologic basin where it reaches its maximum depth. Hence, along the major faults it is drained by several artesian springs. However, there are no boreholes tapping this aquifer till now because of its relatively high degree of confinement within the study area. Despite this it undoubtedly constitutes an important potential water resource for the next decades. This deep aquifer is separated from the overlying Miocene aquifer by impermeable (to slightly permeable) Palaeocene/Eocene carbonate units consisting of phosphatic-rich clayey and marly limestone and dolomite with abundant gypsiferous deposits. Groundwater circulation within this deeper reservoir is not well understood as lateral flow paths are not well defined. However, it is thought that the deep flow regime involves local-scale flow systems, which recharge in the upland highly permeable outcrops and discharge partially to adjacent lowlands via several artesian springs. Far away to the deeper parts of the basin, upward head gradients produce more discharge to the overlying intermediate Miocene flow regime through sub-vertical major faults.

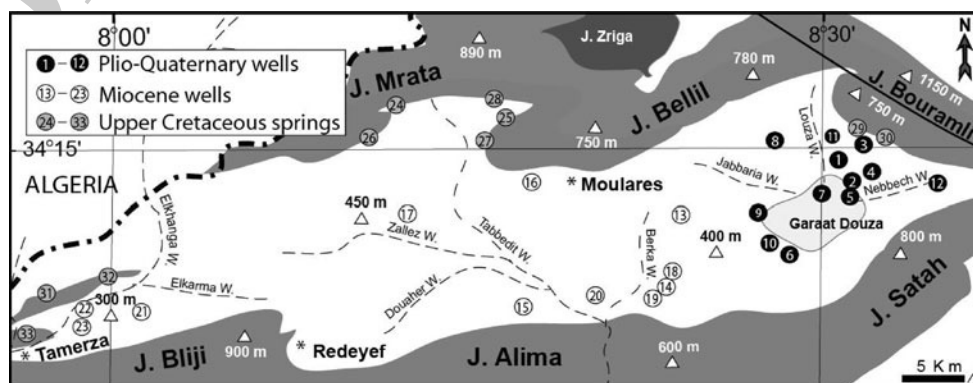
Groundwater sampling and analytical methods

Water samples were collected from private and state-owned wells, and springs tapping the different aquifer levels. Spring waters were sampled as close to the spring orifice as possible. All Upper Cretaceous springs are located in the foot of the bordering mountains, where the aquifer formation crops out (Fig. 3). Wells were pumped for some minutes (ca. 5 min) before sampling. In situ measurements i.e. electric conductivity (EC), temperature (*T*) and pH of the discharge water were monitored, and sample bottles were filled after these parameters stabilised. Sample bottles were kept in a cooler or refrigerator upon collection.

Cation and anion analyses were performed at the laboratory of the “Compagnie des phosphates de Gafsa (CPG)”, Tunisia, using a Dionex DX 100 ion chromatograph equipped with a CS12 and an AS14A-SC Ion Pac columns and an AS-40 auto-sampler. The total alkalinity (as HCO₃) was determined by titration with 0.01 or 0.1 M HCl against methyl orange and bromocresol green indicators (APHA 1998). Charge balances for all samples with HCO₃ data are less than 5%.

Deuterium ($\delta^2\text{H}$) and oxygen-18 ($\delta^{18}\text{O}$) isotope analyses were performed at the laboratory of the IAEA, using mass spectrometer after standard CO₂ equilibration (Epstein and Meyada 1953) and zinc reduction preparation techniques (Coleman et al. 1982), respectively. All oxygen and hydrogen isotopes analyses are reported in the usual δ notation relative to Vienna Standard Mean Oceanic Water (VSMOW). Owing to financial constraints, a limited number of water samples was selected for carbon isotope analysis (^{14}C and $\delta^{13}\text{C}$). Radiocarbon analyses were carried out at the laboratory of the “Ecole Nationale d'Ingénieurs de Sfax, Tunisia, by scintillation counting on C₆H₆ synthesised from BaCO₃ stripped in the field from ca. 150-l water samples. Results are reported as percentage of modern carbon (pmC) (Stuiver and Polach 1977). The $\delta^{13}\text{C}$ was measured at the laboratory of the IAEA, by converting the DIC to CO₂ with 100% phosphoric acid (H₃PO₄)

Fig. 3 Sampling map



312 followed by cryogenic separation and analysis by mass
313 spectrometry (Boaretto et al. 1998). Reproducibility is
314 typically better than $\pm 2\%$ for hydrogen isotopes, $\pm 0.1\%$
315 for oxygen, and $\pm 0.2\%$ for carbon.

316 Discussion

317 Chemical composition of groundwater

318 Water types

319 Analytical results of major ions in groundwater samples
320 and their saturation indexes with respect to some minerals
321 are reported in Table 1.

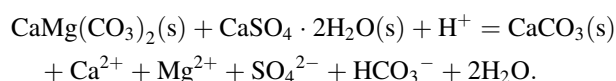
322 In order to classify groundwater samples into different
323 water types and to identify the hydrochemical processes
324 that control the mineralisation within the multilayer aquifer
325 system, a Chadha diagram (Chadha 1999) was used. This
326 diagram is a somewhat modified version of the Piper dia-
327 gram (Piper 1944) and the expanded Durov diagram (Du-
328 rov 1948). The difference is that the two equilateral
329 triangles were omitted (Chadha 1999). When plotted in the
330 Chadha diagram, groundwater samples of the Gafsa-south
331 mining district fall within the field 6, revealing a Ca–Mg–
332 SO_4 water type (Fig. 4). In this field strong acidic anions
333 (Cl^- and SO_4^{2-}) exceed weak acidic anions (HCO_3^- and
334 CO_3^{2-}). Furthermore, alkaline earths (Ca^{2+} and Mg^{2+})
335 exceed alkalis (Na^+ and K^+). The predominance of cal-
336 cium and sulphate over sodium and chloride can be
337 explained by the dissolution of gypsum and/or anhydrite,
338 which dominate the dissolution of halite. However, the
339 dominance of magnesium and the lack of bicarbonate are
340 likely related to the incongruent dissolution of dolomite,
341 which is generally associated with the calcite precipitation
342 and gypsum dissolution.

343 Origin of mineralisation

344 In order to accurately determine the origin of groundwater
345 mineralisation in the Gafsa-south multilayer aquifer sys-
346 tem, the sum of major anions and the sum of major cations
347 were separately correlated to each anion and to each cation,
348 respectively (Fig. 5). The well-defined relationships char-
349 acterising mainly the Cl, SO_4 , Na, Ca and Mg plots lend
350 support to their significant contribution to the groundwater
351 mineralisation. To precisely identify the principal origins
352 of the referred ions, Na versus Cl and Ca versus SO_4 ,
353 bivariate plots were established (Fig. 6). The plot of Na
354 versus Cl shows that the majority of groundwater samples
355 falls on the 1:1 line, suggesting that these ions mostly
356 derived from the same origin; likely in relation with the
357 dissolution of halite (Shouakar-Stash et al. 2007). This

process is, however, confirmed through the negative satu-
ration indexes with respect to the referred mineral, which
exhibit a proportional evolution when correlated to the sum
of ions deriving from the NaCl eventual dissolution (Ben
Moussa et al. 2009) (Fig. 7a).

Most of the groundwater has elevated Ca^{2+} and Mg^{2+}
concentrations relative to HCO_3^- , and is charge balanced by
 SO_4^{2-} . These sulphate-rich waters likely evolved from
gypsum and/or anhydrite (CaSO_4) dissolution as indicated
by the well-defined relationship in the plot of Ca versus SO_4
(Barth 2000) and by the proportional, parabolic, trend
observed in the correlation of the negative saturation
indexes, with respect to the referred minerals, versus the
sum of ions resulting from the CaSO_4 mentioned dissolution
(Kamel et al. 2005) (Fig. 7b, c). Even though all ground-
water is saturated with calcite and dolomite (Table 1), it
is undersaturated with gypsum/anhydrite; the dissolution
of anhydrite continues and the concentration of Ca^{2+} and
 SO_4^{2-} increases further. This causes, according to the
common ion effect, calcite supersaturation and precipita-
tion, which may decrease Ca^{2+} concentrations as the plot of
Ca versus SO_4 reveals. The decrease in HCO_3^- concentra-
tions, resulting also from calcite precipitation, may then
cause de-dolomitization process, adding Mg^{2+} to the waters
and decreasing the Ca/Mg molar ratios (Marfiaa et al. 2004).
This process, which is evidenced by the 1:1 relationship
in the plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + 0.5\text{HCO}_3^-$
(Fig. 8) (McIntosh and Walter 2006), corresponds to the
incongruent dissolution of dolomite (incongruent means
dissolution during which a solid product remains) to form
calcite with a crystalline structure similar to dolomite; cal-
cite formed in this way is called “dedolomite” (Hanshaw
and Back 1979). The net reaction for the de-dolomitization
process is (McIntosh and Walter 2006):



Isotopic composition of groundwater

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents

Deuterium and oxygen-18 isotopes of the water molecule
are indicators of conditions present at the time and place of
groundwater recharge (Faure 1986). They are influenced by
processes affecting the water, rather than the solutes, and
can help identify waters that have undergone evaporation,
recharge under different climatic conditions than the
present, and help further to resolve overall questions
relating to mixing of waters from different sources. (Sacks
and Tihansky 1996). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures of
groundwaters are generally compared to those of the

Table 1 In situ measurements, geochemical data and saturation indexes of groundwaters

Well/Spring	pH	T (°C)	EC (mS/cm)	TDS (mg/l)	Ca	Mg	Na	K (meq/l)	HCO ₃	SO ₄	Cl	NO ₃	Saturation index (SI)				
													Anhydrite	Gypsum	Halite	Dolomite	
Amar B Rmel	7.75	19	3.25	2,350	14	13.56	8.48	0.68	3.61	19.45	10.86	0.98	-0.77	-0.48	-5.77	0.66	1.40
Abedjalil elhani	7.33	17	3.51	2,600	15	15.78	10.00	1.02	4.38	21.96	11.00	0.23	-0.74	-0.42	-5.70	0.31	0.70
Ali B Salah	7.65	18	4.20	3,850	17.25	13.56	13.48	1.04	4.00	24.02	12.97	0.19	-0.65	-0.35	-5.50	0.65	1.26
Med B Hamed	7.80	18	4.99	3,840	26	11.84	22.00	1.48	4.00	28.95	23.01	0.39	-0.47	-0.17	-5.06	0.92	1.60
Hmeda B Gayed	7.84	18	2.94	2,280	15	8.55	14.00	0.62	1.60	18.97	14.02	0.41	-0.74	-0.44	-5.44	0.42	0.66
Chan II bis	8.10	17	5.25	6,850	28.25	16.03	23.91	1.66	4.35	34.94	23.97	0.58	-0.40	-0.09	-5.00	1.24	2.30
Med Sadouk	7.90	18	15.85	15,600	29.75	15.62	25.65	1.92	5.25	36.61	26.79	0.84	-0.37	-0.07	-4.90	1.15	2.10
Jabaria I	8.01	20	1.95	2,010	16	4.52	5.22	0.22	3.61	16.33	4.94	0.18	-0.70	-0.42	-6.36	1.03	1.60
Chanoufia II	8.03	22	7.20	5,380	28	9.86	30.00	1.22	4.30	33.95	26.03	0.13	-0.36	-0.11	-4.89	1.22	2.13
Chanoufia I	8.04	21	3.23	2,400	14	7.89	14.00	0.14	3.39	15.97	14.02	0.24	-0.79	-0.53	-5.45	0.96	1.78
Nazia	8.00	21	2.95	2,400	19	5.34	5.44	0.35	3.53	16.02	13.71	0.14	-0.66	-0.40	-5.80	1.08	1.71
H.H.Gallel	8.01	22	2.80	2,300	16	6.99	15.22	0.29	3.77	16.85	14.44	0.24	-0.72	-0.47	-5.40	1.04	1.84
Mazreg chames	7.02	18.5	3.25	1,560	10.75	6.41	17.91	0.25	3.12	16.02	12.97	0.08	-0.80	-0.61	-5.36	-0.21	-0.57
Berka 4	7.04	20	3.70	3,800	15	6.90	19.00	0.82	3.80	19.97	17.03	0.30	-0.75	-0.44	-5.24	0.01	-0.20
Tarfaya 8	7.72	22	1.59	1,340	11	4.93	3.00	0.23	2.39	14.98	1.97	0.26	-0.31	-0.56	6.94	0.46	0.70
Mratta II	8.10	19.5	5.65	4,850	21.25	9.21	21.09	1.38	4.43	30.37	24.11	0.32	-0.50	-0.22	-5.06	1.18	2.10
O.O.Sardouk	7.48	19	3.55	2,600	14	5.92	17.00	0.41	3.30	17.97	15.03	0.16	-0.77	-0.48	-5.33	0.37	0.44
Barhoumi	7.50	18	11.20	8,250	28	15.21	25.13	1.99	4.59	33.07	24.11	0.90	-0.41	-0.12	-5.00	0.70	1.21
Ali Messaoui	7.70	16	8.97	8,240	14	9.86	10.00	0.35	2.80	15.97	12.01	1.20	-0.83	-0.51	-5.60	0.50	0.86
Salah Mabrouki	7.82	20	10.7	8,080	30.5	12.82	24.57	1.54	5.25	36.40	26.79	0.88	-0.33	-0.06	-4.96	1.11	1.96
T.SONEDE	7.75	19	4.27	3,250	15.2	20.49	22.80	0.18	4.17	28.63	16.02	0.29	-0.68	-0.39	-5.21	0.68	1.59
S.Tamerza	7.9	20	2.1	1,760	15.9	3.87	9.01	0.20	2.70	15.28	4.82	0.27	-0.72	-0.45	-6.09	0.80	1.09
Rmitha	8	19.5	1	800	5.4	4.12	1.39	0.10	2.34	6.89	2.00	0.36	-1.32	-1.04	-7.24	0.49	0.95
Ain Gatâa	7.80	23	0.66	540	3.5	1.97	1.00	0.06	3.30	2.16	5.50	0.05	-1.85	1.60	-6.93	0.40	0.64
Ain Wssaief	7.32	24	1.96	1,700	12	7.40	7.00	0.13	4.71	11.90	8.52	0.07	-0.89	-0.66	-5.96	0.42	0.78
Ain Damous	7.90	21	1.83	1,440	10	4.93	5.00	0.06	1.79	10.98	8.35	0.05	-0.97	-0.71	-6.10	0.49	0.77
Ras El Mâa	8.1	20	2.38	2,200	14	7.89	9.00	0.05	3.00	17.97	10.01	0.09	-0.74	-0.47	-5.78	0.95	1.75
Ejnan	7.25	19	0.84	700	4.1	1.97	2.96	0.04	3.69	2.70	1.78	0.04	-1.74	1.46	-6.94	-0.10	-0.46
Ain Sarraguiya	7.54	20	2.34	2,260	14	7.89	11.00	0.04	3.00	19.97	9.02	0.07	-0.71	-0.44	-5.74	0.40	0.65
Ain El Mourra	7.4	21	2.44	2,100	13.2	7.15	8.61	0.05	2.74	18.30	7.05	0.08	-0.74	-0.47	-5.95	2.20	0.23

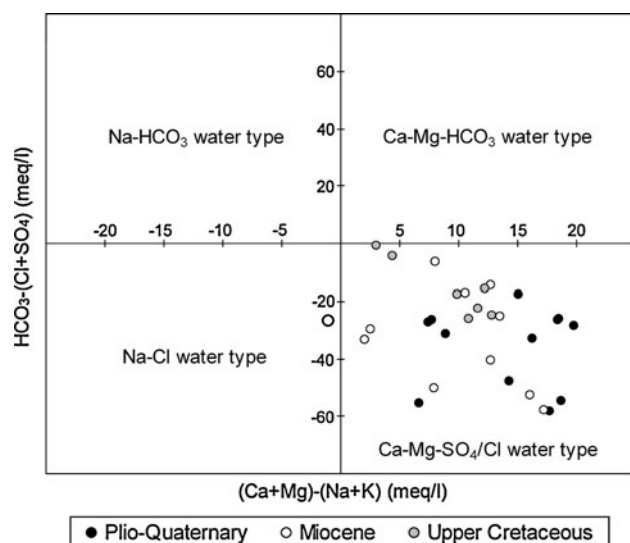


Fig. 4 Chadha diagram showing the water type of the groundwater samples

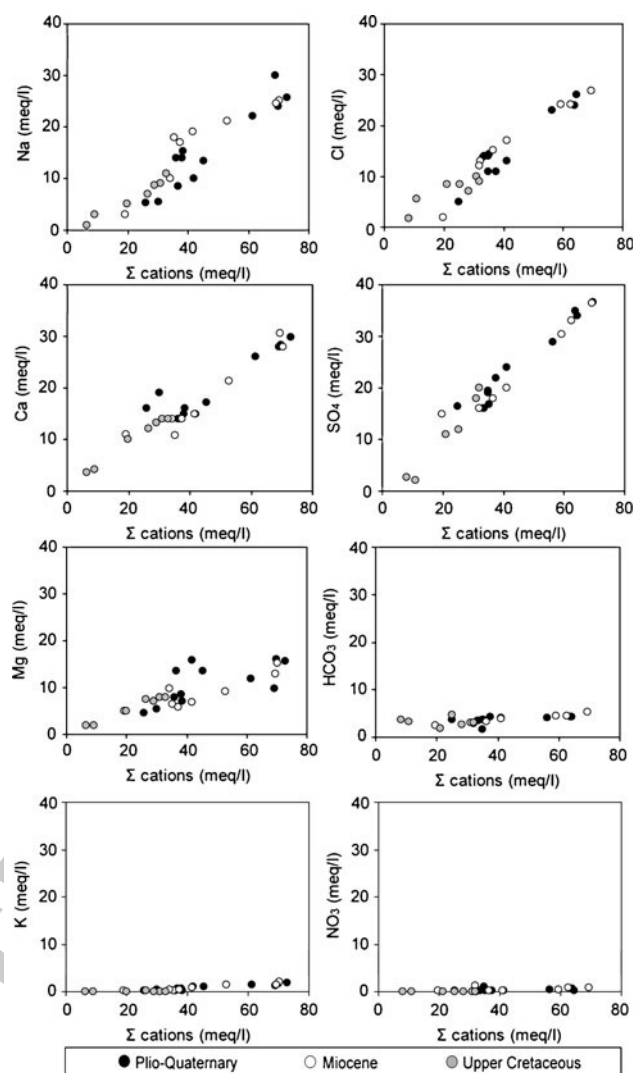


Fig. 5 Plots of Σ anions versus each anion and Σ cations versus each cation

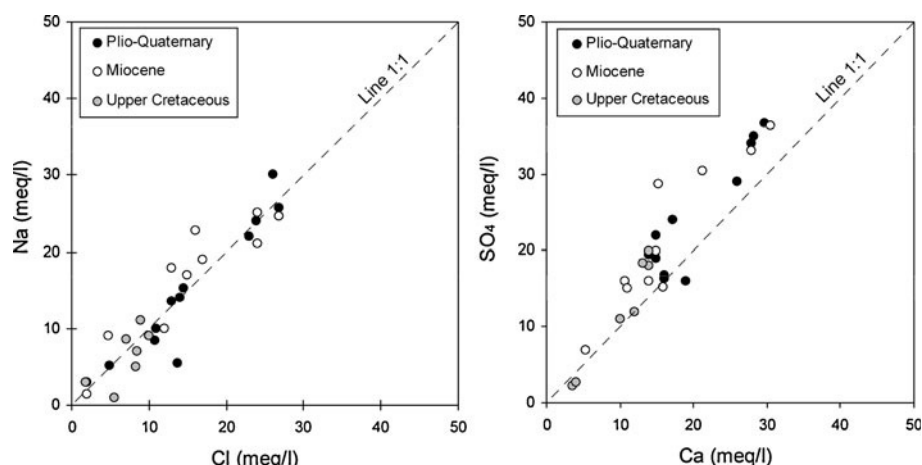
precipitation represented by the Global Meteoric Water Line (GMWL) (Craig, 1961) and the Regional Meteoric Water Line (RMWL). Stable isotope values that plot along the meteoric water lines are compared to local precipitation mean values to determine if groundwaters derive from recent local recharge or they originate from water that recharged the aquifer under climatic condition different than the present. Deviations from the meteoric lines indicate modification of the groundwater by evaporation or extensive water–rock interactions (Uliana et al. 2007).

One major impediment for understanding the relationship between isotopic compositions of precipitation and groundwaters is long-term stable isotope records in the study area. In the present study, oxygen-18 and deuterium values for local precipitation are not well documented. A general estimate, however, can be derived from data and study results from nearby areas. Data from the nearest Global Network for Isotopes in Precipitation (GNIP) station, located in the Sfax coastal city (GNIP station 7622500), at an elevation of about 10 m have yearly weighted means of oxygen-18 and deuterium of -4.60 and -23.30 ‰, respectively (IAEA/WMO 1999). The meteoric water line established from these data, generally used as a RMWL in southern Tunisia studies, has the equation: $\delta^2\text{H} = 8\delta^{18}\text{O} + 13.5$ (Maliki 2000; Maliki et al. 2000).

The isotopic composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of all groundwaters of the Gafsa-south mining basin, range from -8.29 to -6.33 ‰ and from -55.8 to -35.30 ‰, respectively (Table 2). When plotted in the $\delta^{18}\text{O}/\delta^2\text{H}$ standard diagram (Fig. 9), waters from different aquifers of the multilayer system show several observations in relation to each other and to the local modern rainfall. Firstly, they fall practically around the GMWL and do not show patterns of

enrichment that could be attributed to either evaporation of meteoric water during recharge (Allison 1982) or extensive mineral–water interactions following recharge (Banner et al. 1989). The $\delta^{18}\text{O}$ contents reflect, therefore, the conditions present at the time of aquifers recharge. Secondly, they are all strongly depleted in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relative to the weighted mean of the modern local rainfall by up to 3.6 ‰ in ^{18}O , indicating lower condensation temperature of the precipitation that contributes to the recharge. This could be related either to an altitude effect (recent high-altitude recharge) or to a paleoclimatic effect i.e. recharge under colder climatic conditions than at present. Thirdly, the whole groundwater samples from the deeper aquifer, outcropping at higher altitudes, show greater depletion (difference up to 2 ‰ $\delta^{18}\text{O}$) relative to waters from the shallower Miocene and Plio-Quaternary aquifers that crop out at lower altitudes, which brings insight to an altitude

Fig. 6 Plots of Na versus Cl and Ca versus SO₄



effect of the deep waters. Fourthly, water samples from the unconfined Plio-Quaternary and the confined Upper Cretaceous aquifers constitute two agglomerations with isotopically homogenised compositions, while, samples from the confined/unconfined Miocene aquifer scatter along a linear trend with relatively heterogeneous ¹⁸O and ²H compositions, indicating that they derive from more than one origin.

The more depleted waters of the Plio-Quaternary aquifer, which show the largest difference with the isotopic composition of the modern local precipitation (difference of about 3‰ δ¹⁸O), likely represent recharge during cooler climatic conditions rather than altitude. In fact, they are comparable to depleted Late Pleistocene and Early Holocene paleo-groundwaters identified at local (Edmunds et al. 2003; Dassi et al. 2004, 2005; Kamel et al. 2005, 2006) and continental scales (Gonfiantini et al. 1974; Fontes et al. 1983; Fontes 1985; Edmunds et al. 1997; Guendouz et al. 2003). These paleo-groundwaters, observed elsewhere across Africa (Clark and Fritz 1997; Edmunds 2005), were interpreted as evidence of continental effect as Atlantic air masses travelled away from their source (Sonntag et al. 1978).

The more enriched waters from the Upper Cretaceous aquifer, which crops out in the surrounding mountains, have an average δ¹⁸O composition of −6.62, being some 2.0‰ lighter than the weighted mean of the modern local rainfall. This discrepancy in isotopic contents could be attributed to the recharge at a higher altitude than that of the GNIP station, where δ¹⁸O of the modern precipitation was measured. In fact, air masses rise adiabatically owing to increases in elevation, which forces rainout; decreasing air temperature with increasing elevation causes isotopic fractionation so that rainfall becomes increasingly isotopically depleted (Fritz et al. 1992; Leybourne et al. 2006). To confirm this altitude effect it is necessary to estimate quantitatively the recharge altitude of the deep

groundwaters and verify whether it actually matches with the elevation of the aquifer outcrops in the recharge areas. This estimation can be made on the basis of the known heavy isotope content of precipitation and altitude effect in the considered region, by using the simple equation (e.g. Grabczak and Kotarba 1985)

$$H_R = H_{GN} + 100 \times (D/AG)$$

where H_R is the estimated recharge altitude and H_{GN} is the altitude of the GNIP station (in m), D is the difference between oxygen-18 compositions in precipitation and Upper Cretaceous groundwaters ($D = \delta^{18}O_{\text{Precipitation}} - \delta^{18}O_{\text{Groundwater}}$, per mil), AG is the local altitude gradient for oxygen-18 (per mil per 100 m). By assuming an oxygen-18 altitude effect (AG) between 0.25 and 0.35‰ per 100 m with regard to the global variation range of 0.15–0.5‰ per 100, suggested by Gat (1981) as well as by Clark and Fritz (1997), the approximate altitudes of the potential recharge areas calculated with the aid of the above equation and values vary between 581 and 810 m. This range, which matches practically with the elevation of the recharge areas of Upper Cretaceous aquifer in the surrounding mountains, may confirm the assumption of its recharge by modern rainfall at higher altitudes.

Waters from the confined/unconfined Miocene aquifer have an intermediate and relatively wide range of ¹⁸O and ²H contents. They plot along an approximately linear trend, which involves the same paleowaters, already identified in the unconfined Plio-Quaternary unit; more or less mixed with the relatively modern waters deriving from the underlying confining Upper Cretaceous aquifer. The isotopic composition of these mixed waters is largely controlled by extent of the upward leakage from the deeper aquifer, which naturally occurs along the major faults of the study area but may be locally enhanced by pumping or interconnection of wells open to both aquifer systems.

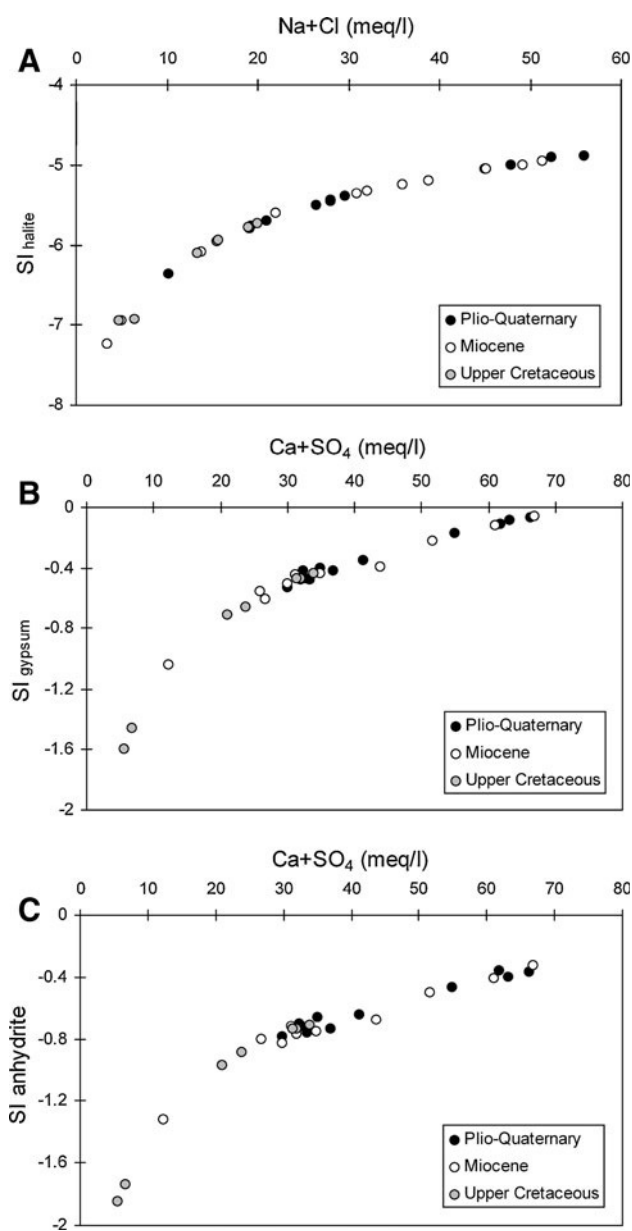


Fig. 7 Plots of (Na + Cl) versus SI_{halite} (a), (Ca + SO_4) versus SI_{gypsum} (b), (Ca + SO_4) versus $SI_{anhydrite}$ (c)

^{14}C activities and $\delta^{13}C$ contents

The ^{14}C of dissolved inorganic carbon (DIC) still gains interest as an alternative practical radioactive tracer due to its potential dating range that makes it the most useful tool for reliable estimation of the mean groundwaters residence time over timescales to ca. 30 ka (Clark and Fritz 1997). However, the interpretation of radiocarbon activities to provide absolute ages, which permit more reliable dating resolution, is limited by geochemical complications related to water–rock interaction and requires knowledge of carbonate hydrochemistry added by understanding of the $\delta^{13}C$

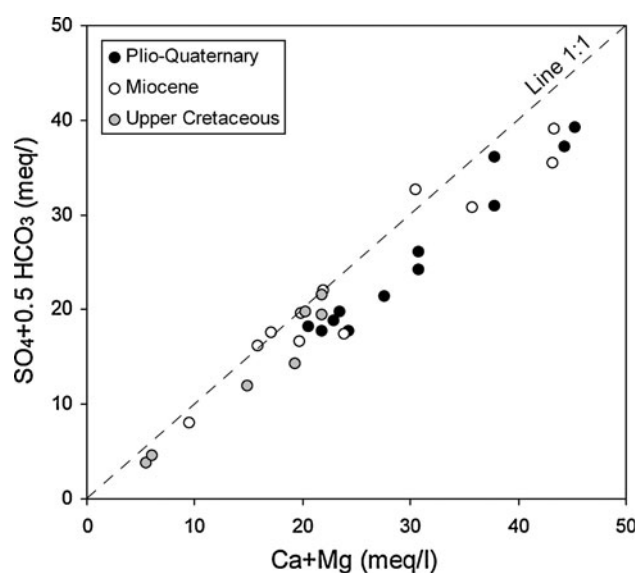


Fig. 8 Plot of (Ca + Mg) versus ($SO_4 + 0.5HCO_3$)

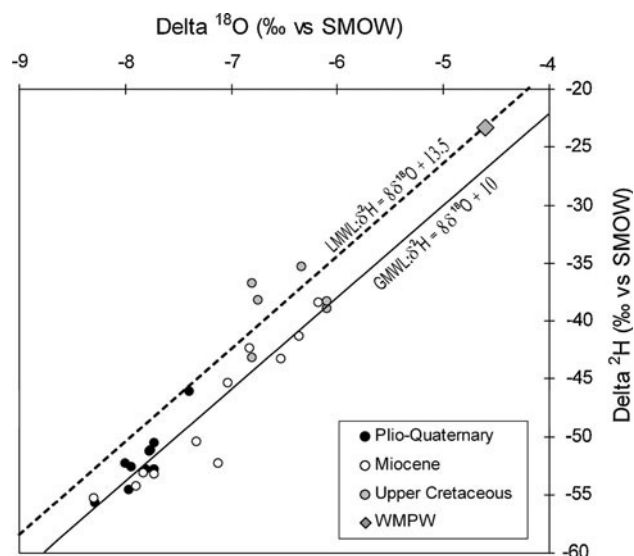
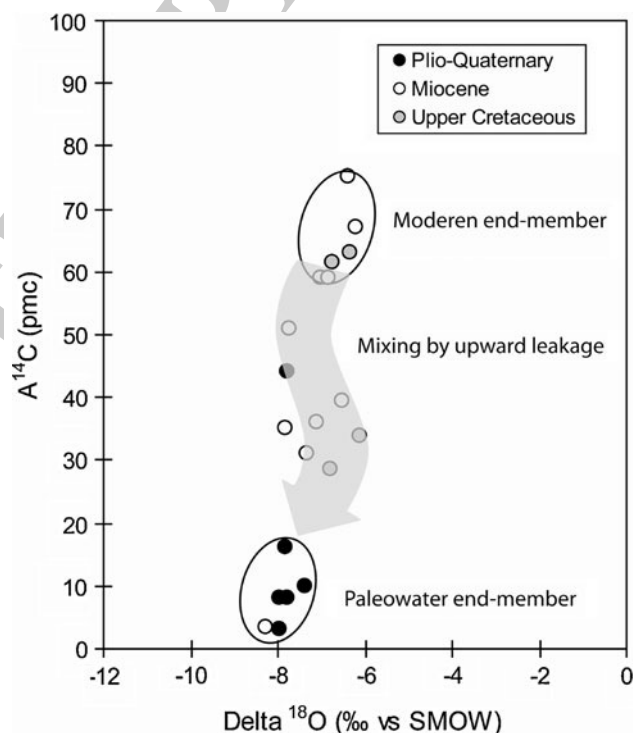
evolution (Clark and Fritz 1997; Edmunds and Smedley 2000).

Carbon-14 activities and $\delta^{13}C$ contents in DIC (mainly HCO_3) of the groundwater in the Gafsa-south aquifer system range from 3 to 75.3 pmC and from -11.3 to -4.98% versus PDB, respectively (Table 2). The variations of ^{14}C activities with $\delta^{18}O$ and $\delta^{13}C$ contents are shown in Figs. 10 and 11, respectively. Groundwater samples collected from the Plio-Quaternary unconfined aquifer show the lowest values of ^{14}C activities ranging from 3 to 44.2 pmC, with a mean value of 14.9 pmC, and the heaviest $\delta^{13}C$ contents varying from -6.32 to -4.98% versus PDB, with a mean value of -5.72% versus PDB. Low ^{14}C activities agree with relatively depleted ^{18}O and ^2H contents of these groundwaters and verify their old paleoclimatic origin. This enriched $\delta^{13}C$ and low ^{14}C activities can be explained by the long groundwater residence times leading to the extended interaction with pedogenic calcite nodules and carbonate conglomerates particularly, abundant within this unconfined aquifer, where the influence of renewable soil CO_2 is negligible (Grassi and Cortecchi 2005).

Water from the Upper Cretaceous carbonate aquifer displays ^{14}C activities ranging between 26.4 and 63 pmC. High activities in some samples lend support to the recent origin of these deep groundwaters, already confirmed by the enriched ^{18}O and ^2H signatures, while, relatively low activities that characterise other samples provide insight to the interaction with old carbonate rocks in this confined aquifer. Indeed, these low ^{14}C -samples show slightly enriched $\delta^{13}C$ contents, varying from -7.5 to -6.8% versus PDB, relative to high ^{14}C -samples, which have $\delta^{13}C$ values between -9.4 and 7.8% versus PDB. In any case, as

Table 2 Isotopic data of groundwaters

Well/Spring	$\delta^{18}\text{O}$ (‰ vs SMOW)	$\delta^2\text{H}$ (‰ vs SMOW)	^{14}C (pmC)	^{13}C (‰ vs PDB)
Amar B Rmel	-8.28	-55.80	-	-6.32
Abedjalil elhani	-7.72	-50.60	-	-
Ali B Salah	-7.80	-52.80	16.00	-6.07
Med B Hamed	-8.00	-52.30	-	-
Hmeda B Gayed	-7.72	-50.60	-	-5.04
Chan II bis	-7.39	-46.10	-	-
Med Sadouk	-7.76	-51.20	44.20	-
Jabaria I	-7.77	-51.30	8.00	-5.94
Chanoufia II	-7.39	-46.10	10.00	-5.68
Chanoufia I	-7.73	-52.80	-	-
Nazia	-7.94	-52.60	8.20	-4.98
H.Gallel	-7.96	-54.60	3.00	-6.03
Mazreg chames	-7.03	-45.40	59.00	-9.83
Berka 4	-7.83	-53.20	35.00	-
Tarfaya 8	-8.29	-55.30	3.40	-
Mratta II	-6.82	-42.40	59.00	-8.63
O.Sardouk	-7.12	-52.30	36.00	-9.91
Barhoumi	-7.73	-53.30	51.00	-
Ali Messaoui	-6.36	-41.30	75.30	-
Salah Mabrouki	-7.33	-50.50	31.00	-
T.SONEDE	-7.90	-54.30	18.00	-11.30
S.Tamerza	-6.18	-38.48	67.20	-8.56
Rmitha	-6.53	-43.30	39.40	-8.32
Ain Gatâa	-6.74	-38.24	61.40	-8.18
Ain Wssaief	-6.80	-36.80	28.60	-7.39
Ain Damous	-	-	-	-
Ras El Mâa	-6.33	-35.30	63.00	-7.80
Ejnan	-	-	-	-
Ain Sarraguiya	-	-	-	-
Ain El Mourra	-	-	-	-
Ain Morchen	-6.10	-39.00	34.00	-7.50
Ain Tahar	-6.10	-38.30	26.40	-6.80
Ain Makhfia	-6.80	-43.20	-	-9.40

**Fig. 9** Conventional diagram of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ **Fig. 10** Plot of $\delta^{18}\text{O}$ versus ^{14}C activity

571 a carbonate aquifer, the Upper Cretaceous does not show
 572 highly enriched $\delta^{13}\text{C}$ contents, deriving from massive
 573 exchange with heavy CO_2 , comparatively to the Plio-
 574 Quaternary non-carbonate aquifer. The slightly enriched
 575 $\delta^{13}\text{C}$ values of the Upper Cretaceous groundwaters (pre-
 576 senting an average value of ca. -8‰ vs PDB) likely
 577 suggest significant contribution of modern recharge by
 578 meteoric waters equilibrated in due time with atmospheric
 579 CO_2 that has $\delta^{13}\text{C}$ ranging between -9 and -7‰ versus
 580 PDB (Deines 1980; Traganos et al. 1995).

581 Waters from the confined/unconfined Miocene aquifer
 582 exhibit wide ranges of ^{14}C activities and $\delta^{13}\text{C}$ contents,
 583 ranging from 3.4 to 75.3 pmC and from -11.3 to -4.98‰

584 versus PDB, respectively. Higher ^{14}C and depleted $\delta^{13}\text{C}$
 585 are consistent with the presence of a greater component of
 586 younger water through upward leakage from the under-
 587 lying Upper Cretaceous confined aquifer. While, lower
 588 ^{14}C and relatively enriched $\delta^{13}\text{C}$ plead in favour of some
 589 contribution from the overlaying Plio-Quaternary uncon-
 590 fined aquifer. However, in general, a significant proportion
 591 of the carbon likely comes from plant respiration and
 592 production of CO_2 in the soils. C_4 plants, represented in the



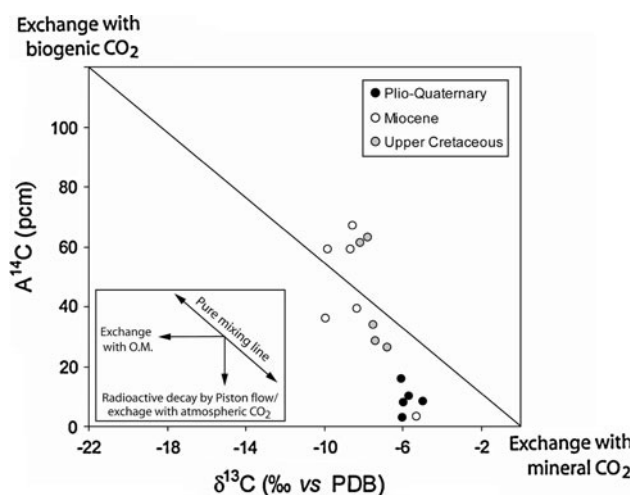


Fig. 11 Plot of $\delta^{13}\text{C}$ versus ^{14}C activity

area by semi-arid halophytes and annual terrestrial xerophytes, have $\delta^{13}\text{C}$ values of -17 to -9‰ versus PDB (Romanek et al. 1992; Vogel 1993). Isotopically light CO_2 liberated by decay of C_4 organic matter in the soil enters the soil waters and likely equilibrates with the Miocene groundwaters making lower $\delta^{13}\text{C}$ and higher ^{14}C (Fig. 11).

Conclusion

Groundwaters in the Gafsa-south mining district play a significant role in the development of the phosphate mining sector in Tunisia. The results of this study provide important information that can be useful for the management and the preservation of this valuable resource. Major ions investigation shows that the Ca-Mg-SO_4 groundwaters within the Gafsa-south multilayer aquifer system acquire their mineralisation through water-rock interaction processes, involving the dissolution of halite, gypsum and/or anhydrite as well as the incongruent dissolution of dolomite. Oxygen-18 and deuterium signatures were very effective in identifying the origin and the migration pathways of groundwaters. Indeed, the more depleted values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the Plio-Quaternary surficial groundwaters lend support to their old recharge likely in relation with Late Pleistocene and Early Holocene cooler, humid periods. Likewise, the more enriched values in the deeper Upper Cretaceous aquifer groundwaters provide insight to their recent recharge occurring probably at higher altitude outcrops. However, intermediate values in the Miocene aquifer groundwaters highlight the mixture between these old and recent end-members. Stable and radiogenic isotopes of the DIC agree with the above-mentioned origins of the different groundwaters and provide supplementary

valuable information about the interaction with carbon from different sources.

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