

An appraisal of natural fluorine contamination of paleogroundwater in Tozeur oases, southern Tunisia, with emphasis on the anthropogenic impact

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ABSTRACT

In southern Tunisia, environmental threat related to fluorine contamination of the “Complex Terminal (CT)” main aquifer paleogroundwater in one of the most important and strongly vulnerable oases was assessed. Emphasis was placed to hydrogeological and hydrochemical processes controlling the occurrence and the transfer of fluorine to paleogroundwater. It has been demonstrated that the fluorine is released from the Carbonate fluorapatite (CFA) deposit underlying the contaminated aquifer. The liberation of F⁻ is ensured by its exchange with hydroxyl and/or by the CFA dissolution through the passage of hot waters ascending from the deep “Continental Intercalaire (CI)” aquifer. The transfer of F-rich waters to the CT aquifer is occurred mainly through deep faults, aquitard windows and through leakage behind casing. This transfer is due to the potentiometric contrast between the two superimposed aquifers, which is enhanced by anthropogenic processes i.e. the overpumping of the CT groundwater and the CI wellbore integrity failure.

1. Introduction

The Tozeur region has an amazing beauty with numerous canyons, sand dunes and Saharan oases. The Tozeur oases are by far the most important in North Africa, for there are found in perfection some of the finest varieties of the date palm in the world (Kearney, 1906). They were occupied, since the Christian era, by Romans; then by Berber, nomadic Arabs and other tribes of the desert. These oases make part of the global environmental network of the International RAMSAR convention for the conservation and wise use of wetlands and their resources. However, these oases, which constitute a fragile ecosystem whose regeneration largely depends on climatic conditions, are strongly vulnerable to anthropogenic impacts. In fact, fossil groundwater of the CT aquifer, which represents the main water reservoir in this region, becomes highly overexploited due to the large expansion of oasis domain (Dassi et al., 2018). This overexploitation has led to several deleterious impacts such as the depletion of the aquifer storage, the decline of groundwater level and the disturbance of hydraulic gradients and groundwater flow schemes (Dassi and Tarki, 2014).

Besides to the above mentioned anthropogenic impacts, another environmental concern arises in the Tozeur region during the last decade's (Tarki, 2017). Widespread fluorosis among children has been

recognized in the Tozeur area and the Metlaoui neighboring mining basin as long as 50 years ago. This concern is related to the high concentration of fluorine element in the groundwater of CT main aquifer. This problem, which represents one of the most important toxicological environmental hazards, has drawn particular attention worldwide due to its considerable impact on human organism metabolism. The presence of fluorine in drinking water in suitable doses (less than 1 mg/L) is beneficial for the teeth and helps to prevent dental caries (Abu Jabal et al., 2014). However, excessive concentrations lead to dental fluorosis and other harmful diseases in relation with the chronic fluorine poisoning such as calcification of ligaments and rheumatic or arthritic pain.

Keeping aside the sources in relation with the anthropogenic activities, mainly the application of phosphate fertilisers, which adds more than 2.3 Mt per year of fluoride to soils (Fuge, 2019), natural origins of high fluoride in groundwater remain subject to great debate among scientists and often involve speculation beyond a certain extent (Abu Rukaha and Alsokhny, 2004). However, during the last decades, many efforts have been made to study the genesis and hydrochemistry of high fluoride groundwater (Handa, 1975; Corbett and Manner, 1984; Sarma and Rao, 1997; Gosselin et al., 1999; Wang and Reardon, 2001; Abu Rukaha and Alsokhny, 2004). The review of relevant background

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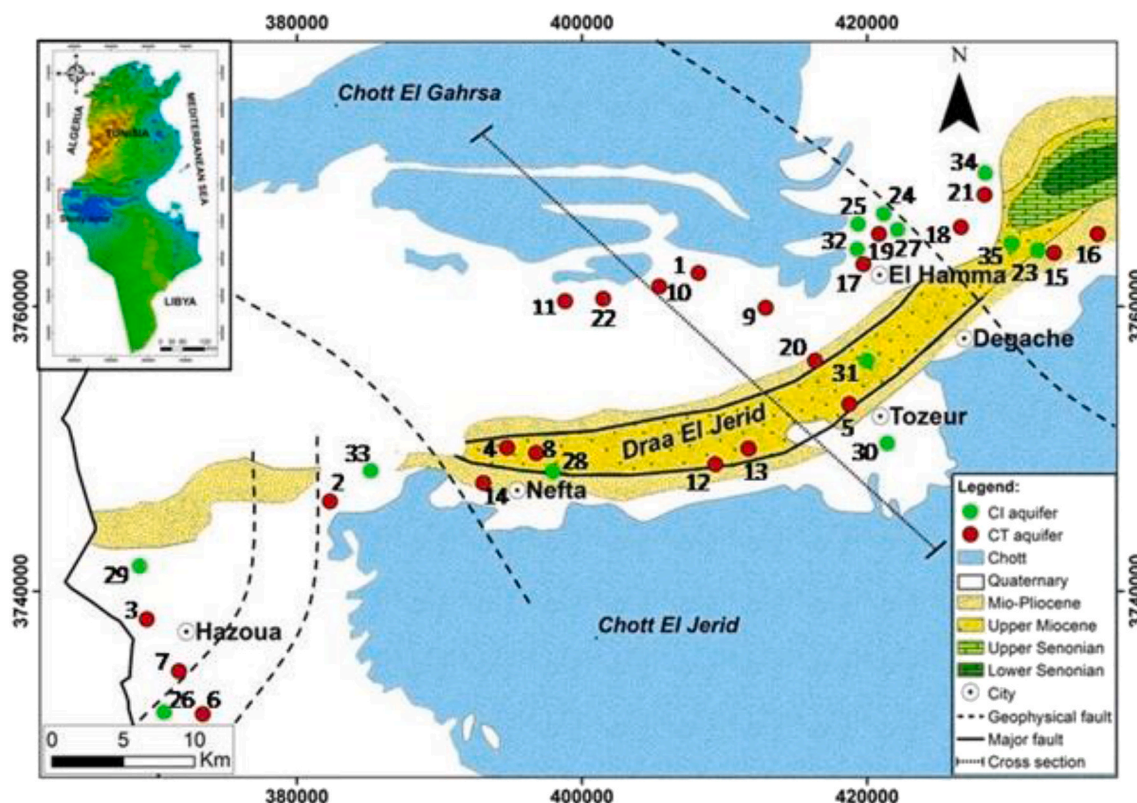


Fig. 1. Geological and sampling map showing the location of groundwater samples.

geochemical literature on this issue indicates that the leaching of rocks and enriched soils is the main cause of excessive fluoride contents in water environments (Beg, 2009). Fuge (2019) reported that the majority of the F occurring in the secondary environment originates from natural weathering with some soils derived from fluoride-rich parent rocks containing over 1% F. The most common natural sources of fluoride are mainly related to the dissolution of fluorite, fluorapatite, micas weathered from silicates, some igneous and sedimentary rocks, especially shale (Datta et al., 1996). Shale and other unstable clay minerals such as sepiolite and palygorskite may also have a dominant control on F^- distribution in groundwater (Wang et al., 1993; Jacks et al., 2005; Guo et al., 2007). Hydrochemical processes controlling the occurrence of fluoride in groundwater include dissolution precipitation reaction, adsorption-desorption processes, and dispersion of chemical formation complex (Lloyd and Heathcote, 1985).

The Fluorine enrichment, exceeding the World Health Organization (WHO) standard of 1.5 mg/L (WHO, 2000; Rango et al., 2014, 2012), in the groundwater of the Tozeur area has been mentioned by several authors (Edmunds et al., 1997, 2003). Nevertheless, this issue has never been carefully investigated. Although, Edmunds et al. (1997) have mentioned the relationship between this enrichment and the ascension of geothermal groundwater from the deep CI artesian aquifer, however, they did not describe the hydrogeological and hydrochemical processes controlling the occurrence of fluorine in the CT groundwater. It is believed that the underlying fluoride-bearing minerals slowly dissolved, releasing F^- to percolating CT groundwater which is being used for irrigation and human water supply in the Tozeur oases and in the whole fringes of the Saharan desert.

The present study is designed to assess and describe the origin of elevated F contents in the CT groundwater. Special emphasis is given to the hydrogeological process by which fluorine is transferred to groundwater.

2. Study area

The Tozeur region covers an arid area of about 5000 km² (Fig. 1). It constitutes the northeastern extremity of the Bas Saharan Artesian Basin (Bryant et al., 1994), which extends over the most part of the Algerian and Tunisian Sahara down to the north of Libya, enclosing the whole of the Grand Erg Oriental (Roberts and Mitchell, 1987).

Physiographically, the climate in the study area is typically Mediterranean arid type with a mean annual precipitation and potential evapotranspiration of 100 mm and 1700 mm, respectively (Dassi et al., 2018). The regional hydrology is characterized by a relatively light drainage network pattern, which consists of non perennial rivers, locally called “Wadis”. These wadis collect surface runoff from the Draa El Jerid anticline toward the continental depression of Chott El Jerid outlet (Meckelein, 1977). This anticline, which is characterized by a large radius of curvature, is constituted by Miocene sands and Eocene limestone. These sedimentary series lie on the phosphate deposits Early Ypresian of the Chouabine Formation (Gallala et al., 2016).

The regional geological and hydrogeological features of the study area have largely been described by (Tarki et al., 2011, 2012; Dassi and Tarki, 2014; Tarki, 2017; Dassi et al., 2018). An overview of the relevant hydrogeological characteristics is provided in Fig. 2.

3. Sampling and analyses

A total of 34 representative groundwater samples were collected from deep boreholes tapping the CT and the CI aquifers (Fig. 1). Physico-chemical parameters of collected samples, including water temperature, Electrical Conductivity (EC), pH and Total Dissolved Solids (TDS), were measured *in situ* using a Consort C535 analyzer. Chemical analyses of major and trace elements (F and Sr) were established using Ion Chromatography, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), in the laboratories of the “Groupe Chimique de Gabès (GCG)”, in

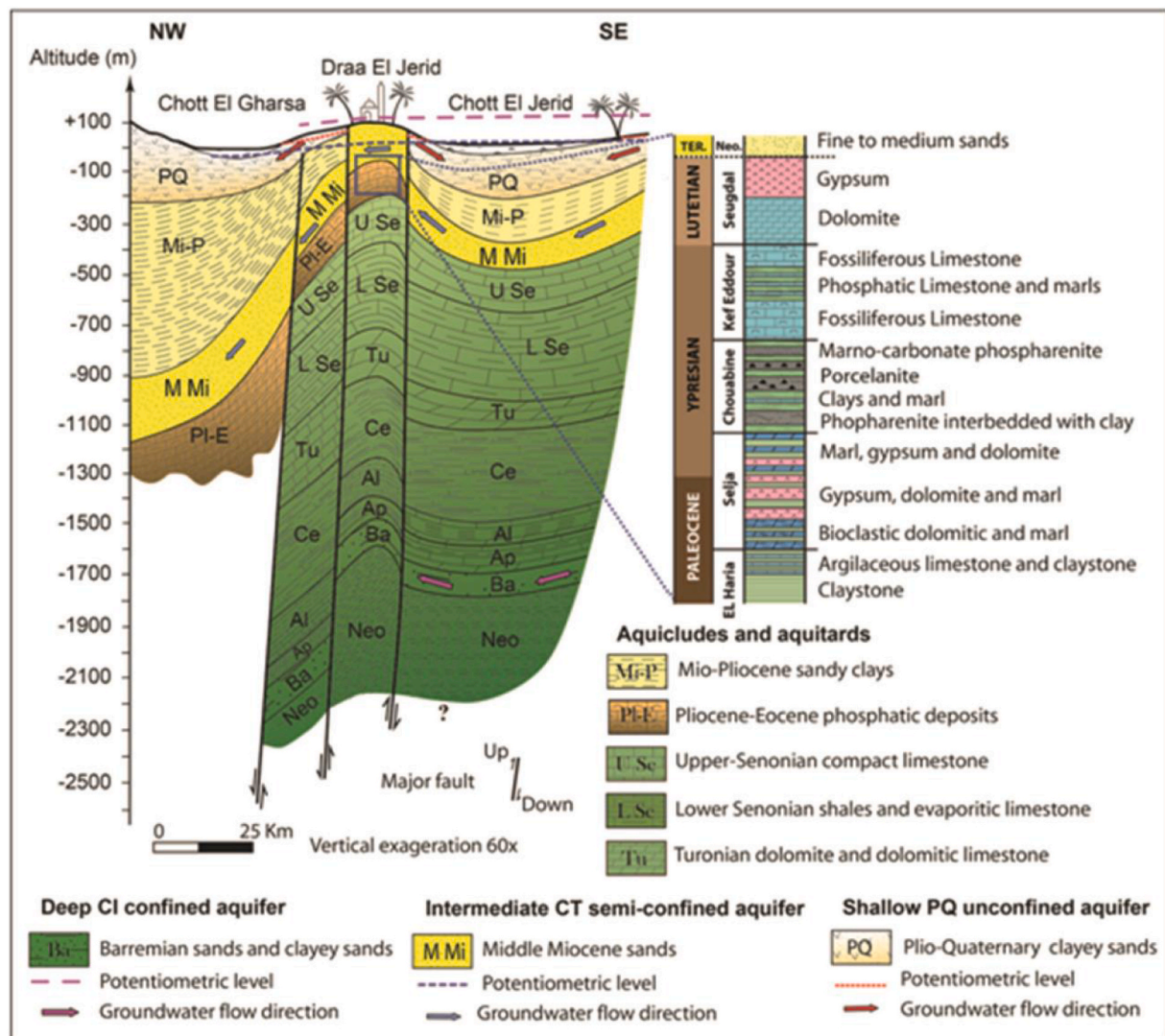


Fig. 2. Cross section of the Tozeur aquifer system (Dassi et al., 2018) and lithostratigraphic column (Ahmadi et al., 2019).

Tunisia. In order to calculate equilibrium concentrations, activities of chemical species and saturation indices of phases in solution, the geochemical modelling program PHREEQC (Parkhurst, 1995) was used, through the water quality database "Diagrammes".

In order to determine the origin of fluorine, mineralogical and geochemical studies were undertaken. Four representative specimens of phosphate sediments, (DJ3, DJ8, DJ10 and DJ11) were sampled from the main levels of the phosphate layer in the Draa El Jerid mining trench (Fig. 3), to the west of Tozeur city. The mineralogy of phosphate samples, ascribed by dark colors, was identified using Philips PW PANalytical X Pert Pro MPD (0-20) diffractometer equipped with CuK α radiation source. XRD data were measured in the following conditions: 40 kV, 40 mA an angular range between 5 and 65 2 θ and a step size of 0.017 $^\circ$ s. This analysis was performed on the finely powdered bulk rocks at the research centre of the CPG and the laboratories of the GCG in Tunisia. Major oxides were analyzed by X-ray fluorescence spectrometry using a Thermo scientific device Niton FXL FM-XRF Analyzer at the Mineralogy laboratory of department of earth science, Sfax University, Tunisia.

4. Results and discussion

4.1. Mineralogy of phosphates

XRD patterns of collected samples show that CFA, also called francolite (a CFA with >1% fluorine and appreciable amounts of CO₂ (Sandell et al., 1939; McConnell, 1973), constitutes the major mineral phase (Fig. 4). The characteristic reflections of CFA appear clearly at 0.81 nm; 0.27 nm; 0.26 nm and 0.26 nm. Other mineral phases such as Calcite (Ca), clinoptilolite (Cl), gypsum (Gy) and quartz (Q) are also present. Their highest reflections appear at 0.30 nm; 0.89 nm; 0.75 nm and 0.33 nm, respectively. These results are coherent with previous studies (Felhi et al., 2008; Tlili et al., 2011; Haj Ahmed et al., 2014; Enneili et al., 2019), which indicate that the Ypresian phosphorites are composed predominantly of the francolite mineral, commonly associated with gangue minerals including calcite, dolomite, quartz, clinoptilolite, gypsum and occasionally clay.

The estimated percentages of minerals (Table 1) indicate that the CFA exhibits the greatest percentages in the four samples. Respective percentages for DJ 3, DJ 8, DJ 10 and DJ 11 are 72%, 90%, 95% and 82%. The percentage of calcite does not exceed 10% and the highest value was computed for the sample DJ 8. The samples DJ 3 and DJ 11 exhibit the presence of clinoptilolite and gypsum minerals in addition to CFA (Fig. 4).

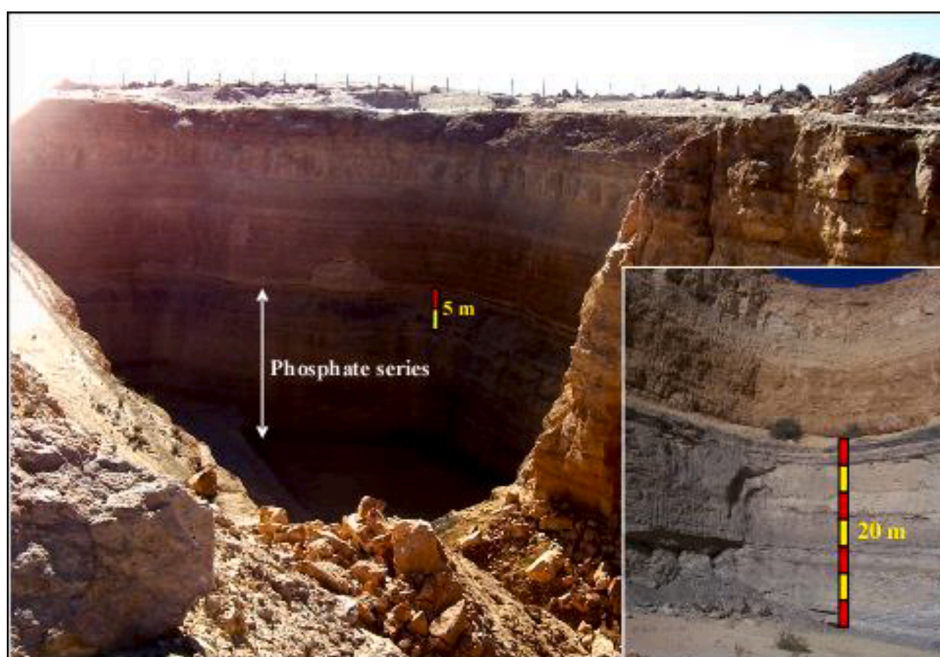


Fig. 3. The mining trench of the Draa El Jerid.

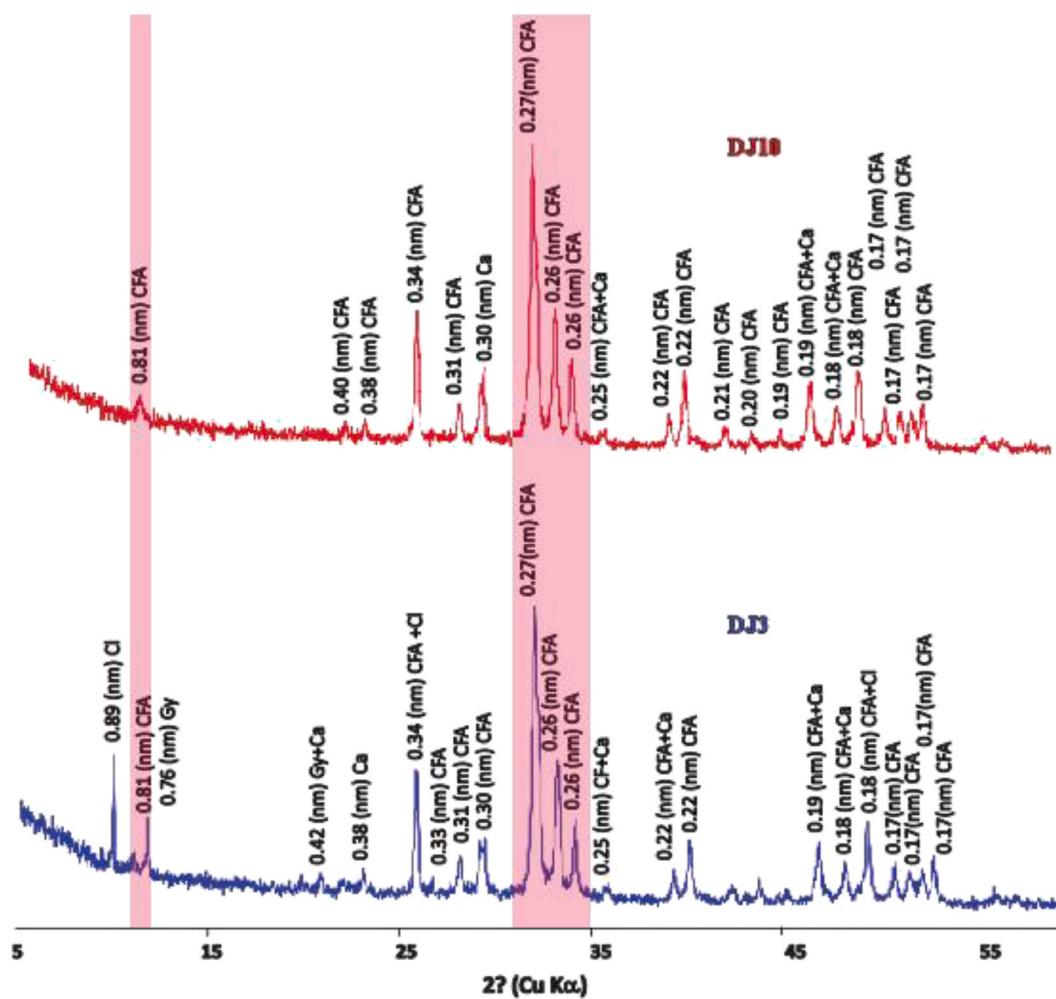


Fig. 4. X-ray diffraction (CoK α radiation) of Draa El Jerid samples (Cl: Clinoptilolite; Gy: Gypsum; Q: Quartz; Ca: calcite and CFA: Carbonate-Fluorapatite).

Table 1
Bulk-rock mineralogy in percent of Draa El Jerid samples.

Samples	CFA	Calcite	Dolomite	Gypsum	Quartz	Clinoptilolite
DJ3	72	5	0	5	2	16
DJ8	90	10	0	0	0	0
DJ10	95	5	0	0	0	0
DJ11	82	7	2	0	5	4

Table 2
Chemical composition of bulk rock samples.

Samples	DJ3	DJ8	DJ10	DJ11
Major elements and F (%)				
SiO ₂	7.73	7.68	4.36	7.37
TiO ₂	0.05	0.05	0.03	0.05
Al ₂ O ₃	1.65	1.82	1.05	1.44
Fe ₂ O ₃	0.53	0.32	0.18	0.25
MgO	1.52	nd	1.77	2.25
CaO	43.6	44.32	46.47	44.77
K ₂ O	0.15	0.2	0.18	0.3
P ₂ O ₅	22.68	23.14	24.75	23.77
SO ₃	5.85	3.82	4.27	3.5
F	3.53	3.7	3.73	3.83
LOI	12.22	13.45	13.14	12.18
% Total	99.51	98.5	99.93	99.71
CaO/P ₂ O ₅	1.92	1.91	1.87	1.88
Sr (mg/g)	1849	1841	1790	1705

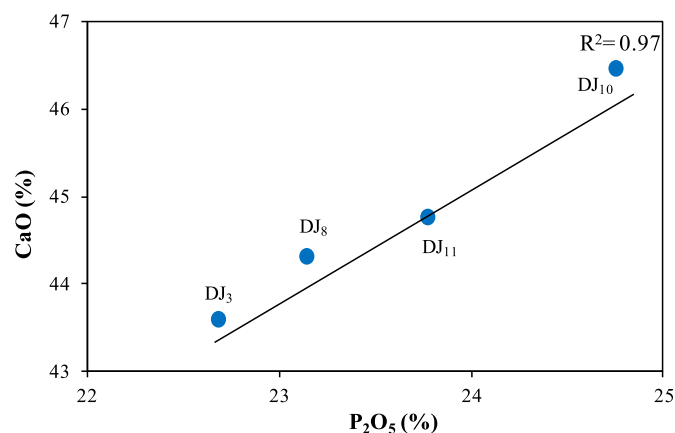


Fig. 5. Correlation between P₂O₅ and CaO contents.

4.2. Geochemistry of phosphates

The geochemical data of the phosphorite samples, collected from the main levels in the phosphate layer, show that the predominant major oxides are CaO and P₂O₅. Other elements (SiO₂, SO₃, Al₂O₃, MgO and F) are also present in moderate proportions. While, Sr trace element exhibits relatively low concentrations, which did not exceed 1%.

The contents of the predominant oxides (CaO and P₂O₅) indicate that the francolite is the primary mineral phase in the phosphorites of the Draa El Jerid. It is associated with subordinate minerals such as calcite, clinoptilolite, gypsum and quartz. The percentages of CaO and P₂O₅ vary from 43.6% to 46.47% and from 22.68% to 24.75%, respectively (Table 2). These relatively high values provide evidence that these oxides form the crystal lattice of the CFA mineral. This is confirmed by the high positive correlation ($R^2 = 0.97$) observed in the plots of P₂O₅ versus CaO (Fig. 5). The relatively high percentages of lime (CaO), with reference to that of the francolite (1.82), indicate that this component occurred as a part of carbonate mineral, mostly calcite. This is coherent with the slightly elevated CaO/P₂O₅ ratios for the samples DJ3 (1.922) and DJ8 (1.915), which are higher than the stoichiometric value of the apatite (1.66) (Galfatit et al., 2010) (Table 2).

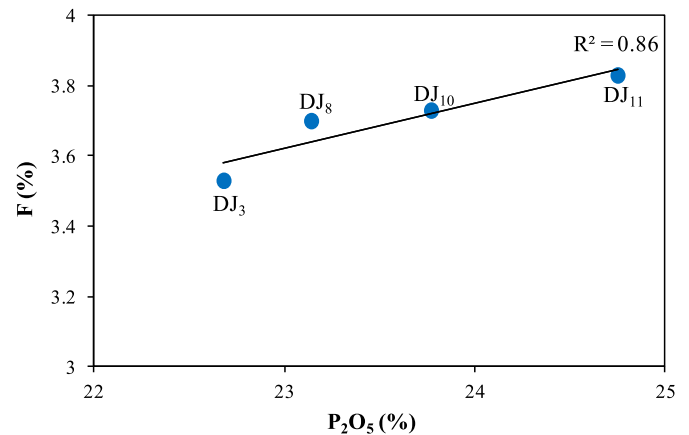


Fig. 6. Plot of F versus P₂O₅.

The SO₃ content varies between 3.5 and 5.85%. This relatively high content is likely attributed to the occurrence of gypsum as revealed by XRD of the samples DJ3 and DJ10 (Fig. 4). The SO₃ oxide corresponds also to constituent in the phosphate lattice (McArthur, 1985; Jarvis et al., 1994). SiO₂ concentrations are rather high; they vary in a relatively wide range between 4.36 and 7.3%. This may reflect, to a large extent, the changing proportion of clinoptilolite (Table 2). This statement is consistent with the Al₂O₃ content, which shows a similar variation. The MgO oxide is detected in the samples DJ3, DJ10 and DJ11, are relatively low; it has an average of 1.84%. The Mg element is obviously detected in the CFA. According to Sader et al. (2013), numerous substitutions occur in all of the apatite sites (the two Ca sites, the PO₄ sites and the F site), and not all of them have the same valance as the original ion. Elliott et al. (2002) established that CO₃²⁻ group and Mg²⁺ are commonly the main component in the crystal lattice of phosphate minerals. The CO₃²⁻ group slightly substitutes PO₄³⁻ group in apatite mineral, which needs the incorporation of F⁻ in the structure of phosphate minerals. This explanation agrees with the rather high concentrations of F⁻ in the analyzed samples (from 3.53 to 3.83%, with a mean value of 3.69%). These percentages indicate that this element is incorporated in the crystal lattice of the CFA as confirmed by the well-defined relationship observed for the major samples in the plot of F versus P₂O₅ ($R^2 = 0.86$) (Fig. 6). While, the presence of measurable Sr concentration brings insight to the substitution of Ca by this element in francolite (Jarvis et al., 1994).

4.3. Hydrogeological basis for the fluorine contamination

Excessive F⁻ contents in groundwater depend on many factors such as the geological, hydrogeological and physical characteristics of aquifers (Jacks et al., 2005; Abu Rukaha and Alsokhny, 2004). Groundwater hydrochemistry, temperature, age and residence time (Kim and Jeong, 2005) may also have control on this element. In order to understand how the hydrogeology controls F⁻ concentrations in the CT groundwater it is essential to apprehend the geological and hydrogeological features within the whole multilayer aquifer system in the Tozeur region. In fact, these features have been largely described in our previous works (e.g., Tarki et al., 2011, 2012; Dassi and Tarki, 2014; Tarki, 2017). So, an account is given here only of the essential aspects relevant to hydrogeological features that clarify the mechanism of F transport by the upward leakage of geothermal waters from the deep aquifer. A special attention is provided to the explanation of natural and anthropogenic factors enhancing the ascending fluxes. This explanation seems to be essential to answer the question whether the transport and the inflow of F⁻-rich waters to the underlying CT aquifer is insured by the upcoming of hot waters.

The variation of the piezometric contour map of the CT aquifer was

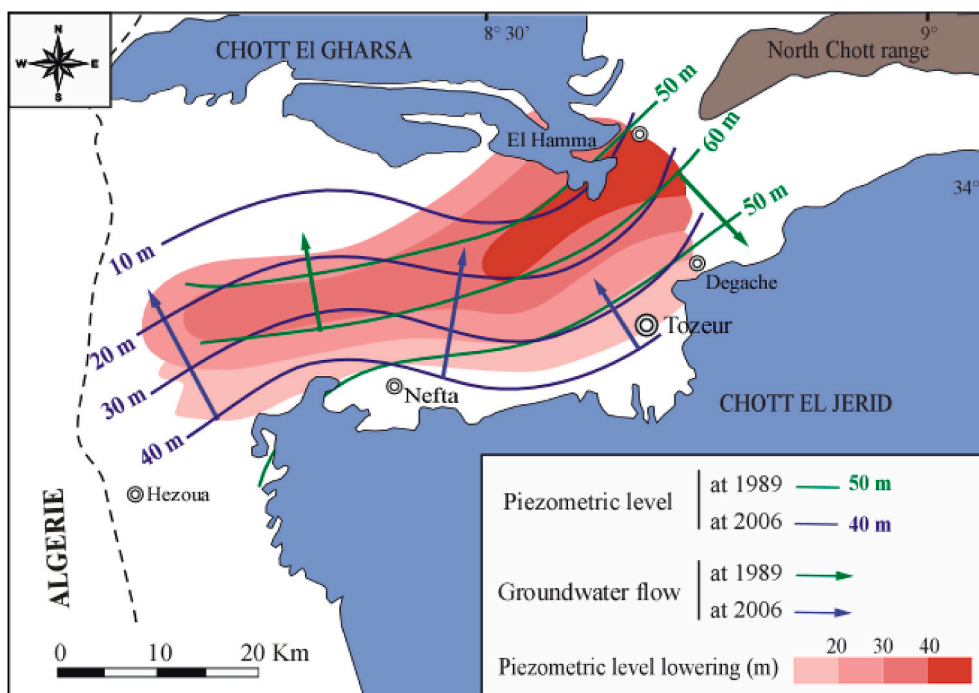


Fig. 7. Variation of the piezometric contour map of the CT aquifer.

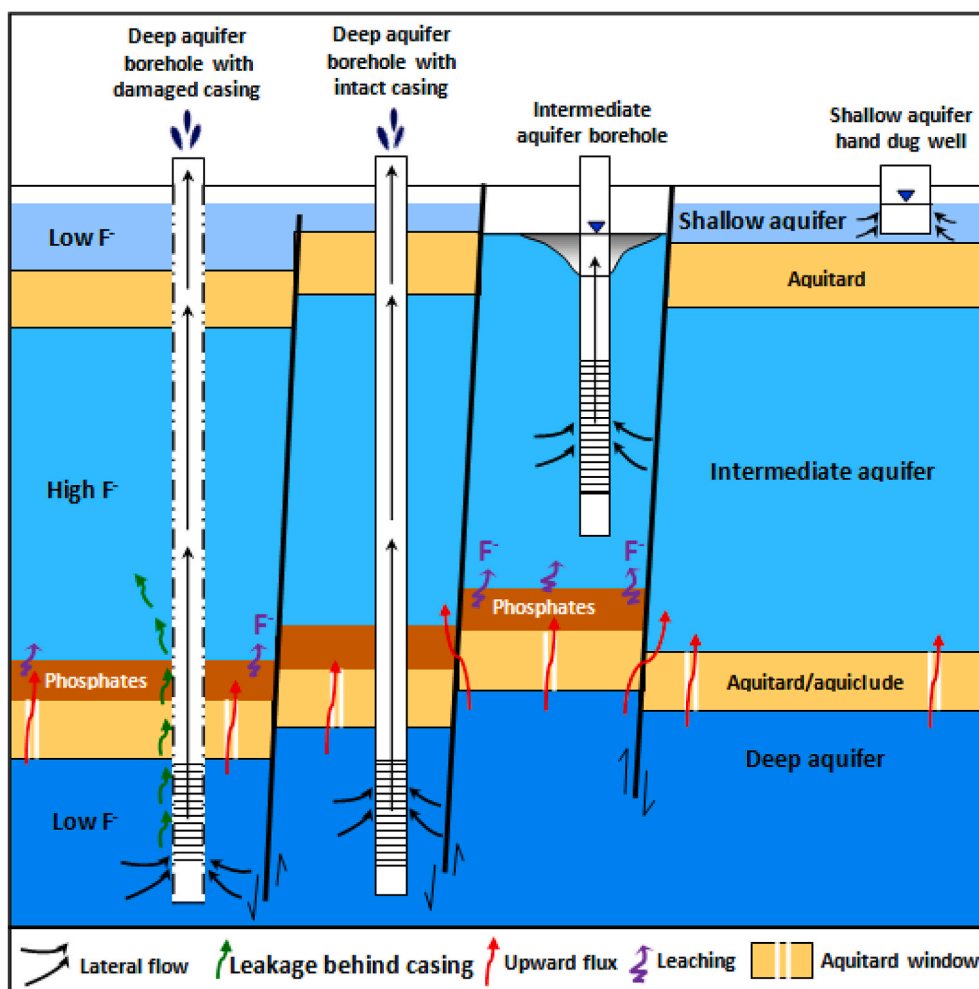


Fig. 8. Conceptual model illustrating the origin and mechanisms of the upward leakage of deep hot waters.

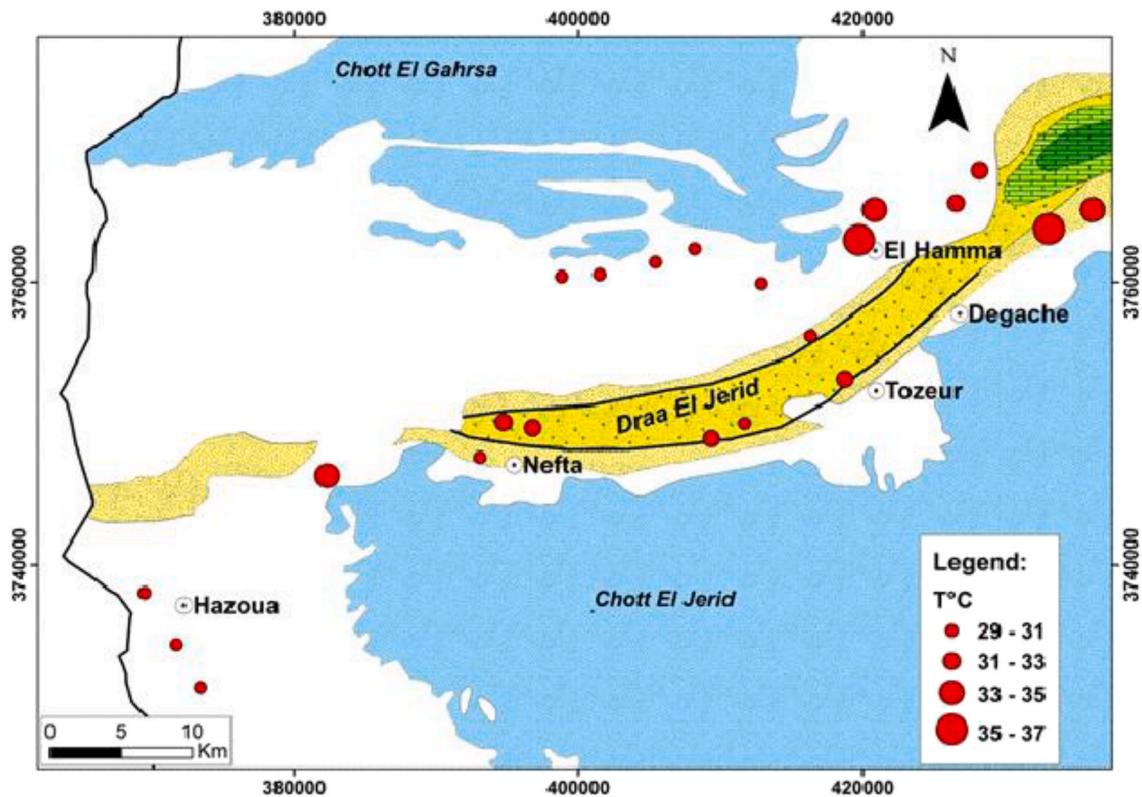


Fig. 9. Spatial distribution of the groundwater temperatures of the CT aquifer.

examined using the work of Mamou (1990) and Tarki et al. (2012), which refer to two groundwater surveys conducted on 1989 and 2006, respectively (Fig. 7). It has been found that the groundwater flow patterns in the more recent potentiometric state (of 2006) are considerably different from those found at 1989 i.e. prior to the significant onset of drilling. In fact, excessive pumping of groundwater for irrigation has

lowered the water table for more than 45 m. However, the CI underlying aquifer, which is slightly exploited, is always characterized by high artesian pressure. The piezometric contrast between the two superposed aquifers has resulted in an upward leakage of the CI geothermal waters through deep faults, heterogeneities, thin parts in confining units and aquitard windows. This upward leakage permits the discharge of the CI

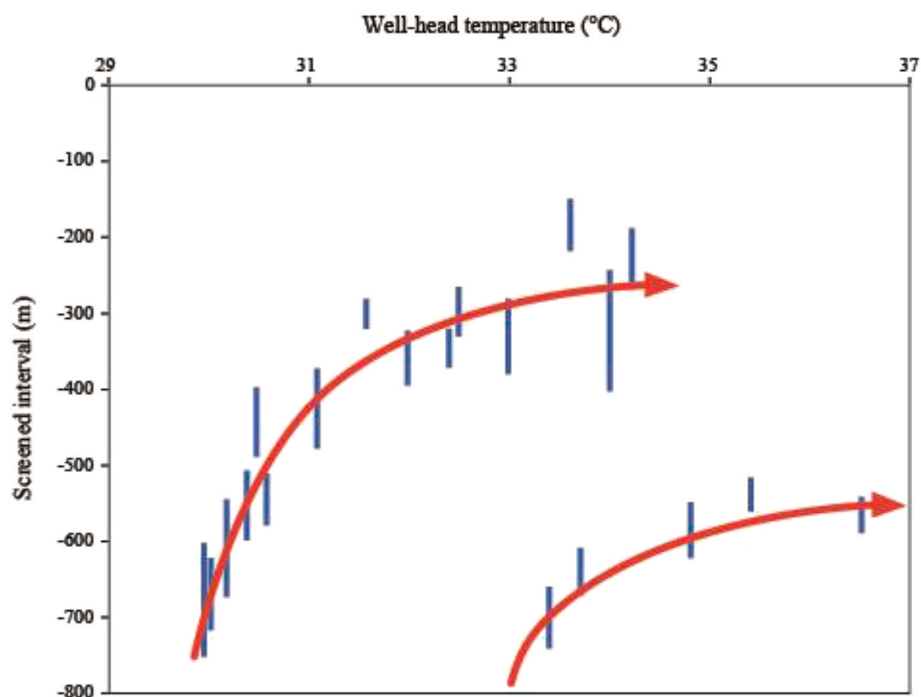


Fig. 10. Well-head temperature vs. screened interval of the CT groundwaters.

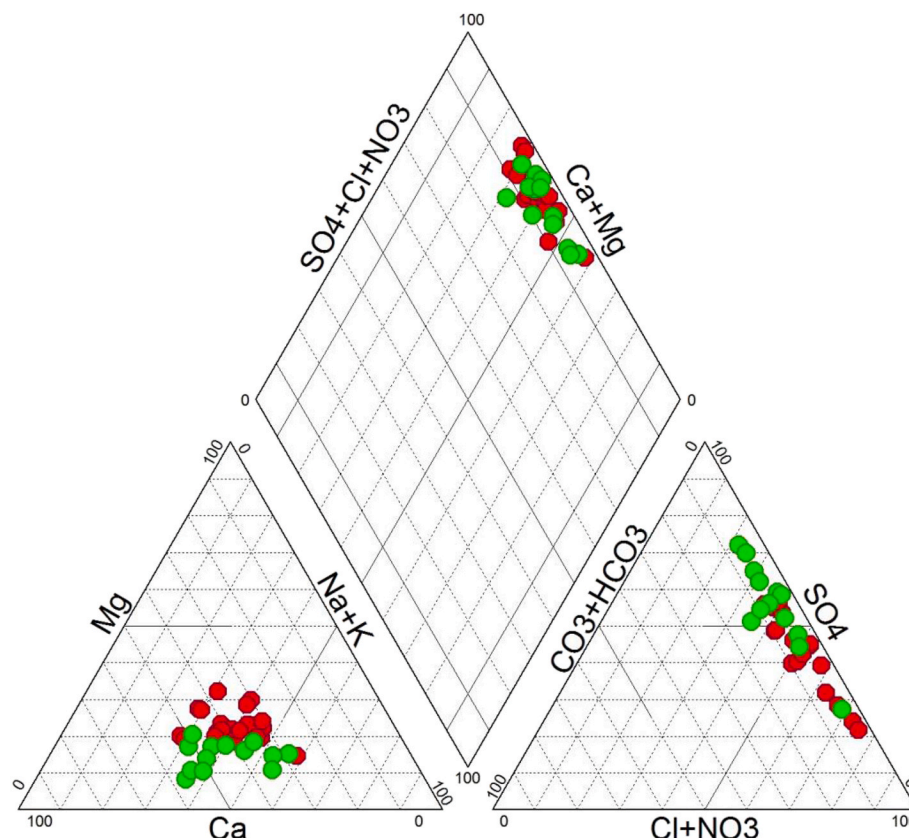


Fig. 11. Piper diagram of the CT and CI samples.

deep waters into the underling CT aquifer. The Upward flux may also occur through the leakage in the annulus behind the casing of the CI deep boreholes (Wayne et al., 1997). This undesired leakage is a consequence of the failure of wellbore integrity (Ekseth et al., 2007), which is most likely to occur as a result of the corrosion of bore casing due to poor construction techniques (inappropriate selection of construction materials, poorly sealed annulus), inadequate monitoring or lack routine maintenance of bore casing (Teodoriu, 2013). In some abandoned deep wells, where casing has been partially or completely damaged, bore holes have become like man-made aquitard windows, which resulted in a high rate of upward leakage behind the broking casing.

In any case, as discussed above, multiple mechanisms or modes of transport of subsurface geothermal water can take place. A conceptual model illustrating the origin and mechanisms of the upward leakage of deep hot waters is proposed in Fig. 8. Though, whatever the source and mechanism of the upward flow, it is almost certain that, the passage of hot waters through the fluoride-bearing rocks, which constitute the major part of the substratum of the CT aquifer, may engender the partial weathering or the complete dissolution of CFA and thus enhancing the release of F^- .

4.4. Hydrochemistry

4.4.1. Hydrochemical characterization

The pH values of the CT groundwater vary from 7.0 to 8.0, with a mean value of 7.5. Those of the CI range from 7.40 to 8.00, with a mean value of 7.6. These values indicate that groundwaters in both aquifers are near-neutral to weakly alkaline. The slightly alkaline character of water with relatively high TDS and EC values (1.2–5.1 g/L and 2400–7930 $\mu\text{S}/\text{cm}$ for the CT, 1.9–5.3 g/L and 2600–6660 $\mu\text{S}/\text{cm}$ for the CI) exhibits fresh to brackish groundwater in nature, which can be attributed to extended water-rock interaction i.e. dissolution and cation

exchange processes. In a such long term geothermal aquifer system, these processes are very expected due to the elevated groundwater temperature and relatively high residence times (up to 71 °C and 30 ka according to several studies (Edmunds et al., 1997, 2003; Kamel, 2007) as well as the presence of highly reactive aquifer materials such as halite and gypsum (Mamou, 1990; Edmunds et al., 2003; Dassi and Tarki, 2014; Tarki, 2017).

Well-head temperatures of the CT boreholes vary between 29.7 and 36.8 °C, with a mean value of 31.8 °C. Those of the CI samples range from 62.7 °C to 71.1 °C, with a mean value of 66.3 °C. The spatial distribution of the groundwater temperatures of the CT aquifer illustrated in Fig. 9 shows that relatively high values characterize the Draa El Jerid uplifted area, with obvious temperature anomalies in the eastern and western parts, where are located the transversal faults of El Hamma and Hezoua. The high temperatures along the Draa El Jerid bring insight to the upcoming of geothermal waters from the deep CI aquifer and inflow of F-rich waters through fluoride bearing bedrocks into the overlying CT aquifer. The upward leakage of hot groundwater is again coherent with the plot of the well-head temperature of the CT boreholes against their screened interval (Fig. 10). Groundwaters in this plot show inversely proportional trends, which cannot be attributed to the effect of the natural geothermal gradient. Shallower wells in these trends are characterized by higher water temperature, which confirms the mixing of CT water samples with various percentages of hot water ascending from the deep CI geothermal aquifer.

The cations and anions abundance orders for most CT water samples are $\text{Ca}^{2+} \geq \text{Na}^+ > \text{Mg}^{2+} \gg \text{K}^+$ and $\text{Cl}^- \geq \text{SO}_4^{2-} \gg \text{HCO}_3^-$, respectively. Those for most CI water samples are $\text{Ca}^{2+} \geq \text{Na}^+ \gg \text{Mg}^{2+} > \text{K}^+$ and $\text{SO}_4^{2-} \gg \text{Cl}^- \gg \text{HCO}_3^-$, respectively. Analysis of hydrochemical water-types on the Piper diagram (Fig. 11) reveals that the major hydrochemical facies for the CT and CI groundwater are Ca–Na–Cl– SO_4 , and Ca–Mg–Cl– SO_4 , respectively. These water-types together with mineral saturation states (Table 3) confirm that the dominant control of associated

Table 3
Statistics for the hydrogeochemical parameters of groundwaters.

Well No.	Aquifer	pH	T (°C)	CE (μS/cm)	TDS (g/L)	Cl (meq/L)	Na	SO ₄	Ca	HCO ₃	Mg	K	F (10 ⁻³)	Sr (10 ⁻³)	SI Anhydrite	SI Gypsum	SI Calcite	SI Fluorine
1	CT	7.75	30.00	4410	3.08	20.45	18.32	23.81	21.16	4.50	12.18	0.63	25.45	103	-0.50	-0.33	1.03	1.12
2		7.75	33.70	4190	3.66	22.99	13.08	26.54	20.96	4.70	13.23	0.67	37.87	61	-0.43	-0.30	1.08	1.40
3		7.75	29.70	4190	3.00	23.33	20.99	18.35	14.97	4.40	8.89	0.66	25.25	-	-0.70	-0.50	0.91	1.00
4		7.83	31.10	3530	2.93	22.16	20.33	21.66	14.50	2.40	10.30	1.27	39.58	69	-0.64	-0.48	0.71	1.37
5		7.50	32.00	3180	3.42	22.68	14.86	17.67	17.96	3.50	8.89	0.50	38.17	-	-0.60	-0.46	0.68	1.45
6		7.86	30.00	3950	3.16	18.79	19.03	26.70	14.97	3.00	14.81	0.68	29.39	92	-0.60	-0.42	0.80	1.08
7		7.98	29.70	4000	4.30	21.24	20.40	30.15	16.87	3.48	15.21	0.54	11.98	127	-0.51	-0.34	1.00	0.33
8		7.95	33.00	3830	4.80	16.22	14.20	25.02	17.47	3.53	15.31	0.58	20.81	225	-0.54	-0.38	1.80	0.81
9		7.53	30.40	4350	3.39	21.35	18.76	27.67	20.48	2.60	10.99	1.54	23.92	86	-0.45	-0.28	0.56	1.05
10		7.00	30.20	4000	3.40	20.87	18.87	27.42	19.70	2.60	9.08	1.53	22.20	83	-0.45	-0.29	0.02	1.00
11		7.20	30.00	4190	3.47	21.27	19.74	25.97	15.08	2.50	10.75	1.01	4.99	25	-0.58	-0.41	0.10	-0.42
12		7.49	32.00	3400	4.34	46.63	28.07	19.69	28.87	2.99	16.33	1.32	31.00	77	-0.52	-0.36	0.75	1.33
13		7.53	30.60	3490	2.72	20.33	15.83	19.70	18.76	2.60	9.86	1.08	9.58	220	-0.56	-0.42	0.57	0.27
14		7.41	30.00	5280	5.06	47.55	23.03	32.27	35.81	2.50	22.44	1.50	17.17	68	-0.29	-0.13	0.60	0.85
15		7.20	36.50	2400	2.64	24.95	16.83	12.68	14.14	2.30	9.51	0.61	29.11	155	-0.78	-0.47	0.20	1.08
16		7.10	35.00	5580	4.82	53.89	30.62	17.91	28.66	2.30	16.54	1.45	18.36	1177	-0.54	-0.41	0.30	0.83
17		7.78	36.80	6820	3.80	44.95	24.97	38.35	47.71	2.40	18.51	1.14	6.69	274	-0.13	0.03	1.04	0.14
18		7.50	32.60	7930	4.30	50.98	29.58	16.75	20.93	2.20	16.60	1.97	30.75	770	-0.67	-0.53	0.50	1.20
19		7.00	34.20	6800	2.96	45.18	25.65	39.10	47.89	2.40	17.85	2.12	8.41	329	-0.09	0.04	0.33	0.42
20		7.69	30.00	3180	3.70	21.03	16.98	17.17	13.16	2.30	7.70	1.01	14.76	110	-0.73	-0.57	0.54	0.55
21		7.60	32.60	7080	2.55	67.93	49.26	19.43	24.21	2.70	13.14	2.92	35.21	-	-0.61	-0.45	0.72	1.36
22		7.66	30.20	7590	1.16	20.78	19.00	29.91	24.26	2.30	11.09	1.20	18.14	83	-0.37	-0.20	0.70	0.87
23	CI	7.75	71.10	3540	2.59	14.75	13.39	18.00	13.65	1.70	5.71	2.54	0.21	75	-0.38	-0.47	0.93	-3.50
24		7.56	67.40	4440	3.54	28.36	30.94	28.15	16.79	2.50	8.95	2.19	0.40	75	-0.28	-0.40	0.89	-2.90
25		7.65	63.00	3650	3.15	10.84	17.65	24.04	12.16	2.20	5.40	2.04	0.15	-	-0.44	-0.48	0.80	-3.80
26		7.55	62.70	2600	3.09	9.17	7.08	13.35	14.17	3.50	4.74	1.61	0.27	-	-0.50	-0.55	1.04	-3.15
27		7.40	66.30	3650	2.76	9.36	21.74	30.70	15.17	2.62	4.74	2.22	0.22	-	-0.24	-0.30	0.71	-3.35
28		7.72	66.60	3540	2.90	11.21	11.56	31.74	22.31	2.40	9.45	2.57	0.19	46	-0.06	-0.15	1.12	-3.44
29		7.66	68.00	2680	1.92	22.19	14.74	19.71	20.54	2.50	7.79	1.94	0.22	36	-0.27	-0.34	1.13	-3.33
30		8.00	65.50	4670	5.13	24.85	23.01	39.34	39.52	2.20	5.82	1.81	0.14	-	0.12	0.06	1.46	-2.50
31		7.70	66.00	6660	4.02	34.28	29.17	51.43	41.38	2.30	11.88	2.83	0.55	180	0.18	0.12	1.22	-2.40
32		7.68	66.00	3730	3.30	15.65	20.75	30.54	17.56	3.00	9.15	2.18	0.35	-	-0.22	-0.28	1.08	-3.00
33		7.42	63.50	3160	2.47	14.81	11.33	22.39	19.96	2.70	3.95	1.80	0.13	-	-0.23	-0.28	0.88	-3.70
34		7.48	69.50	3200	2.15	13.37	13.78	20.31	16.97	3.60	7.08	2.37	0.12	-	-0.16	-0.25	1.00	-3.90

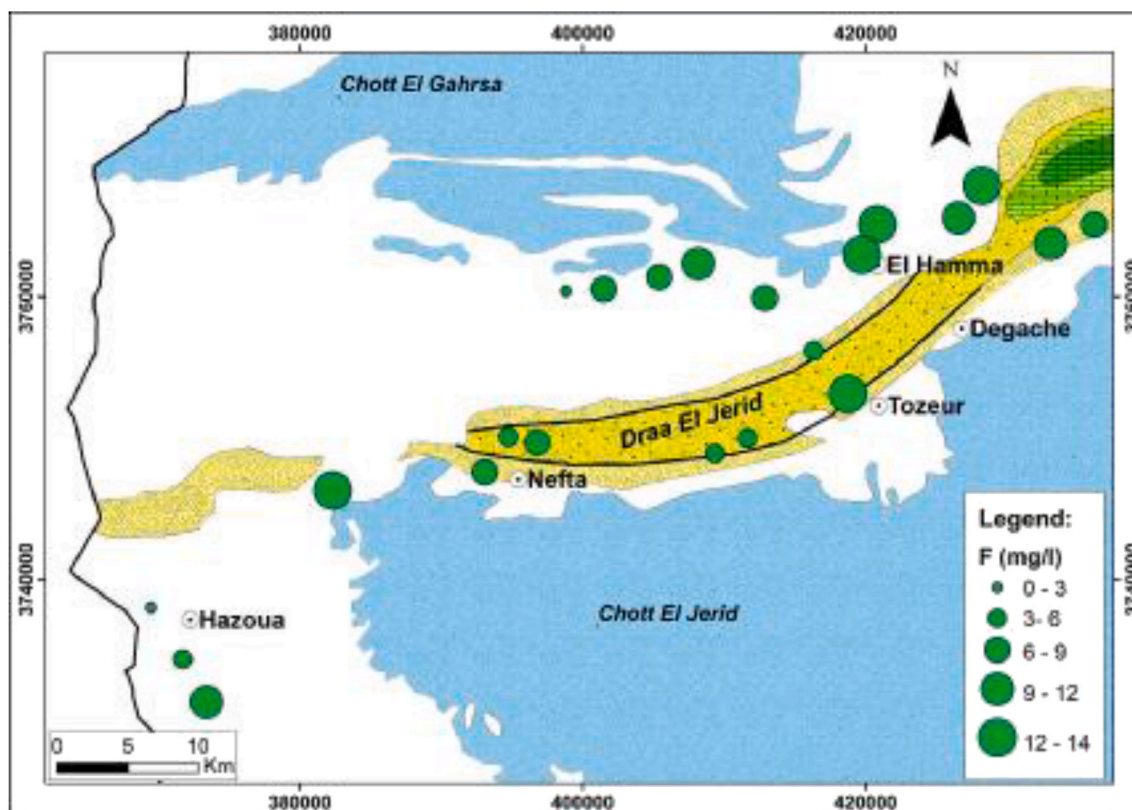


Fig. 12. Spatial distribution of the fluorine in the CT groundwaters.

hydrogeochemical natural processes are evaporate mineral dissolution, mixing, ion exchange and the residence time during the groundwater which is bring in contact with rock materials.

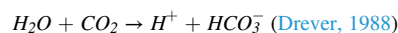
4.4.2. Mechanisms of fluorine contamination

Groundwater F^- concentrations in the deep CI aquifer are typically less than 0.30 mg/L ($0.55 \cdot 10^{-3}$ meq/L), which corresponds to natural background values (Table 3). However, within the CT shallower aquifer, these concentrations are generally high (Fig. 12). They vary from 1.80 to 14.30 mg/L ($5\text{--}40 \cdot 10^{-3}$ meq/L), with mean and median values of 8.20 and 8.85 mg/L ($23 \cdot 10^{-3}$ meq/L and $23.06 \cdot 10^{-3}$ meq/L), respectively; which signifies that they are above the prescribed limits of 1.5 mg/L for drinking water (Table 3). The F^- concentration of seawater is about 1.3 mg/L (Hem, 1985) and cannot directly account for the larger concentrations of fluoride in the CT groundwater. Alternatively, fluoride is present in solid form within some marine sediments as fluoride-bearing minerals composed mainly of CFA ($Ca_{10}(PO_4)_6F_2 \cdot 2x(CO_3)_x$, with $0 \leq x \leq 1$) (Matthews, 1977), which makes part of the substratum of the CT groundwater (Gallala et al., 2016).

Furthermore, higher F^- concentrations in the CT aquifer (Fig. 12) are randomly distributed in the Tozeur area, which may indicate that there is a relationship between the water geochemistry and the mineralogical composition of aquifer sediments or the formations crossed by the CT groundwater. This statement probably signifies that the CFA plays a significant role in the occurrence of fluorine in the CT aquifer groundwater. Two assumptions are plausible: either the CFA releases F^- to groundwater by ion exchange with carbonate hydroxyl (OH^-) to form hydroxyl-apatite ($Ca_5(PO_4)_3OH$); or $Ca_{10}(PO_4)_6F_2$ mineral is slowly dissolved, releasing fluorine to percolating groundwater.

a- Ion exchange with hydroxyl Adsorption of hydroxyl: Ion exchange with hydroxyl adsorption results from an increase in its concentration in groundwater, thereby displacing adsorbed F^- into groundwater (Guo et al., 2007; Abu Jabal et al., 2014). Dissolved OH^- concentrations, which vary directly with pH, results from an increase of HCO_3^- (Subba

Rao, 2003; Tiwari et al., 2008; Kantharaja et al., 2012). Thus, an increase in bicarbonate concentration such as observed in the CT groundwater also correspond to F^- desorption. The HCO_3^- ion may have three different sources: (i) the dissolution of calcium carbonate in groundwater, (ii) the solution of CO_2 in water and (iii) the incongruent dissolution of dolomite. However, both CI and CT groundwaters are oversaturated with respect to calcite, which makes the dissolution of calcium carbonate implausible. In contrast to the preceding source of HCO_3^- , the solution of CO_2 in water is most likely to occur in our case of study. Water infiltrating the land surface along the Draa El Jerid recharge area, where the CT aquifer is unconfined, combines in with carbon dioxide originating from soil organic material to form carbonic acid (hydrogen ions and bicarbonate anions):



As a result of the continued supply of carbon dioxide under "open system" conditions (Freeze and Cherry, 1979), pH values of the groundwater may vary over a relatively small range, between 7 and 8 (Table 3). This range is, however, in coherence with the pH values of the CT groundwaters. On the other hand, with downward percolation of the CO_2 -equilibrated recharge water to the CT aquifer, followed by upward flow of deep aquifer geothermal water through the aquiclude dolomitic units, water and hydrogen ions react with minerals making up subsurface sediments. These complex chemical reactions are as highly varied as the many mineral species with which the water can come in contact. For instance, in the Gafsa-Metlaoui neighboring basin, one of the most widespread reactions in silica-rich rocks within phosphatic formations is the incongruent dissolution of dolomite (Tlili et al., 2010, 2011). This reaction, which represents another potential source of bicarbonate, may also explain the Mg enrichment in the CT groundwater. Incongruent dissolution of dolomite is coupled to gypsum and/or anhydride dissolution as confirmed firstly by the undersaturated state of the CI and CT samples respecting to the mentioned minerals; and secondly through the

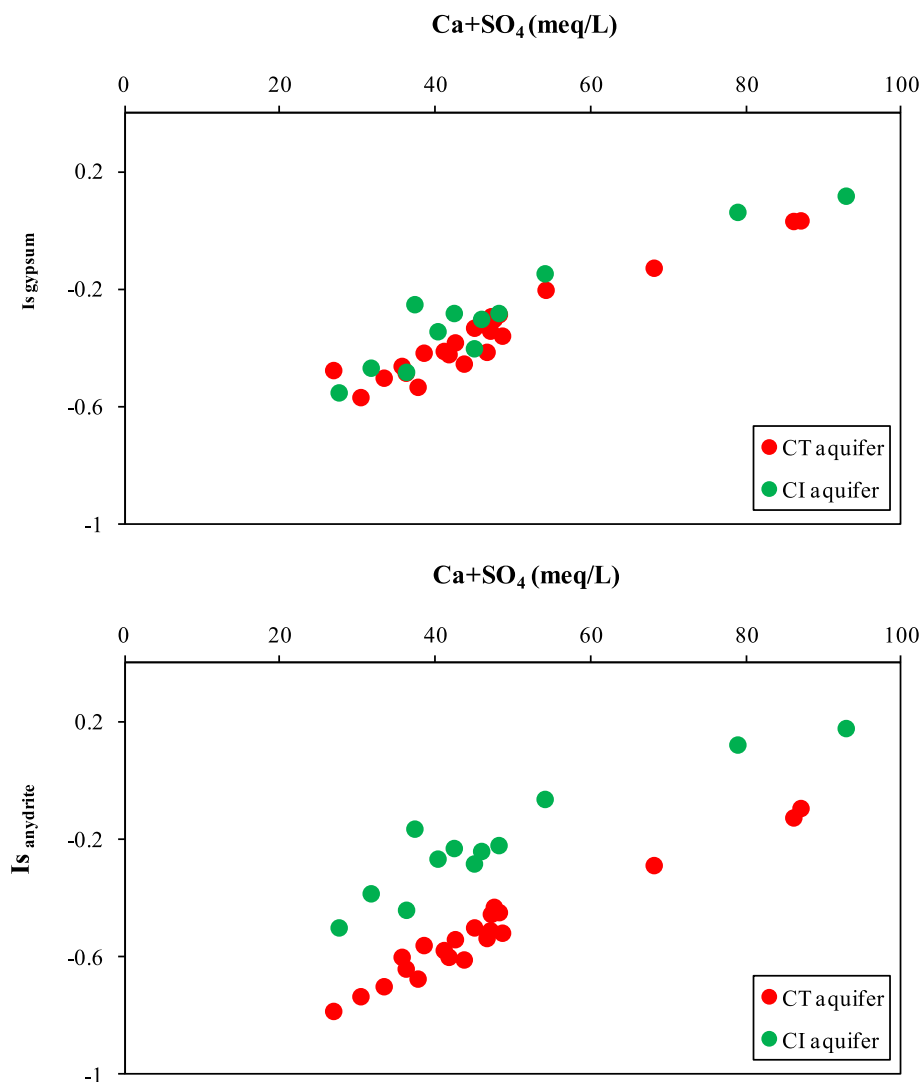


Fig. 13. Plots of $(Ca + SO_4)$ vs. SI_{gypsum} and $SI_{\text{anhydrite}}$ of the CT and CI samples.

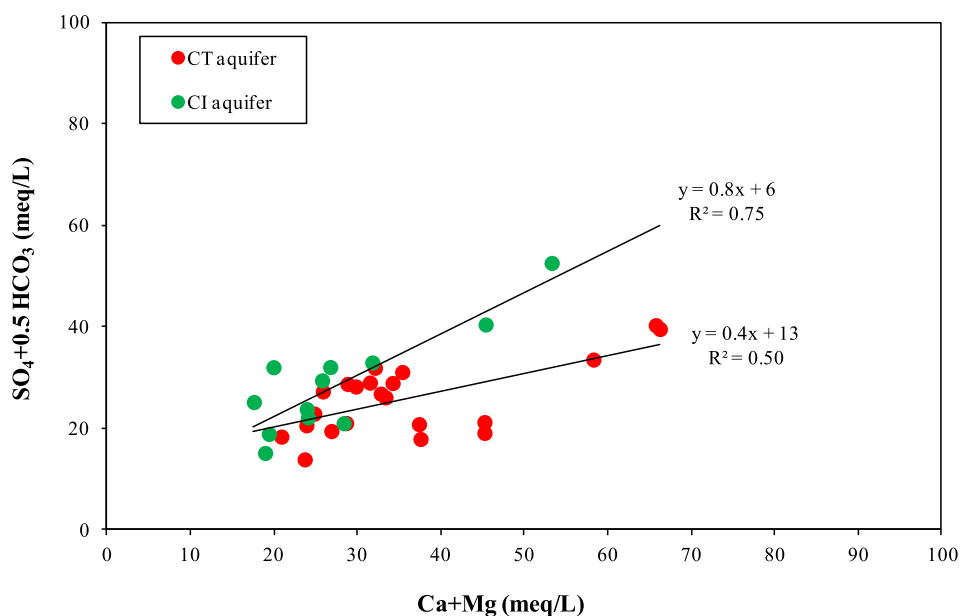


Fig. 14. Plot of $(Ca + Mg)$ vs. $(SO_4 + 0.5HCO_3)$ of the CT and CI samples.

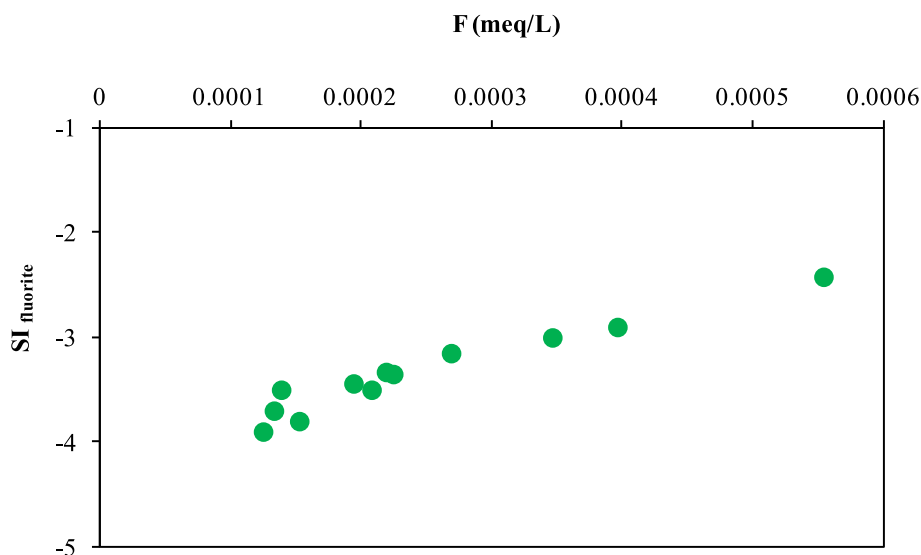
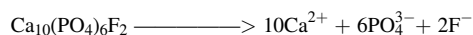


Fig. 15. Plot F vs. SI_{fluorite} of the CI groundwaters.

parabolic proportional relationships in the plots of (Ca + SO₄) versus the saturation indexes (SI) of gypsum and anhydrite, respectively (Fig. 13). As the dissolution of gypsum and/or anhydrite continues, Ca and SO₄ concentrations increase more and more, which resulted in calcite supersaturation and precipitation due to the common ion effect. As a result of calcite precipitation, HCO₃ concentrations decrease, which sets off the dedolomitization process, adding Mg to waters and decreasing the Ca/Mg molar ratios (Marfiaa et al., 2004). This geochemical process, which produces calcite with a crystalline structure similar to dolomite called “dedolomite” (Hanshaw and Back, 1979) is evidenced by the well observed relationship in the plot of (Ca + Mg) vs. (SO₄+0.5HCO₃) (McIntosh and Walter, 2006) (Fig. 14). The net reaction for the dedolomitization process is (Marfiaa et al., 2004):



b- Dissolution of Ca₁₀(PO₄)₆F₂ mineral: As mentioned above, the other explanation of F⁻ enrichment in the CT groundwater is the dissolution of CFA by the geothermal water ascending from the CI deep aquifer. A dissolution mechanism has been proposed for the release of F⁻ in natural waters according to the equation (Pettenati et al., 2013):



Nevertheless, this mechanism can happen only under acid condition (Subba Rao, 2003; Tiwari et al., 2008; Kantharaja et al., 2012). So, it cannot explain the elevated F⁻ contents in the Tozeur area, where groundwater is near-neutral to weakly alkaline. In fact, contrary to what has been found in other studies (Subba Rao, 2003; Guo et al., 2007; Tiwari et al., 2008; Rafique et al., 2009; Kantharaja et al., 2012), water alkalinity do not appear to have a major role in the F⁻ distribution within the groundwater. Similarly to some other studies (Chairat et al., 2007; Abu Jabal et al., 2014), the fluorapatite dissolution in our case of study seems to be pH independent as there is no obvious relationship between F and pH values, which vary in a relatively narrow range. In such a condition of water alkalinity, the fluorapatite can be dissolved according to two-step mechanism (Chairat et al., 2007; Abu Jabal et al., 2014; Banerjee, 2015). During the first step, the fluoride bearing mineral dissociates and produces the fluorite (CaF₂) according to the following equation (Chairat et al., 2007):

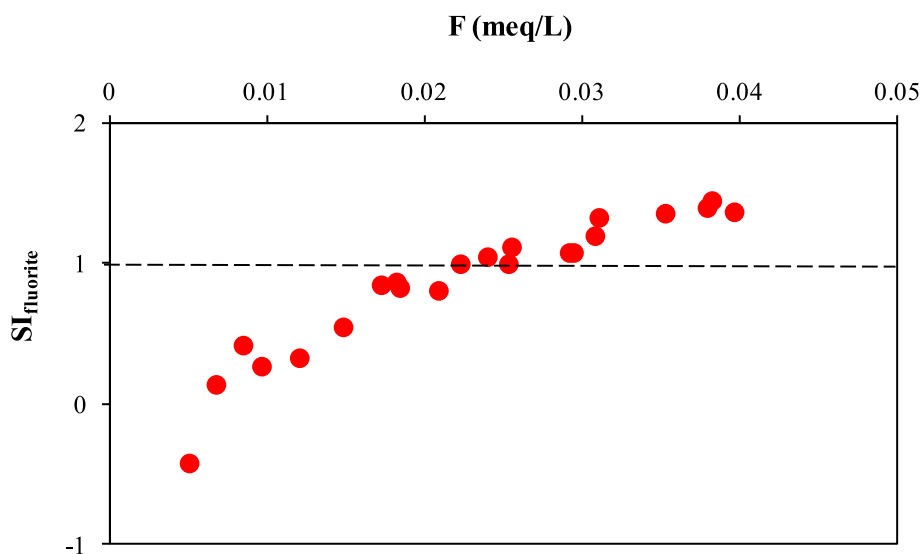


Fig. 16. Plot F vs. SI_{fluorite} of the CT groundwaters.

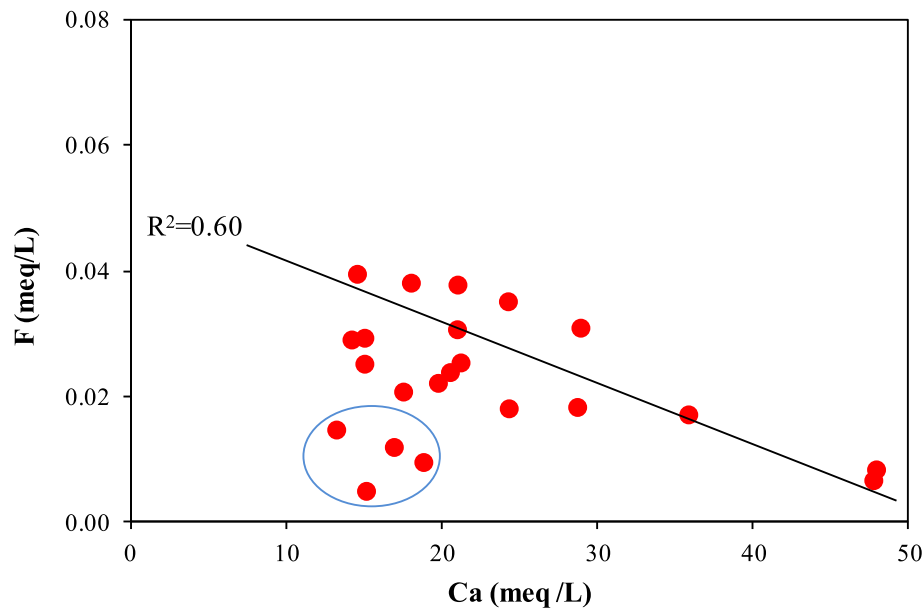


Fig. 17. Plot Ca vs. F of the CT groundwaters.

Then, the fluorite starts to dissociate producing fluorine according to equation (Handa, 1975):



This dissolution, which agrees with under-saturated state of the CI groundwater to fluorite, is confirmed by the parabolic and proportional relationship observed in the plot of F^- versus $\text{SI}_{\text{fluorite}}$ (Fig. 15). This plot indicates that there is an increasing trend of the $\text{SI}_{\text{fluorite}}$ with an increase of F^- concentration. This well defined correlation indicates that F^- ions are controlled by the solubility of CaF_2 by geothermal waters ascending from the CI deep aquifer. However, the plot of F^- versus $\text{SI}_{\text{fluorite}}$ of the CT (Fig. 16), shows that about 64% of the samples with relatively low F^- concentration fall within the equilibrium range ($-1 < \text{SI} < 1$), which may indicate the likely dissolution of fluorite. While, for about 36% of the samples, there is an oversaturation of the CT to fluorite, which is likely

due to high availability of CaF_2 .

Although the solubility of fluorite (CaF_2) is relatively low under normal condition, it would be enhanced by the presence of geothermal waters as it is temperature-dependent. On the other hand, the release of F^- is mainly controlled by the availability of free Ca^{2+} in the groundwater (Jacks et al., 2005). In other words, more Ca^{2+} ions are subtracted from the water more CaF_2 is dissolved and there will be an increase in F^- concentration in the waters leaking to the CT (Abu Jabal et al., 2014). This is corroborated by the negative relationship ($R^2 = 0.60$) observed for the majority of samples in the correlation between F^- and Ca^{2+} (Fig. 17).

As mentioned in the discussion of the first assumption of F^- enrichment, the CI and CT samples are oversaturated with respect to gypsum and or anhydrite which engender calcite/anhydrite precipitation according to Fig. 13 ($\text{Ca} + \text{SO}_4$ vs. $\text{SI}_{\text{gypsum}}$ and $\text{SI}_{\text{anhydrite}}$). Thus, a

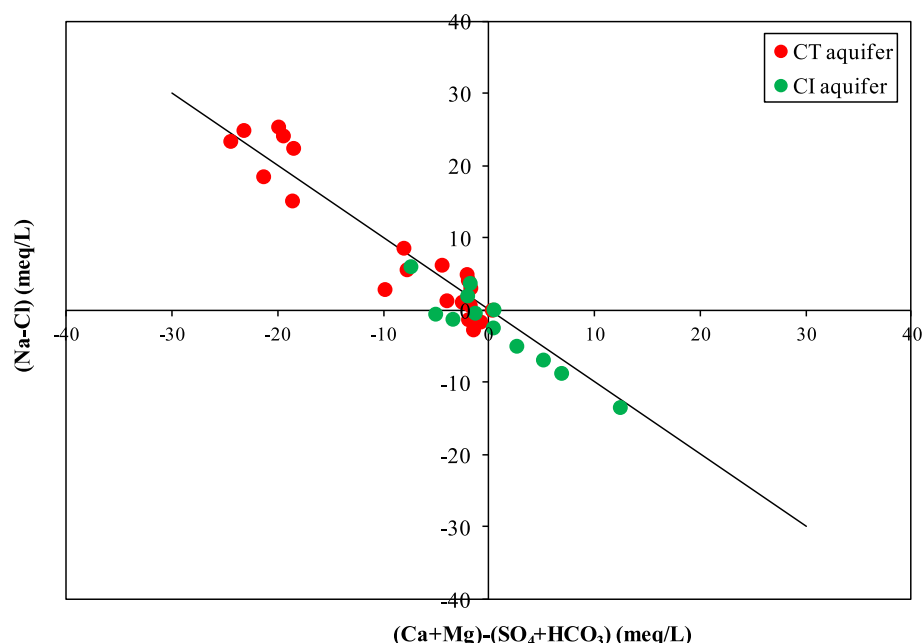


Fig. 18. Plot of $(\text{Na} + \text{K} - \text{Cl})$ vs. $(\text{Ca} + \text{Mg} - \text{SO}_4 - \text{HCO}_3)$ of the CT and CI samples.

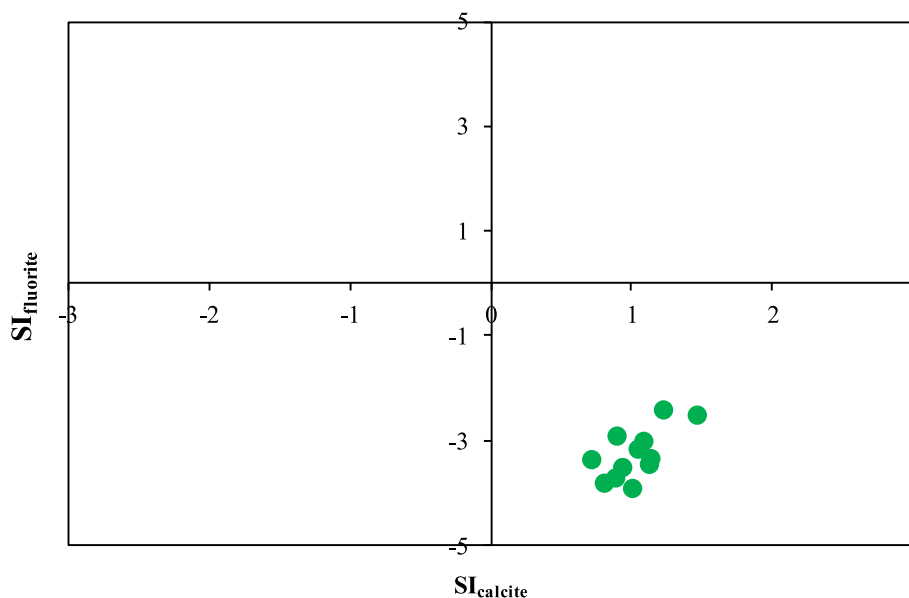


Fig. 19. Plot of SI_{CaCO_3} vs. SI_{CaF_2} of the CI groundwaters.

geochemical equilibrium will be developed between groundwaters in contact with both $CaCO_3$ and CaF_2 based on the solubility of the two solid phases. The net reaction for this equilibrium state is as follows (Handa, 1975):



with $K_{calcite-fluorite} = a(HCO_3^-)/a(H^+).a(F^-)^2 = 1.06 \times 10^{-10.58}$ at 25 °C, where, $K_{calcite-fluorite}$ represent the constant of the solubility product for $CaCO_3/CaF_2$ and a is the activity for HCO_3^- , F^- and H^+ ions.

The above equations signify that as long as the pH is fairly invariable, as it is the case for the CT and CI groundwaters, any increase in HCO_3^- changes the chemical equilibrium in the direction of the F^- formation and vice versa (Handa, 1975). However, calcite is less soluble than fluorite in the CI groundwaters and will precipitate earlier, which in reduce Ca^{2+} , enhancing the dissolution of CaF_2 (Saxena and Ahmed, 2001) and leaving more F^- ions into the groundwater (Abu Jabal et al., 2014). Another supplementary geochemical process that can be accounted for the Ca^{2+} consumption is the cation exchange between Na^+ -rich clay minerals (Garcia et al., 2001; Dassi et al., 2018). The phenomenological evidence for this cation exchange is the proportional inverse relationship (with a slope close to -1) shown in the bivariate plot of $[(Ca^{2+} + Mg^{2+}) \cdot (HCO_3^- + SO_4^{2-})]$ against $(Na^+ + K^+ - Cl^-)$ (Mc Lean et al., 2000). In the absence of this process, all data should plot close to the origin (Garcia et al., 2001) (Fig. 18).

These different assumptions are, indeed, favored by the arid climate in the Tozeur region, where high temperature in summers and low rain intensity in winter increase the alkalinity in the soil and groundwater due to evapotranspiration (Jacks et al., 2005). In such a condition, groundwater becomes more and more oversaturated with respect to $CaCO_3$, which enhances its precipitation. This will further reduces Ca^{2+} concentration and thus promoting dissolution of CaF_2 and increasing F^- concentration in the groundwater (Gupta et al., 2012).

In order to provide evidence for each mechanism of F release: the exchange of OH for F and the simple dissolution of CFA, Ca^{2+} , SO_4^{2-} , and OH^- ions have been correlated with F^- . Nevertheless, no well defined relationship has been observed. This finding is likely due to the fact that F release does not happen within the CT or the CI aquifers; but it took place within the intermediate phosphate layer by the ascending CI geothermal waters. After that the F-rich groundwaters percolates into the CT underling aquifer and mixes with CT groundwater from regional flow. This mixing modifies the chemistry of ascending groundwater and

masks any evidences which can confirm or deny either hypothesis. However, the presence of relatively high amount of Sr trace element confirms the importance of water-rock interaction process and pleads in favor of the dissolution CFA (Galfatit et al., 2010). Whilst, moderate to low Sr concentrations in the deep CI aquifer are likely related to the dissolution of gypsum bearing rocks and possibly to celestine.

As a result, the groundwater composition in the CT aquifer in the Tozeur region, where the Ca^{2+} , F^- , and HCO_3^- activities are mutually dependent, is controlled by the solubility products of CaF_2 and $CaCO_3$ (Abu Rukaha and Alsokhny, 2004; Ghrefat et al., 2014). The release of F^- into the groundwater is then governed by the degree of saturation of both calcite and fluorite reflected by the saturation indexes of groundwaters relative to the referred minerals (SI_{CaCO_3} and SI_{CaF_2}), which express the intensity of soluble minerals that is quantitatively described as the deviation of water from equilibrium in respect of dissolved minerals (Nordstrom and Jenne, 1977; Carrillo-Rivera et al., 2002; Cidu et al., 2009; Mamatha and Rao, 2010). The variation of the SI_{CaCO_3} and the SI_{CaF_2} to each other (Fig. 19) shows that all CI samples are undersaturated respecting to fluorite and supersaturated with respect to calcite. This suggests that fluorite dissolution by the ascending CI geothermal waters in the Tozeur region is enhanced by the ongoing process of calcite precipitation. However, for the CT groundwater, in which fluorite is already dissolved, around 64% samples are approaching equilibrium respecting to both $CaCO_3$ and CaF_2 , which indicates that the fluorite process coupled to calcite precipitation is slowly progressing. While, 36% of the samples are oversaturated with respect to both CaF_2 and $CaCO_3$ highlighting the ending of the process of fluorite dissolution.

5. Summary and conclusion

In this study, integrated hydrogeological, hydrochemical and mineralogical analyzes, were used to assess the F contamination of the CT groundwater and to refine understanding of the associated hydro-geochemical processes. The most important findings and conclusions can be summarized as follows:

- The source of fluorine in the CT groundwater is the CFA mineral which makes part of the substratum the aquifer,
- The mechanism of the F^- release from the CFA is governed by several factors i.e. the chemistry of CT and CI groundwaters, the high temperature of ascending waters, the geothermal character of the CI waters and the chemistry of the CFA mineral,

- The liberation of F^- is controlled by its exchange with hydroxyl and/or by the CFA dissolution through the passage of hot water ascending from the deep Continental Intercalaire (CI) aquifer,
- The transfer of F-rich waters to the overlain CT aquifer by the upward leakage of deep geothermal groundwaters is mainly through deep faults, aquitard windows and through leakage behind casing,
- This transfer of F-rich waters is engendered by the potentiometric contrast between the two superimposed aquifers, which is enhanced by anthropogenic processes i.e. the overpumping of the CT groundwater and the CI wellbore integrity failure.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2020.104661>.

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