

Geoeconomic interest of minerals assemblage of sebkhah El Melah, southeastern Tunisia

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Abstract

This work aimed to study the formation of salt through a progressive evaporation of sebkhah El Melah brine. The precipitated salt in the case of sebkhah El Melah is variable along the progressive evaporation. Weights of salt after each phase of precipitation indicate a heterogeneous evaporation process cumulating at 315 g L⁻¹. With an increasing evaporation of El Melah brine, the number of precipitated mineral species increased. The cumulative number of species along the evaporation process reached 20, including principally: Halite (NaCl) (73–95%), epsomite (MgSO₄·7H₂O) (7–14%), bischofite (MgCl₂·6H₂O) (1%), Kieserite Mg(SO₄)(H₂O) (0–2%), magnesite (MgCO₃) (1–4%), polyhalite (K₂Ca₂Mg(SO₄)₄·2H₂O). Also, the thermodynamic theoretical modeling of the El Melah brine shows convergence with geochemical and mineralogical experimental data. At an evaporation rate of 60%, the sebkhah of El Melah annually provides with 315,000 tons of salt. The majority of salt (80%) is halite. The remaining 20% contains different species having a huge economic interest. From an industrial viewpoint, our study shows that the purity of halite is guaranteed at low rates of evaporation. Evaporation between 50 and 75% produces a mixture dominated by halite. Evaporation higher than 75% needs further studies to find the mineralogical composition and the phase of each mineral precipitation. The saline system of El Melah represents a geoeconomic interest due to the cheap natural process of production, its large quantity of halite with varieties of other accessory minerals, and cheap procedure of exportation.

Key words: El Melah, geochemistry, mineralogy, progressive evaporation, southeastern Tunisia

Highlights

- The cumulative number of species along the evaporation process reaches 20: Halite (NaCl) (73–95%), epsomite (MgSO₄·7H₂O) (7–14%), bischofite (MgCl₂·6H₂O)(1%), Kieserite Mg(SO₄)(H₂O)(0–2%), magnesite (MgCO₃) (1–4%), polyhalite (K₂Ca₂ Mg(SO₄)₄, 2H₂O).
- The purity of halite is guaranteed at low rates of evaporation. Evaporation between 50 and 75% produces a mixture dominated by halite.

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INTRODUCTION

Economic geology (Emmons 1918; Max *et al.* 2005; Pohl 2011; Neukirchen & Ries 2020) is a branch of geology dealing with the location and exploitation of industrial materials. It is concerned with materials that can be used for economic and/or industrial purposes. These materials include precious and base metals, nonmetallic minerals, construction-grade stone, petroleum minerals, coal, and water. The techniques employed by other earth science disciplines such as geochemistry, mineralogy, geophysics, petrology and structural geology might all be used to understand, describe, and exploit natural resources. Economic geology is basically studied and practiced by geologists. Nonetheless, it may be of interest to other professions such as engineers, environmental scientists, and conservationists because of the far-reaching impact that extractive industries could have on the society, the economy, and the environment (Bastin & Hill 1911; Neukirchen & Ries 2020). From the beginning of time, salt has been considered of important geoeconomic interest (e.g. Shah 1980; Warren 2016). Worldwide, brines within salt lakes have recently attracted researchers' attention for the extraction of some chemical elements such as lithium (Liu *et al.* 2019; Zhang *et al.* 2019) and magnesium (Zhang *et al.* 2020) and the recovery of some minerals (Lwanyaga *et al.* 2019). The sebkhas of North Africa contain high volumes of natural brine, which represents enormous resources for extraction of dissolved salt. Actually, during the natural isothermal solar evaporation of the brine related to the arid climate, mineral salts may be recovered. Starting from the original brine, the precipitation sequences of the different salts is a function of the composition and the density of the initial brine (Zatout *et al.* 2017). Tunisia is marked by the presence of endorheic as well exoreic saline depressions including Chott Djerid (Haddadi 2018) and sebkhas of Sidi El Hani (Essefi *et al.* 2013; Tagorti *et al.* 2013), Oum El Khialate (Tagorti *et al.* 2014, 2016; Essefi 2021); Mchiguig (Essefi *et al.* 2020) and Boujmel (Ben Smida 2016). Salt is accumulated within endorheic and exoreic saline systems progressive brine evaporation. In endorheic saline systems, this brine accumulated due to either dissolution by water (e.g. rivers) of the outcropping rocks along the hydrological basin (Ehya & Moghadam 2017) or the groundwater-rock interaction along the hydrogeological basin (Ehya & Marbouti 2018; Chen & Gui 2019). Added to these processes, in exoreic systems, saline water is accumulated mainly due to seawater contribution (Ben Smida 2016). Since the beginning of the 19th century, saline systems have caught the attention of scientists and economists. The geological and economic studies began early in the 20th century. The Tunisian sebkhas and chotts are different from the usual salt lakes or closed seas. They appear as areas covered by a salt crust hiding a spongy soil soaked with briny water. Sometimes in winter, when much rain falls, they acquire the aspect of lakes for some months. These salty lakes contain similar ions to the seas, but the concentration of salts is 10 to 15 times more important than in sea water and varies between 300 and 430 g/l. They can be a significant resource of useful salts. The major elements contained in sebkhas or chotts are sodium, potassium, magnesium, calcium, chloride, sulfate, and carbonate. Other elements such as lithium, boron, bromine, iodine, etc. are present but at a lower concentration; they are the minor elements. There are also many other elements, but as traces (Kbir-Ariguib *et al.* 2001). The geo-economic interest of some minerals within Tunisian sebkhas has been recently discussed by numerous studies (Tagorti *et al.* 2014; Essefi *et al.* 2020; Essefi 2021). Mineral assemblages do have their geo-economic values due to their quantities and/or their qualities. Some minerals such as halite (Essefi *et al.* 2020), in spite of their low prices, acquire their geoeconomic interest from their production in large quantities. On the other hand, other minerals such as mirabilite (Essefi 2021), in spite of their small quantities, acquire their geoeconomic interest due to their high prices.

At the level of sebkha El Melah, the salt deposit was discussed by many authors. In terms of mineralogy, some minerals including halite, gypsum, dolomite, magnesite, carnallite (Perthuisot 1971) and huntite (Perthuisot *et al.* 1990) are deposited at the sebkha of El Melah. In terms of the process of mineral formation, Fezei *et al.* (2009) artificially recuperated halite, epsomite, carnallite, hexahydrate and bischofite. Nonetheless, the natural process of salt formation, which is economically the most

important since it has low cost, was not explicitly discussed. As was mentioned by Neukirchen & Ries (2020), economic geology not only describes the most important deposit types, but also understands the natural processes involved in their formation.

In this vein, this work is meant to carry out a comparative study along the process of progressive evaporation between brine on the recovered salt of the exoreic saline systems of El Melah. On the one hand, salt recovered after each evaporation phase was investigated based on XRD. The refinement of XRD allows the identification of evaporite minerals and their percentages. On the other hand, the geochemistry of the residual brine after each evaporation phase was analyzed. In addition, the theoretical modeling of mineral precipitation allowed the comparison between experimental and theoretical results. The study has a geoeconomic approach giving special care to the quantitative and qualitative investigation of salt resources within this saline system.

STUDY AREA

The sebkha of El Melah (also called the sebkha of Zarzis) is a Saharan salt flat of southern Tunisia; it has an area of approximately 150 km² (Figure 1). The level is slightly below the sea (Perthuisot 1974; Busson & Perthuisot 1977). The potential evaporation in the region of Zarzis ranges between 1,200/mm yr and 1,500/mm yr (Ferchichi 1996). The scarce rainy days barely exceed 200 mm (Ferchichi 1996). Sometimes, it communicates with the sea. There are holes in the surface from which the brine gushes out. Each hole is a kind of well 6 to 8 m deep. The brine of this sebkha is homogeneous (Kbir-Arigoib *et al.* 2001). Fluvial basin excavation of sebkha El Melah appeared at the beginning of the Würmian Quaternary period (Perthuisot 1974). Around 40,000 BP, the lagoon was highly desalinated by freshwater arrivals. At the upper Würm, seawater withdrew and the basin evolved to a temporary lake or continental sebkha. More recently, around 8,000 years BP, the lagoon evolved into an evaporite basin. The sebkha sediments are of several saliferous layers of rock salt and gypsum (calcium sulfate) and/or polyhalite (sulfate of potassium, calcium, and magnesium) (Perthuisot 1971). The previous sedimentological and geochemical studies conducted on several cores taken from sebkha El Melah have led

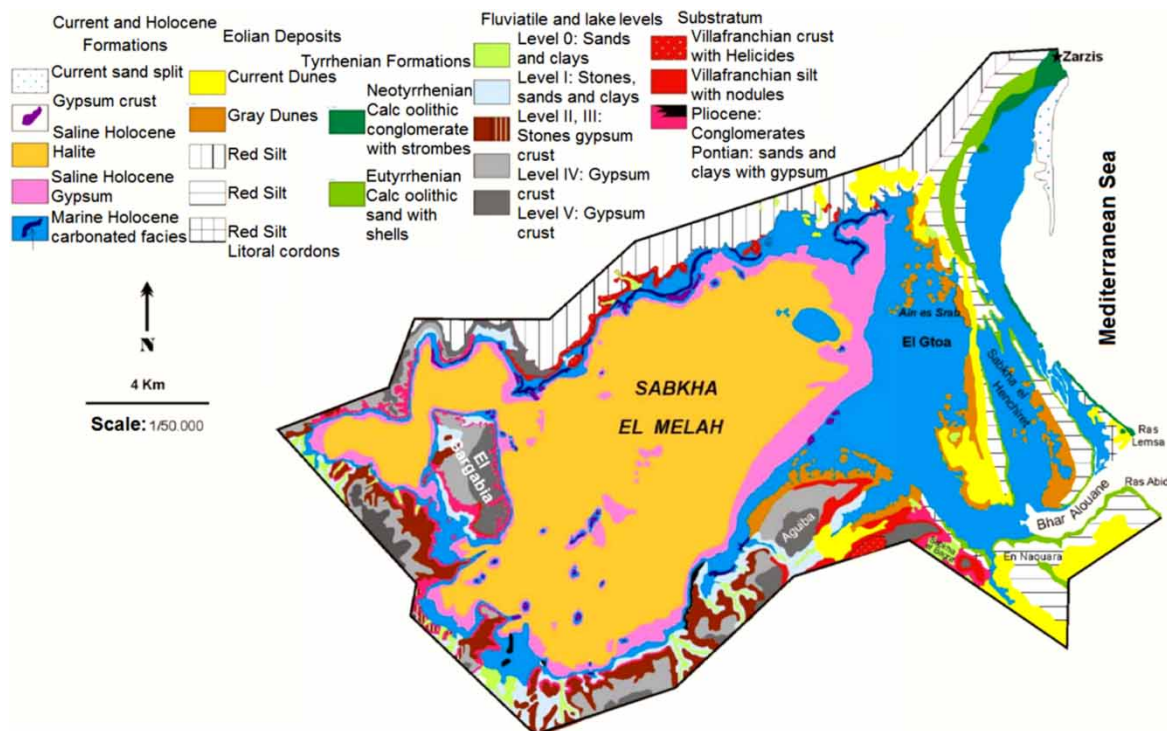


Figure 1 | Geological map of sebkha El Melah and its vicinity (Perthuisot & Florida 1973).

to the elaboration of a sedimentological model explaining the facies pattern as well as the controlling factors of the Würmian–Holocene sedimentary record (Perthuisot 1974). The sebkha of El Melah is near the commercial port of Zarzis (10 Km). Our field expeditions (Ben Smida 2016) show good conditions of transportation between the sebkha and the port. On the southern shore of the Gulf of Gabes, the port of Zarzis mainly handles sea salt and crude oil exports.

METHOD AND MATERIALS

Experimental

Water was recuperated from the surface of sebkha of El Melah (June 2017) to undergo a progressive evaporation and a series of analyses including water geochemistry, water pH, salt geochemistry, and salt mineralogy. The initial brine (M00) underwent analyses; then, it evaporates under natural conditions simulating the evaporation process taking place during the natural extraction within successive basins of salt from Tunisian saltworks. Contrary to the other industrial processes of desalination and salt recovery (e.g. Aliyu *et al.* 2018), the natural extraction of salt based on the solar energy has low cost, hence giving more economic profitability.

Water geochemistry was carried out based on high-performance liquid chromatography (HPLC). HPLC was commonly used to measure the concentration of some components such as herbicide (Mahesh & Manu 2019), phenolic extract (Neffa *et al.* 2020) and brine geochemistry (Essefi 2021; Essefi *et al.* 2020). Most HPLC instruments also have a column oven that allows for adjusting the temperature at which the separation is performed. In our work, the brine was diluted to save the HPLC from the damage. Then, a Hewlett Packard model 1100 HPLC equipped with a Spherisorb ODS column 5 μm (diameter 6×250 mm) and UV diode array detector (DAD) installed with an Agilent Chemstation 1990–2000 software was used for data acquisition, integration and processing. After the evaporation from brines, the recuperated salt is of great importance to investigate the selective precipitation. Also, it is of great importance to compare the salt and the remaining water. Salt geochemistry was studied by dissolving 1g of the solid salt within one liter of bidistilled water. After the measurement of ion contents in this water, we were able to calculate the percentages of chemical elements (Na, Cl, Mg, K, Ca, SO_4) within the salt. The mineralogical composition of the precipitated salt was also determined by X-ray diffraction (XRD). The used diffractometer was a Philips X-PERT with a Cu anticathode (K α). The recording and the digital processing of the data were carried out using the software X'PERT HighScore Plus[®]. The X-Ray Diffraction-Webmineral database was used to identify minerals. In addition, the MAUD software as well as MATCH software combined with FULLPROOF were used for refinement of spectra and detection of minor mineralogical fractions. Minerals were identified based on the Crystallography Open Database Identifier (COD ID) and Crystallography Identifier File (CIF). Cell parameters are as mentioned (a Å, b Å, c Å, Alpha, Beta, Gamma, cell volume Å³). The MATCH software combined with FULLPROOF.

Theoretical modeling

For the simulation of the natural brine evaporation, a thermodynamic modelling package, PHREEQC 3.4.0 (Parkhurst & Appelo 2017), was used. PHREEQC is an interactive modeling code with extensive interaction models, which account for the non-ideality of aqueous solutions. It iteratively calculates mineral solution-gas equilibria in complex brine systems. Due to the high ionic strength of the solutions of sebkha El Melah, the Pitzer database was used. The simulations were made using the chemical composition of the initial (M00) and final (M60) solutions from El Melah sebkha.

RESULTS AND DISCUSSION

Experimental study of El Melah salt and brine

Water geochemistry

As is shown in Figure 2, the Na^+ and Cl^- are by far the dominant ions, hence explaining the precipitation halite as the primary mineral (Ben Smida 2016). Along the progressive evaporation, the concentration of Na^+ slightly decreases due to its consumption by halite. On the other hand, the Cl^- concentration remains stable to the end of the evaporation process. Mg^{2+} , K^+ , Mg^{2+} and SO_4^{2-} amounts significantly increase until a rate of evaporation of 30% is reached. Then, they seem to stabilize, probably due to the precipitation of polyhalite in sebkha El Melah (Perthuisot 1971) and other potassic minerals. The Ca^{2+} and HCO_3^{2-} ions leading to the formation of carbonate minerals started with low concentrations and further decreased due to the progressive evaporation. This radical change in the already heterogeneous ionic content is accompanied by slight modification of pH values.

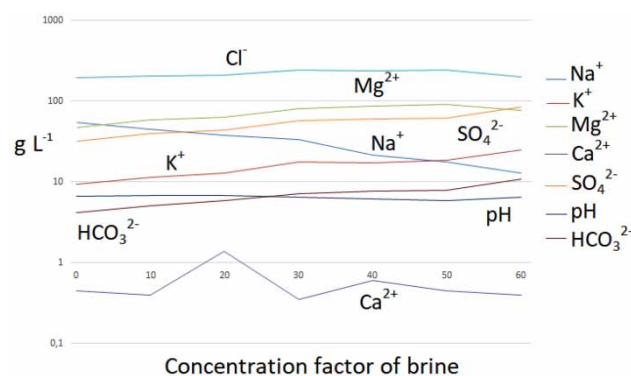


Figure 2 | Evolution of water geochemistry during the evaporation process of 60%.

Evolution of the competitive salt precipitation

Chemical analyses indicate that the potential salt from a liter of sebkha El Melah water is 349 g. Until an evaporation rate of 60%, 90% of salt precipitates. The precipitated salt in the case of sebkha El Melah is variable along the progressive evaporation (Table 1). Weights of salt after each phase of precipitation indicate a heterogeneous evaporation process. Precipitation begins rapidly with 144.7 g of salt, hence consuming 44.4% of the total salt. Then, it falls to the range of 20% of the total salt at the evaporation of 30 and 40%, to accumulate at 85%. At the evaporation process of 50 and 60%, precipitation of salt dramatically decreases.

Table 1 | Weight of the precipitated salt from El Melah water after each phase of evaporation

Rate of evaporation [%]	Weight of salt recuperated from sebkha El Melah (g)	Percentage from the potential total salt [%]
10	144.7	41.4
20	71.5	20.4
30	74.5	21.2
40	17.6	5
50	4.3	1.3
60	2.4	0.7
Sum	315.0	90

Salt geochemistry

Salt geochemistry during the evaporation process (Figure 3) shows variability related to the availability of ions within brine solution and the competing precipitation of minerals according to their constants of precipitation. At the evaporation rate of 10%, the Na and Cl are by far the dominant chemical elements, hence explaining the precipitation of halite as the primary mineral. At the evaporation rate of 20%, the concentrations of these elements slightly decrease, but remain high compared to other elements. At the evaporation rates of 30 and 40%, Na and Cl contents return to increasing accompanied by a dramatic decrease of Mg, K, Ca and SO₄ contents. At the evaporation rates of 50 and 60%, salt geochemistry shows a radical change with an increase of Mg, K, and SO₄ amounts, whereas the Ca amount remains constantly weak. In spite of its decrease, the amount of Cl remains higher than Mg, K, and SO₄ amounts; on the other hand, Na content rapidly decreases due to its consumption not only by halite but also by other similar minerals to become lower than SO₄, K and Mg amounts at evaporation rates of 52, 57.6, and 58% respectively.

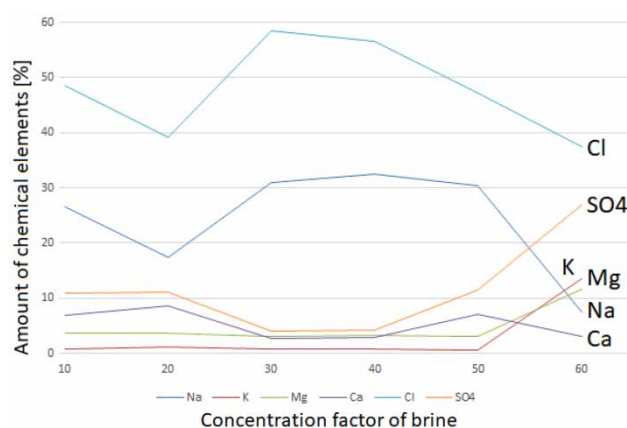


Figure 3 | Evolution of salt geochemistry during the evaporation process of 60%.

Salt mineralogy

Halite domain. As for the salt Me10 and Me20, the investigation of the XRD pattern (Figure 4) as well as the Rietveld refinement with Maud software show the precipitation of basically the halite NaCl₍₄₃₀₀₁₈₀₎ (Jürgens *et al.* 2000) (3.25 Å, 2.82 Å, 1.99 Å, 1.62 Å, and 1.41 Å). This type of halite crystallized in a cubic system with a cell parameter of 5.6393 Å and a volume of crystal cell of 179.34 Å³; it belongs to the space group Fm-3 m. The intensity of the peak reach its maximum 21,310 and 12,628 for Me10 and Me20 respectively. This range of evaporation between 10 and 20% is the domain of pure halite, with consumption of Na⁺ and Cl⁻ and stability of all the other elements.

Domain of appearance of minor minerals. The investigation of the XRD pattern of salt Me30 (Figure 5(a)), as well as the Rietveld refinement with Maud software, show the precipitation of basically halite (NaCl) (95%), lithium carnallite (Cl₃H₁₄LiMgO₇) (1%) (Schmidt *et al.* 2009), magnesite MgCO₃ (2%). The hanksite (Na₂₂K(SO₄)₉(CO₃)₂Cl) and bischofite (MgCl₂·6H₂O) (1%). The refinement shows that halite is of NaCl₍₁₀₀₀₀₄₁₎ type (Abrahams & Bernstein 1965). This type of halite crystallized in a cubic system with a cell parameter of 5.62 Å and a volume of crystal cell of 177.5 Å³; it belongs to the space group Fm-3 m. Halite reaches the highest intensity of 41,828. On the other hand, the other minerals are of minor amounts. The magnesite is of MgCO₃₍₂₁₀₁₀₅₇₎

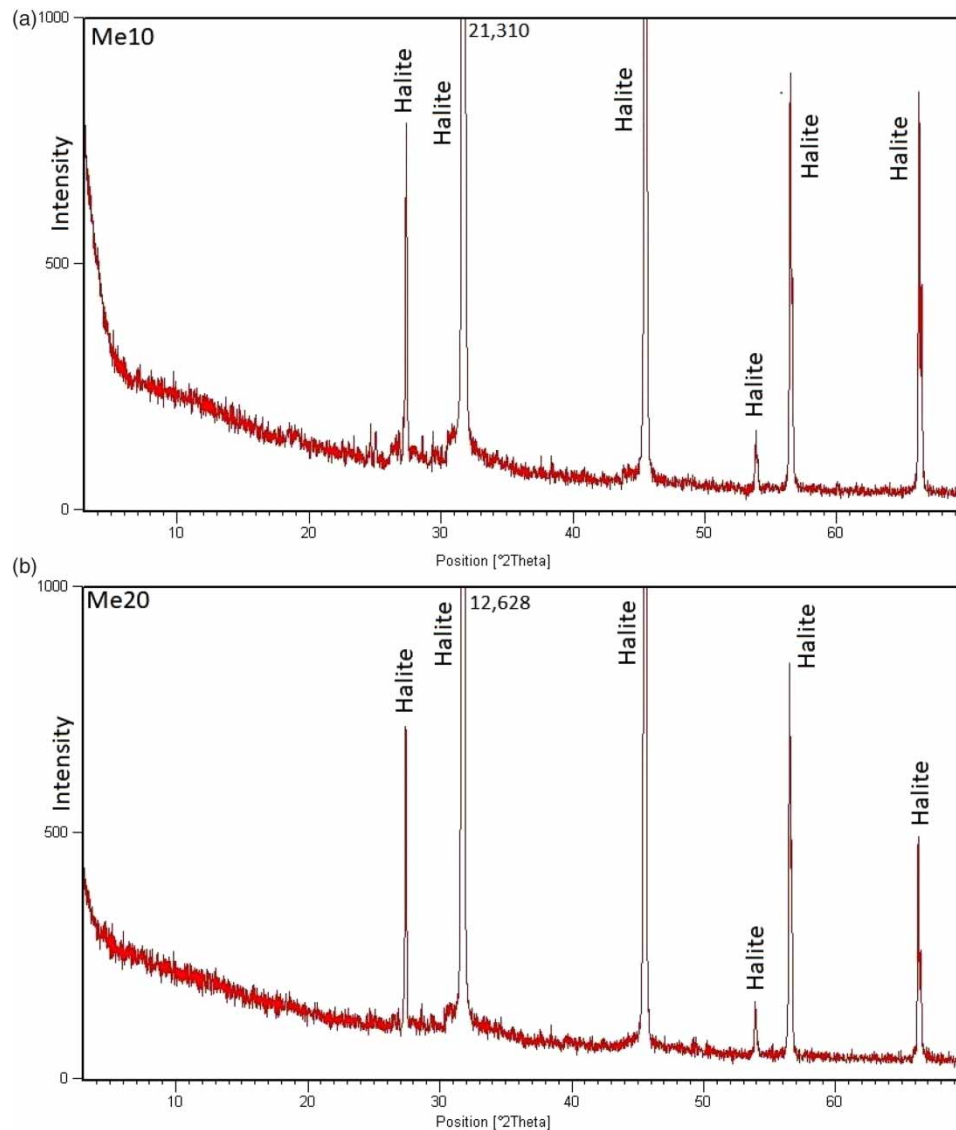


Figure 4 | X-ray diffraction patterns of the recovered salts of El Melah 10 and 20%.

type (Maslen *et al.* 1993); crystallizing in the orthogonal system, it belongs to the space group $R\bar{3}c$:H and the cell parameters are (4.635; 4.635; 15.023; 90; 90; 120; 279.5 Å). The bischofite is of $(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})_{(9011352)}$ type (Agron & Busing 1985), belongs to the space group $C12/m1$ and the cell parameters are (9.8607; 7.1071; 6.073790; 93.758; 90; 424.736 Å³). The hanksite is of $(\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl})_{(9011352)}$ type (Araki & Zoltai 1973), crystallizing in the hexagonal system it belongs to the space group $P63/m$ and the cell parameters are (10.465; 10.465; 21.191; 90; 90; 120; 2,009.74 Å). At the evaporation of 40% (Me40), halite intensity decreases to 12,628 and minor minerals disappear except magnesite. The investigation of the XRD pattern of salt Me50 (Figure 5(a)), as well as the Rietveld refinement with Maud software, show the precipitation of basically halite (NaCl) (98%) and Kieserite $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})$ (2%). The refinement shows that halite is of $\text{NaCl}_{(1000041)}$ type (Abrahams & Bernstein 1965). Kieserite is of $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_{(2003025)}$ (Aleksavska *et al.* 1998); crystallizing in the monoclinic system, it belongs to the space group $C12/c1$ and the cell parameters are (7.14; 8.05; 7.84; 90; 118.1; 90; 398 Å³). It is worth noting that the purity of Melah 50% decreases comparably to the other phases with a maximum intensity peak slightly exceeding 6,000.

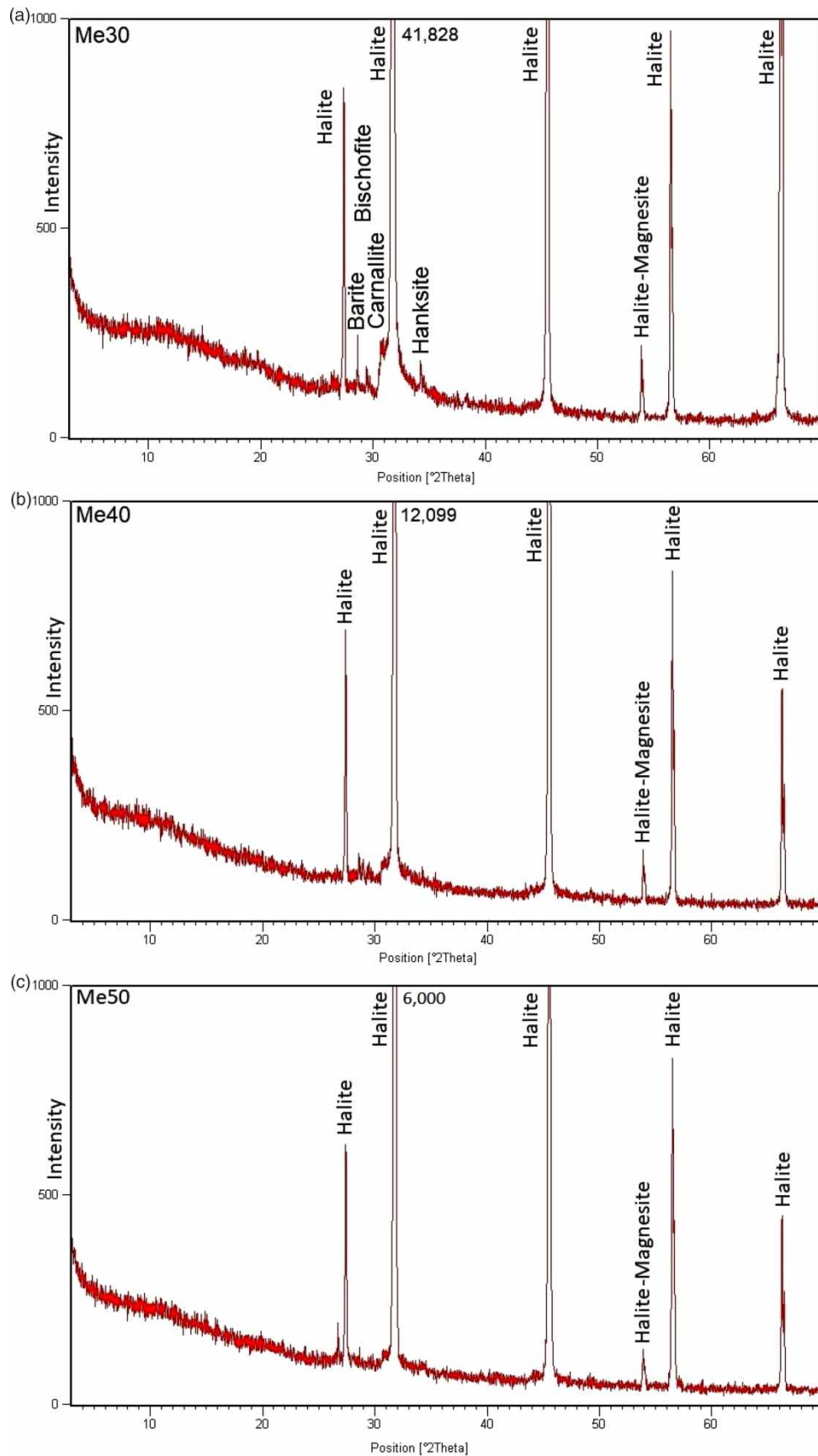


Figure 5 | X-ray diffraction patterns of the recovered salts of El Melah 30% (a), 40% (b) and 50% (c).

Domain of transition towards halite disappearance. In terms of current mineralogy, the competing precipitation of some minerals including halite, gypsum, dolomite, magnesite, and carnallite would have taken place at the sebkha of El Melah (Perthuisot 1971). Fezei *et al.* (2009) artificially recuperated halite, epsomite, carnallite, hexahydrate and bishofite. At an evaporation rate of 60%, the mixture of different minerals becomes more complicated. It is not so evident to find out the exact mineralogical composition. The Rietveld refinement may be useful to estimate the amount of each mineral.

As for the salt Me60, the preliminary investigation of Me60 through the X-Ray Diffraction-Webmineral database shows the precipitation of basically five minerals including the Kainite ($\text{KMg}(\text{SO}_4)\text{Cl}\cdot 3\text{H}_2\text{O}$) (5.17 (1), 2.64 (0.9), 2.63 (0.7), 2.8 (0.5), 2.46 (0.3), 2.61 (0.3), 4.16 (0.3), 5.85 (0.3), and 4.16 (0.3)), halite (NaCl) (3.25, 2.82, 1.99, 1.62, and 1.41), aragonite (CaCO_3) (3.396 (1), 1.977 (0.65), and 3.273 (0.52)), polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4\cdot 2\text{H}_2\text{O}$) ((2.9 (1), 3.18 (0.7), and 2.85 (0.16)), magnesite (MgCO_3) (2.742 (1), 2.102 (0.45), and 1.7 (0.35)). Another ten minor minerals would have precipitated including urancalcarite (8.06 (1), (4.02 (0.8), 3.488 (0.7)), Hexahydroborite ($\text{CaB}_2(\text{OH})_8\cdot 2(\text{H}_2\text{O})$) (7.73 (1), 3.118 (0.9), 3.37 (0.9)), uranosilite ($(\text{UO}_2)\text{Si}_7\text{O}_{15}$) (7.3(1), 6.19 (0.9), 11.58 (0.9)), Buetschliite ($\text{K}_2\text{Ca}(\text{CO}_3)_2$) (2.86 (1), 3.02 (0.3), 1.044 (0.2), 1.614 (0.2), 1.69 (0.2), 0.933 (0.2), 2.07 (0.1), 2.69 (0.1)), Hydroglauberite ($\text{Na}_4\text{Ca}(\text{SO}_4)_3\cdot 2(\text{H}_2\text{O})$) (3.08 (1), 2.78 (0.9), 9.2 (0.9)), Rutherfordine ($(\text{UO}_2)(\text{CO}_3)$) (4.6 (1), 3.21 (0.9), 4.29 (0.8)), Jacquesdietrichite ($\text{Cu}_2\text{BO}(\text{OH})_5$) (4.734 (1) (200), 3.941 (0.9) (102), 1.922 (0.5) (322), 2.489 (0.5) (220), 2.545 (0.45) (302), 1.712 (0.4), 1.838 (0.4)), Burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$) (2.78(1), 2.58 (0.8), 3.78 (0.8)), Artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH})_2\cdot 3(\text{H}_2\text{O})$) (2.736 (1), 5.34 (0.65), 3.69 (0.5)), and allanite ($\text{Ce}_{1.2}\text{Ca}_{0.6}\text{Y}_{0.3}\text{Al}_{2.25}\text{Fe}_{0.75}^{3+}(\text{SiO}_4)_3(\text{OH})$) (5.84 (20), 5.15 (30), 4.93 (100), 3.65 (30), 3.26 (40), 3.03 (20), 2.95 (30), 2.79 (20)). It is worth noting that the purity of Me60 is minimal compared to the other phases, with more pronounced intensity peaks slightly exceeding 1,500 of halite hence indicating a tendency towards halite disappearance. The Rietveld refinement of the recovered salt Me60 through MAUD and MATCH is relevant, with the mixture of the major minerals showing comparable amounts (Figure 6). The halite₍₁₀₀₀₀₄₁₎ (23%–16%), kainite (72%–77%), magnesite₍₂₁₀₁₀₅₇₎ (2%–4%), aragonite (2%–2%), and polyhalite (1%–1%). The kainite is of ($\text{KMg}(\text{SO}_4)\text{Cl}\cdot 3\text{H}_2\text{O}$)₍₉₀₀₀₂₈₂₎ type (Robinson *et al.* 1972); crystallizing in the monoclinic system, it belongs to the space group C 1 2/m 1 and the cell parameters are (19.72; 16.23; 9.53; 90; 94.92; 90; 3038.89 Å³). The polyhalite is of ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4\cdot 2\text{H}_2\text{O}$)₍₉₀₀₉₅₆₇₎ type (Schlatti *et al.* 1970); crystallizing in the triclinic system, it belongs to the space group F-1 and the cell parameters are (11.69; 16.33; 7.6; 91.6; 90; 91.9; 1,449.46 Å³). The aragonite is of (CaCO_3)₍₂₁₀₀₁₈₉₎ type (Caspi *et al.* 2005); crystallizing in the Orthorhombic system, it belongs to the space group R -3 c :H and the cell parameters are (4.987; 4.987; 17.058; 90; 90; 120; 367.4 Å³).

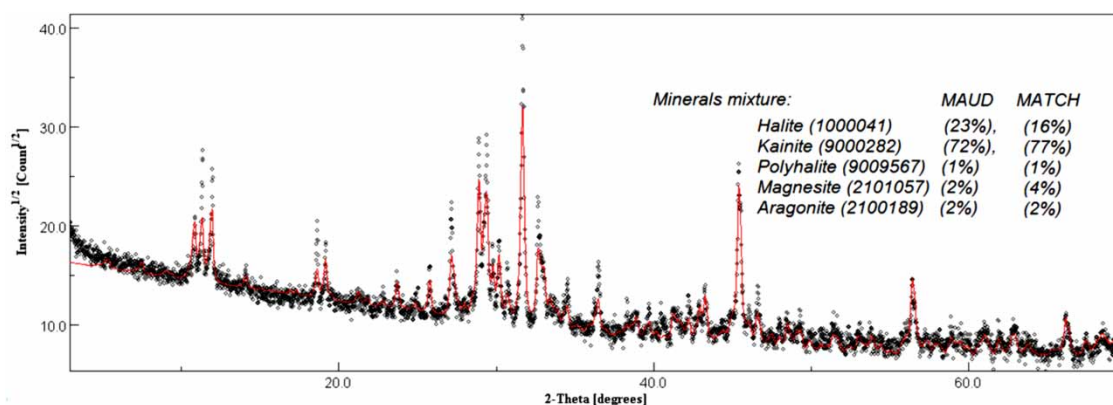
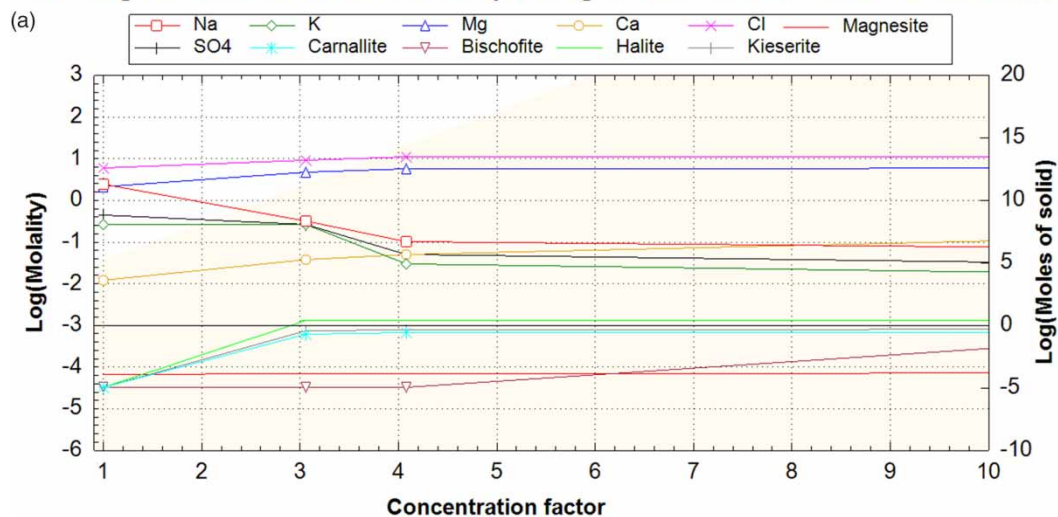


Figure 6 | Rietveld refinement of the recovered salts Me60 based on MAUD software compared with MATCH software values.

Thermodynamic modeling of El Melah brine

Exceeding the limit number of iterations, the thermodynamic theoretical modeling of the El Melah brine between the initial solution and evaporation of 60% did not converge toward a stable solution, neither did it lead to the precipitation of evaporitic minerals. This is due to an open system from which we recover the formed salt after each phase of evaporation. For this reason, the modeling was carried out in two stages. This first stage encompassed the halite domain as well as the domain of appearance of minor minerals (Figure 7(a)) from the initial solution evaporation to the evaporation rate of 50%. The second stage encompassed the domain of halite disappearance between the evaporation rates of 50 and 60% (Figure 7(b)). Taking into account experimental results showing the crystallization of halite, magnesite, bischofite, carnallite, and kieserite, modeling between the initial solution and the evaporation rate of 50% shows twofold convergence with experimental data. On the one hand, from a geochemical viewpoint, the theoretical evolution of the geochemical elements is similar to the evolution values measured during the progressive evaporation. On the other hand, the predicted precipitated minerals are already detected by XRD. In spite of its decrease in high evaporation rates, halite is omnipresent throughout the evaporation process. The magnesite

Modelling minerals and ions within Evaporating Sebkhah El Melah Brine from 0 to 50%



Modelling minerals and ions within Evaporating Sebkhah El Melah Brine from 50 to 60%

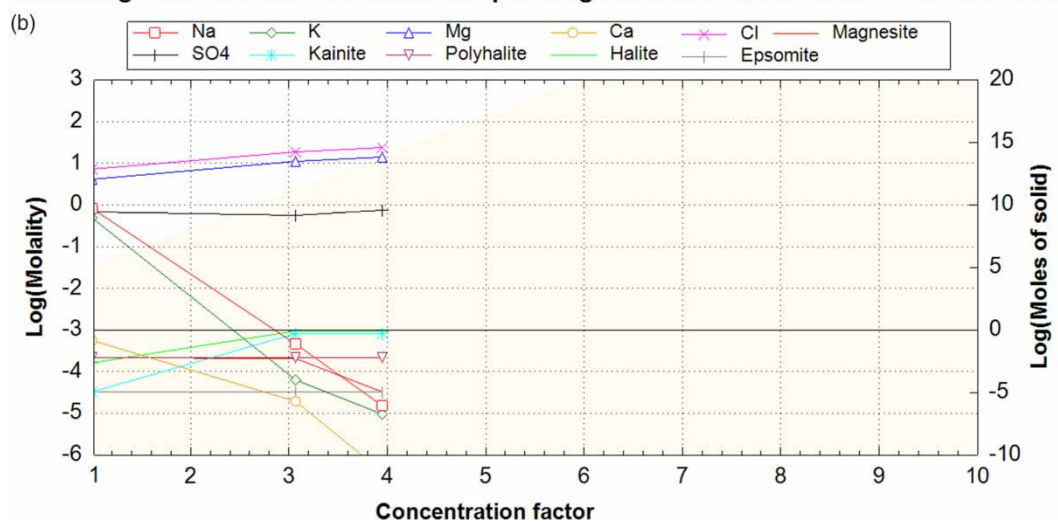


Figure 7 | Thermodynamic modeling of El Melah brine.

(MgCO_3) maintains a weak constant precipitation. Carnallite precipitation increased until a factor of evaporation equal to three. At an evaporation factor of four, bischofite started precipitation. The precipitation of Kieserite does not appear in the model; this absence represents a limitation of this method. In fact, one cannot deny that with the complexity of the ionic composition of the solution and the competitive precipitation of mineral species on the one hand and the absence of some minor minerals species, the modeling does not totally coincide with the experimental data. The modeling between the evaporation 50 and 60% (Figure 7(b)) show a decrease of Na^+ , K^+ and Ca^{2+} ion contents, whereas SO_4^{2-} , Cl^- and Mg^{2+} contents slightly increased in spite of their consumption. In terms of mineralogy, Kainite shows an increasing precipitation to balance the formation of halite.

Geoeconomic interest of sebkha El Melah

The economic interest of sebkha El Melah is twofold. (1) The renewable quantity of salt fed by the ever-present communication with the Mediterranean Sea and huge reserves inherited from thousands of years of saline conditions in the region allow the production of maximum quantities. (2) Different mineral species already cited in previous works (Perthuisot 1971; Perthuisot *et al.* 1990; Fezei *et al.* 2009) are of great economic interest in the international salt markets due to an increasing ratio of demand/supply and prices.

Salt reserves

Salt production in Tunisia is from endorheic as well as exoreic saline systems. Production of salts from inland systems has advantages as well as disadvantages. On the one hand, brines of inland systems are by far richer in salt in terms of quality and quantity than coastal ones (Ben Smida 2016). In terms of quantity, concentration of inland saline system brines with salt is 8 to 10 times higher than seawater. The salt budget within sebkha El Maleh is 349 g L^{-1} . The ordinary production of salt within Tunisia saltworks (rate of evaporation of 60%) allows the production of 315 g L^{-1} (Table 1). The potential evaporation in the region of Zarzis ranges between 1,200/yr mm and 1,500/yr mm (Ferchichi 1996). The scarce rainy days, barely exceeding 200 mm (Ferchichi 1996), could by no means modify the water and salt budgets of sebkha El Melah due to the communication with seawater. In addition, the actual evaporation is radically modified due to an increasing fluid density. The potential evaporation at sebkha El Melah of 1,200 mm/yr and 1,500 mm are corrected by the formula of actual evaporation in Tunisian sebkhas (Essefi 2009) (Actual Evaporation = Potential Evaporation $\times 22.32 \times \text{Exp}^{-3.1113 \times \text{Fluid Density}}$). In doing so, the brine density measured to 1.225 makes an annual actual evaporation ranging between 590 mm/yr and 730 mm/yr. Taking into account the evaporating surface of sebkha El Melah (150 Km^2), the sebkha annually evaporates $100 \times 10^3 \text{ m}^3$ from the initial brine. At an evaporation rate of 60%, the sebkha of El Melah annually provides 315,000 tons of salt. The majority of salt (80%) is halite. The remaining 20% contains different species having a huge economic interest. At an evaporation rate of 100%, Ashmead (1931) reported recovery from the brine of El Melah of 346 g of salt including 158 g of halite (45%), 141 g of bischofite (MgCl_2) (40%), 32 g of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) (10%), 13 g of sylvite (KCl) (3.5%), and 2.24 g (MgBr_2) (1.5%). Added to these annual reserves, sebkha El Melah accumulated within a fossil basin (Busson & Perthuisot 1977) huge quantities of salt (30 m thick along 150 Km^2) since its setting as a sebkha, 6,000 years ago.

Economic interest of sebkha El Melah mineral species

In terms of quality, the salt budget of inland systems is rich with many mineral species. With an increasing evaporation of El Melah brine, the number of precipitated mineral species increased. At

Me10 Me20 and Me30 salts, the halite dominates the precipitated fractions with the presence of carnallite and magnesite. At the end of the evaporation process, the number of species reaches 15 in Me60. The cumulative number of species along the evaporation process reaches 20. Prices of these salt and their uses are really variable. In our case, we will deal with the common price and uses of the major (up to 3%) minerals of El Melah brine redundant in the internet. The price of the more abundant mineral halite is between 20.00-\$100.00/metric ton. With its chemical formula, halite is the most important ore of the elements sodium and chlorine. It is used as food seasoning, road safety to melt snow and ice, as salt licks for cattle and for medicinal purposes. With small amounts, magnesite as such is used as a gem and lapidary material. As a raw material, Magnesite is used to produce magnesium oxide (MgO), serving as a refractory material for the steel industry and chemical industry. According to the amount of MgO, Magnesite price varies from \$205–230/metric ton, \$240–260/metric ton, \$335–355/metric ton, for 90–92, 94 and 96% MgO respectively. Since it is comprised of calcium, magnesium and potassium sulphates, polyhalite is a mineral salt that can be used as a fertilizer. With a price of about \$125/metric ton, it has potential for other industrial applications. Kainite is used as a source of potassium and magnesium compounds, as a fertilizer, and as gritting salt. Kainite is used in the crude state, without any treatment except grinding, as a fertilizer. Some of it is also used for the production of potassium sulphate. Kainite price varies from \$10–20/metric ton.

Natural industrial procedure to recover pure salts

To have a good profitability of salt exploitation, recovery of salt should be natural with the minimum of cost; any industrial procedure would only increase the production cost. In this work, we reached an evaporation rate of 60%. The halite domain is located at an evaporation rate lower than 50%. At this domain, halite production reached its maximum with the highest purity. The evaporation rate between 60 and 75% is not good for the recuperation of pure salts. The more important evaporation phase for the precipitation of other mineral species than halite lies at higher evaporation rates. [Ashmead \(1931\)](#) reported that a total evaporation of one liter of El Melah brine gives a mixture of salt including 158 g of halite, 141 g of bischofite (MgCl_2), 32 g of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), 13 g of sylvite (KCl), and 2.24 g (MgBr_2). Nonetheless, we have no idea about the domain of precipitation of each mineral. Any industrial procedure to separate this mineralogical mixture could only increase the price of each mineral. [Fezei et al. \(2009\)](#) used a protocol to select the successive precipitation of halite, epsomite, carnallite, hexahydrate and bischofite. Really, we have no idea about the cost of this supplementary protocol. From an industrial viewpoint, our study shows that the purity of halite is guaranteed at low rates of evaporation. Evaporation between 50 and 75% produces a mixture dominated by halite. Evaporation higher than 75% needs further studies to find the mineralogical composition and the phase of each mineral precipitation. The modeling of brine with the mixture found by [Ashmead \(1931\)](#) does not converge, hence indicating an error in the mineralogical composition of the mixture and/or in the geochemical composition of our brine.

CONCLUSIONS

Experimental as well as theoretical studies of El Melah brine confirm the abundance of minerals assemblage having a geoeconomic profitability related to their natural process of production, their quantities and qualities and the procedure of their exportation. (1) In this work, the method of progressive evaporation leading to formation of evaporite minerals is similar to the procedure used in the saltwork of sebkha El Melah. In this procedure, it is not required to use industrial procedures to extract a specific mineral. Its domain of crystallization is just located in the evaporation path

and extracted with no supplementary cost. (2) In terms of quantities and qualities of evaporite minerals, the salt reserves within this exoreic saline system are huge due to its communication with the Mediterranean Sea. The climate, dominated by high evaporation, also enhances the formation of salt. Salt recuperated from sebkha El Melah has a relevant geoeconomic interest in terms of quantity and quality. Halite with different subspecies is present in huge quantities, reaching 80% of the precipitated salt. About 20 other mineral species are also present including magnesite (MgCO_3), polyhalite $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, lithium carnallite ($\text{Cl}_3\text{H}_{14}\text{LiMgO}_7$), hanksite ($\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$), aragonite (CaCO_3), kieserite ($\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), urancalcarite ($\text{Ca}(\text{UO}_2)_3(\text{CO}_3)(\text{OH})_6 \cdot 3(\text{H}_2\text{O})$), Hexahydroborite ($\text{CaB}_2(\text{OH})_8 \cdot 2(\text{H}_2\text{O})$), uranosilite ($(\text{UO}_2)\text{Si}_7\text{O}_{15}$), Buetschliite ($\text{K}_2\text{Ca}(\text{CO}_3)_2$), Hydroglauberite ($\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2(\text{H}_2\text{O})$), Rutherfordine ($(\text{UO}_2)(\text{CO}_3)$), Jacquesdietrichite ($\text{Cu}_2\text{BO}(\text{OH})_5$), Burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$), Artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3(\text{H}_2\text{O})$), and allanite ($\text{Ce}_{1.2}\text{Ca}_{0.6}\text{Y}_{0.3}\text{Al}_{2.25}\text{Fe}_{0.75}^{3+}(\text{SiO}_4)_3(\text{OH})$). (3) The procedure of their exportation is not expensive. The commercial port of Zarzis is located at a distance of less than 10 Km. Salt exports from the commercial port of Zarzis are a candidate to increase from one year to another. For instance, in December 2017, it reached 84,367 T, with an increase of 100% compared to the same period of 2016. The potential quantity produced and prices in the international market present a good opportunity for Tunisia to invest in the salt industry.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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