Arid Land Research and Management

Soils and Brine Geochemistry and Mineralogy of Hyperarid Desert Playa, Ouargla Basin, Algerian Sahara

Belhadj Hamdi-Aissa a, Vincent Valles b, Alain Aventurier c, Olivier Ribolzi d

a Université de Ouargla, L. R. de Protection des Écosystèmes en Zones Arides et Semi-Arides, Laboratoire d'Analyses Physico-Chimiques, Département d'Agronomie, Ouargla, Algeria
b Université de Provence, Laboratoire de Chimie & Environnement, Marseille, France
c Unité de Recherches et d'Analyses, CIRAD Montpellier, France
d IRD - Ouagadougou, Burkina, Faso

Online Publication Date: 01 January 2004
To cite this Article: Hamdi-Aissa, Belhadj, Valles, Vincent, Aventurier, Alain and Ribolzi, Olivier (2004) 'Soils and Brine Geochemistry and Mineralogy of Hyperarid Desert Playa, Ouargla Basin, Algerian Sahara', Arid Land Research and Management, 18:2, 103 - 126
To link to this article: DOI: 10.1080/1532480490279656
URL: http://dx.doi.org/10.1080/1532480490279656

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BELHADJ HAMDI-AISSA
L. R. de Protection des Ecosystèmes en Zones Arides et Semi-Arides
Laboratoire d’Analyses Physico-Chimiques
Département d’Agronomie, Université de Ouargla
Ouargla, Algeria
Agronomie & Environnement (AGER-DMOS)
Institut National Agronomique
Paris-Grignon, France

VINCENT VALLES
Laboratoire de Chimie & Environnement
Université de Provence
Marseille, France

ALAIN AVENTURIER
Unité de Recherches et d’Analyses
CIRAD Montpellier, France

OLIVIER RIBOLZI
IRD - Ouagadougou
Burkina Faso

The Ouargla basin is located in hyperarid north Africa and characterized by an endoreic landscape (playa) with Solonchak (accumulated soluble salts) and Gypsisol (accumulated gypsum) soils, and subsurface groundwater. The chemical and mineralogical specificity of this hyperarid ecosystem has been compared to other areas under arid environment (Tunisian sub-Saharan and Algerian steep-lands). Chemical data on the major and minor elements, such as Sr\textsuperscript{2+}, were obtained, and

Received 16 August 2002; accepted 30 November 2003.

The authors thank Dr. Fedoroff, Dr. Bourrié and Dr. Halitim for their constructive revisions, suggestions and comments on the manuscript. They also gratefully thank Mr Hadj-Yahia (Hydraulic Division of Ouargla), Mr. Zekri and Mr. Moudjahed (Civil Engineering Laboratory) for their invaluable assistance during the field work. We are especially grateful to the Saharan Agriculture Institute (Ouargla), Agriculture Ministry (Algeria), National Institute of Agronomy (Paris), and Exterior Ministry (France) for their administrative and financial supports.

Address correspondence to Dr. Belhadj Hamdi-Aissa, AGER-DMOS, INA P-G, BP. 01, 78850 Thiverval-Grignon, France. E-mail: belhamdiaissa@yahoo.fr
geochemical studies of groundwater, soil solution samples and brines have been performed. In total, 84 samples (42 groundwater, 39 soil solutions, 3 brines) were collected. X-ray diffraction and micromorphological observations (SEM with microprobe) were also performed in order to analyze soils and efflorescence. The concentrations of chemical components showed a strong variability (standard deviation of 1.15 for Cl⁻ and 1.08 for Na⁺) which was reduced by an increasing ratio between concentrated and diluted samples. The Principal Component Analyses showed that an increase in the concentration of soluble ions was responsible for 56% of the total variance. When the soluble salt concentration increased, the chemical composition changed from Ca-sulfate dominance to Na-chloride dominance. Thermodynamic equilibrium data indicated that these salt solutions were controlled by the following precipitation sequence: calcite > gypsum > mirabilite > halite. This sequence was confirmed by X-ray diffraction and micromorphology. Genesis of dehydrated forms of CaSO₄·2H₂O were recognized by: (1) partial dehydration of gypsum by sun radiation on the soil surface, and (2) a decrease in water activity (<1) relating to an increase in ionic strength (>3 mol, kg⁻¹ of H₂O) of concentrated solutions. The presence of mixed sulfates (glauberite, bloedite, and others) appears to be a distinctive feature of the hyperarid soil. In this environment they are more stable than simple sulfates. A discrete mineral involving a minor element was observed, and celestite (SrSO₄) was thermodynamically predicted. This mineral results from the coprecipitation of Sr²⁺ with gypsum. Morphologically, celestite crystals occur as inclusions and within the periphery of gypsum crystals. The seasonal and daily thermal amplitudes in the desert environment determine the precipitation pattern into the Na–Ca–SO₄·H₂O system (mirabilite-thenardite-halite paragenesis), controlling the process of dissolution/precipitation of gypsum. The hyperarid environment has a remarkable chemical and mineralogical reactivity because of the high solubility and hydration status of minerals, and its sensitive reactivity to climate variation. Based on these results, dehydrated CaSO₄ is proposed as a diagnostic pedological criterion for delineating hyperarid and arid ecosystems.

**Keywords** ion activity, gypsum, soluble salts, groundwater, micromorphology, desert soil, surface crust, soil salinity

Arid climatic regimes display a strong heterogeneity on a global scale. The Sahara desert is a representative of an aridic climatic regime with mean rainfall of 100 ± 50 mm a⁻¹. This value is considered as the critical limit between an arid and hyperarid region (Le Houérou, 1990, 2000, 2001; UNESCO, 1979) although other authors suggest a lower value of 70 mm a⁻¹ (Monod, 1987). Below this critical limit, great differences in soil, vegetation, and fauna can be observed (Cooke et al., 1993; Dregne, 1976; Dutil, 1971; Le Houérou, 1990, 2000, 2001).

The hyperarid climate of the Ouargla basin in Algeria is characterized by gypsiferous and saline soils (i.e., primary salinization) (Hamdi-Aïssa, 2001a; Hamdi-Aïssa & Girard, 2000). The presence of a surface water table in the lower parts of the landscape (playa) induces very intense salinization, resulting in the formation of brines and salt crusts. However, the processes of salinization may also occur at the highest zones of landscape.

In the subdesertic areas of the Sahara (i.e., sub-Sahara), the geochemical processes responsible for the formation of the saline crusts have been the focus of various studies (Gueddari, 1980, 1984; Rezagui, 1993; Valles et al., 1997). These studies have shown, however, that the simple precipitation sequence (known since the 1980s), calcite → gypsum → halite, must be reexamined. These data suggest that soluble sulfate minerals, such as mirabilite, may be formed in the natural environment, and may contribute to a greater understanding of brine chemistry. Moreover, information on minor elements that are associated with brine formation is extremely rare.
Hyperarid environments, such as the Sahara desert, have received less attention compared to other arid regions (North Africa, Middle East, Central Asia, Australia, and United States of America) where the climate is less arid. The present study reports on the geochemistry and mineralogy of an endoreic landscape (playa) of the Ouargla basin. We have determined the concentration of both the major and minor chemical elements of soil solution and groundwater samples associated with this hyperarid climate, and evaluated the mineralogical nature of their accumulation. Additionally, we made the attempt to address the following question: can the hyperarid character of climate induce mineralogical specificity compared to soils developed in an arid climate? The purpose of this study was to assess the hydration status and complex nature of sulfates specific to the chemistry of hyperarid environments. Special attention was given to a comparison between the salinization processes of arid and hyperarid regions.

This work was performed by using (1) the techniques of X-ray diffraction for the identification of minerals and of their hydration status; and (2) the observations under scanning electron microscope (SEM, equipped with microprobe) to analyze minerals containing trace elements. A geochemical assessment of soil solutions, groundwater, and salt crusts was also performed. The selection of the study area was justified by the hydrochemical simplicity of the Ouargla basin system and the size in the number of artesian wells as the sole source of groundwater (Guendouz, 1985; Hamdi-Aïssa, 2001a; PNUD-UNESCO, 1972).

Materials and Methods

Description of the Area

The study area is located in the northeastern Sahara desert of Algeria “Low-Sahara” near the city of Ouargla (Figure 1), 31°54′ to 32°1′ N and 5°15′ to 5°27′ E, with a mean elevation of 134 m. The area forms a part of the Wadi Mya (a dry paleovalley) which runs from Tadmaï Plateau in Central Sahara to Gulf of Gabes in Tunisia (Dubief, 1953; Rognon, 1980). In this region of the Sahara, the climate is hyperarid Mediterranean. The mean annual rainfall is 40.7 mm (1985–1995) (Hamdi-Aïssa, 2001a), and the mean annual temperature is 22.5°C with a minimum of 10.7°C (January) and a maximum of 34.4°C (August). The mean annual relative humidity is 41.5% while the mean annual evapotranspiration is 2138 mm. High temperature and dry winds favor considerable evaporation. These winds are mostly either from the northeast or from the southwest with an average velocity of 9 m s⁻¹ (20 m s⁻¹ during spring) and mean windy days of 50 da⁻¹.

The investigated area is a plateau dominating the Ouargla basin, characterized by Miocene-Pliocene bedrock composed of a clayey-quartzite sand. A hard calcrete (considered to be Pliocene in age) covers this plateau, the surface of which is in the form of a reg. The clayey-quartzite sand is located on the upper slope and runs east towards a depression that is strongly eroded. The sandy material is covered by mixed aeolian and colluvial deposits on the lower slopes. The bottom of the basin is occupied by a playa sabkha (Briere, 2000), the surface of which is enriched in soluble salts. The accumulation of these salts is closely related to the dynamics of the groundwater. Undoubtedly, the pumping of deep saline aquifers (2 to 8 g L⁻¹) and the parallel urban development have severely altered an equilibrium which had existed over millennia between water input/output in the Ouargla depression. The general rise of the subsurface groundwater in this depression has induced a global salinization of the oasis soils. Moreover, the direct application of untreated sewage water from the city of Ouargla to the playa is a serious cause of pollution of the subsurface groundwater.
Soils

After Hamdi-Aïssa & Girard (2000) and Hamdi-Aïssa (2001a), the Reg plateau soils are classified as Yermic Calcisol (FAO, 1998), consisting of a gypsic crust overlain by a petrocalcic horizon. Soils on the upper slopes are covered by Hypogypsic Petrocalcic and sandstone bedrock Regosol. Loose aeolian sand mixed with colluvial material, classified as a Yermic Arenosol are present on the piedmont. On the edges of the playa, soils are characterized by a surface or subsurface gypsic crust underlain by a calcareous crust lying on a secondary gypsic crust. These soils are classified as Hypogypsic/Petrocalcic Solonchak, and Hyper/Petrogypsic Solonchak. In the center of the playa, the soils are characterized by a wavy and bumpy surface salt crust, characterized by efflorescence and is classified as a Hypogypsic/Gypsic Solonchak.

Field Sampling Procedures

The sampled horizons of the playa and its edges were evaluated in order to understand selected soil chemical properties in relation to the rise of subsurface groundwater. Seven profiles have been studied and described according to World Reference Base (FAO, 1998). These profiles were judged to be representative of soils showing salt crust and gypsic horizons, in allowing for the study of the most relevant aspects of gypsum and soluble salt (secondary) enrichment. Surface salt crusts were sampled (sieved separately) and found to be intermixed with the soil. Saline deposits present a white and dusty appearance and have been sampled, as well as the subsurface crusts. Undisturbed samples of soil horizons, in Kubiana boxes, were used for micromorphological and submicroscopic studies. Additionally, 42 groundwater samples were also collected from piezometers placed in the Ouargla depression.
Chemical Analyzes

The pH, Eh, temperature, and electrolytic conductivity (EC) were measured in the field in nonfiltered samples. The redox potential was measured with a platinum electrode in dark bottle.

The chemical and physicochemical analyses of the groundwater and saturated extracts of the soils were performed in the laboratory: CO$_3^{2-}$ and HCO$_3^{-}$ were measured in situ with H$_2$SO$_4$ titration (Richards et al., 1954), Cl$^{-}$ and SO$_4^{2-}$ were assessed using ion exchange chromatography (Waters ILC-2 ion/liquid chromatograph, with IC-PAK anion columns). Na$^+$ and K$^+$ were determined using flame spectrophotometry, while Mg$^{2+}$ and Ca$^{2+}$ were determined by atomic absorption spectrophotometry. Sr$^{2+}$ was analyzed in only 15 samples (six groundwater, eight soil solution, one brine) and performed by Inductively Coupled Plasma (Argon) - Atomic Emission Spectroscopy (ICP-AES) (Reitznerova et al., 2000). The major elements Cl$^{-}$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$ were analyzed systematically using diluted samples. The pCO$_2$ was calculated by thermodynamic equilibrium from in situ measurement of pH and alkalinity. Chemical analyses were provided by Institut National de la Recherche Agronomique (INRA, Arras).

X-ray Diffraction Analyses and Micromorphology

Each soil and crust sample was studied using a Siemens D 5000 diffractometer with the Cu-Kα radiation, with a Ni filter working at 30 mA and 40 kV. For scanning electron microscopy, a Scanning Electron Microscope (SEM) (Philips 525 M) was used, while clods taken from the undisturbed samples were analyzed by an Energy Dispersive X-Ray Analyzer (EDXRA) microprobe. Thin sections were studied under a light microscope. Additional thin sections with polished surfaces were examined under SEM by way of Back Scattered Electron Images (BSEI). X-ray mineralogy and micromorphology were analyzed in INRA (Versailles-Grignon).

Data Analyses and Activity Coefficient Calculations

Ion activities in solution are usually calculated using two types of models:

- Ion interaction models, which take into account a large number of interactions, from short range to long range, and thus provide accurate estimates of ion activities under strong ionic concentrations (ionic strengths of 5 mol kg$^{-1}$ of H$_2$O and above). These models require many fitting parameters, which are not always available for the type of solution being studied.

- Ion pair models, which have the advantage of requiring no other fitting parameters other than the stability constants of the considered complexes.

These models are usually built around an extension of the Debye-Hückel theory for saline solutions. The Debye-Hückel law itself deals only with electrostatic interactions and gives poor results when applied to brines. Various extensions of this theory have been suggested. The Scatchard extension (Scatchard, 1936) is among the most commonly used. A more effective extension has been recently suggested by Valles et al. (1997) which takes into account the solvent/solute interaction under a strong ionic concentration. It was applied successfully to brines in southern Tunisia, whose chemical characteristics were very similar to those in southern Algeria. This model, called AQUA (Barbiero et al., 2002; Ould Mohamadou et al., 1999; Valles & Bourgeat, 1988; Valles & De Cockborne, 1992), was used for calculations in the present study.

Generalized Residual Alkalinity

Alkalinity is the sum of weak base concentrations multiplied by the number of protons of each base (which may be neutralized), minus the number of protons in the
solution (Bourrie, 1976, 1978). In most soil solutions, this alkalinity is mainly due to carbonate species.

Two scenarios may occur when evaporation concentrates a solution resulting in calcite precipitation. If the calcium equivalent is stronger than the carbonate alkalinity, then the calcium molality increases and alkalinity decreases. If the calcium equivalent is less than the carbonate alkalinity, then molalities change in the opposite direction. The concept of residual carbonates originally derived by Eaton (1950) was later redefined in terms of residual alkalinity and generalized to the successive precipitation of several minerals (Al-Droubi et al., 1976; Chernet et al., 2001; Van Beek & Van Breemen, 1973).

**Statistical Methods**

Chemical data were analyzed using computed software AQUA for statistic and chemical equilibrium. Following an Analysis of Variance (ANOVA) for each parameter, a Principal Component Analysis (PCA) was conducted based on the matrices of correlation utilizing 84 samples (42 groundwater, 39 soil solutions and three brines).

**Results and Discussion**

**Characterization of Chemical Facies of the Groundwater Solutions**

A Piper diagram of the groundwater solutions (Figure 2) shows only one scatter plot suggesting only one geochemical family, however, the chemical facies varies significantly. The facies of the least concentrated water when compared to the most concentrated samples was of the following order: Ca-sulfate > Na-sulfate = Mg-sulfate > Na-chloride. This sequential order of solutes is comparable to other groundwater samples described for North Africa, and especially in the neighboring area of Chott Merouan and Melrhir (Rezagui, 1993; Valles et al., 1997). In the

![FIGURE 2 Piper diagram of ground water and soil solutions.](image-url)
present study the difference between the least and the most concentrated samples is that the least concentrated water is already relatively charged with dissolved solutes that are dominated by Ca-sulfate but may also have significant amounts of Ca-carbonate and Ca-sulfate. The presence of the latter solutes is characteristic of the neutral pathway salinization (Rieu & Cheverry, 1976).

**Geochemical Processes Responsible for the Development of Chemical Facies and Mineralogy**

**Statistical Approach**

The 84 samples showed a strong variability in concentrations and salinity. Thus, the standard deviation of Cl⁻ and Na⁺ reached 1.15 and 1.08, respectively, for average values of 0.723 and 0.681 units. This strong variability, however, was negated by a rising ratio between the concentrated and the diluted samples, ranging from 673 for Cl⁻ to 742 for Na⁺.

The total increase in the concentration of soluble elements (i.e., noncontrolled) due to aridity effects constitutes the main process responsible for the observed chemical changes. The PCA showed that this concentration process was responsible for 56% of the variance. The second source of chemical variability was the anoxic/aerobic status of waters, however, accounting for 18% of the variance.

**Concentration Diagrams**

The sum of sulfate molality and alkalinity equivalents was higher than that of Ca²⁺ (Figure 3). Residual calcite alkalinity plus gypsum was positive. When water concentrates and precipitates gypsum, the sulfate molality parallels the increase in alkalinity, whereas the Ca²⁺ molality remains stable (Ca²⁺ activity decreases). Due to precipitation reactions, the SO₄²⁻ molality increased less quickly than that of

![Concentration Diagrams](image)

**FIGURE 3** Concentration diagrams calculated using chloride as traces.
Cl\(^-\) and Na\(^+\), especially for very concentrated water, suggesting that sulfated minerals other than gypsum precipitate. Lastly, the most concentrated water samples were dominated by Na-chloride and probably lead to halite precipitation.

It is appropriate to note that the Na\(^+\) and K\(^+\) molalities do not seem to be controlled by soil adsorbing processes (as it is the case in other North African systems) implying the exchange of these cations with the soil exchange complex. These results agree with data obtained from Chott El-Jerid (Gueddari, 1984), Chott Melghir and Merouane (Rezagui, 1993; Valles et al., 1997) (Figure 1), suggesting the evaporation of water from the water table in the playa, with a weak influence by the soil clays and associative cation exchange phenomena.

**Equilibrium Diagrams**

**Calcite, Gypsum, Anhydrite, Halite and Sylvite (Table I)**

Results show that the most of solutions were saturated with calcite (Figure 4) and saturated or close to the saturation point with gypsum (Figure 5). However, the most concentrated points were oversaturated with gypsum. These results may be attributed to the precipitation of the Ca-sulfate minerals less hydrated than gypsum as in the case of the brines. Thermodynamic equilibrium with anhydrite (Figure 6) was also reached with the water samples. The most concentrated points were close to saturation values of halite and sylvite (Figures 7 and 8).

**Mirabilite/Thenardite, Bloedite, Glauberite and Celestite (Table I)**

Thermodynamic equilibrium between the water samples and mirabilite was only attained for the brines (Figure 9). Once saturation was achieved, the solutions progressed to the branch of Na domination, paralleling the water/mirabilite
equilibrium diagram (Figure 9) and suggesting the precipitation of halite. Equilibria with bloedite (Figure 10) and glauberite (Figure 11) were also attained for the brine samples, however, for the bloedite samples, equilibrium was less obvious than that of glauberite. This difficulty in recognizing equilibrium conditions relates to only some of the samples and appears less frequently for glauberite and especially bloedite. These results are significant because they confirm the presence of Na-sulfates (mirabilite evolving into thenardite under natural conditions) for these north Saharan zones. The presence of this mineral was previously recognized by Gueddari (1984) during experimental evaporation experiments carried out in tank reactors, but until recently, only found in abundance under natural environmental conditions.

**TABLE 1** Chemical formulae of mineral names used in text

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Name</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>Hexahydrate</td>
<td>Mg(SO₄)·6H₂O</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>(Mg, Al)₈(Si, Al)₂₀·₈H₂O</td>
<td>Epsomite</td>
<td>Mg(SO₄)·7H₂O</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>Bloedite</td>
<td>Na₂Mg(SO₄)₂·4H₂O</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>Loeweite</td>
<td>Na₂Mg(SO₄)₂·2.5H₂O</td>
</tr>
<tr>
<td>Basanite</td>
<td>CaSO₄·0.5H₂O</td>
<td>Glauberite</td>
<td>Na₂Ca(SO₄)₂</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td>Eugsterite</td>
<td>Na₄Ca(SO₄)₃·2H₂O</td>
</tr>
<tr>
<td>Celestite</td>
<td>SrSO₄</td>
<td>Syngenite</td>
<td>K₂Ca(SO₄)₂·H₂O</td>
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<tr>
<td>Mirabilite</td>
<td>Na₂SO₄·2H₂O</td>
<td>Halite</td>
<td>NaCl</td>
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<td>Thenardite</td>
<td>Na₂SO₄</td>
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**FIGURE 4** Equilibrium diagram of solutions with respect to calcite (dashed line represent theoretical equilibrium).
**FIGURE 5** Equilibrium diagram of solutions with respect to gypsum (dashed line represent theoretical equilibrium).

**FIGURE 6** Equilibrium diagram of solutions with respect to anhydrite (dashed line represent theoretical equilibrium).
FIGURE 7 Equilibrium diagram of solutions with respect to halite (dashed line represent theoretical equilibrium).

FIGURE 8 Equilibrium diagram of solutions with respect to sylvite (dashed line represent theoretical equilibrium).
FIGURE 9 Equilibrium diagram of solutions with respect to mirabilite (dashed line represent theoretical equilibrium).

FIGURE 10 Equilibrium diagram of solutions with respect to bloedite (dashed line represent theoretical equilibrium).
(Rezagui, 1993). However, the possible formation of mixed sulfates, such as glau-berite and bloedite, represents additional knowledge on the salt weathering model obtained from hyperarid environments (Goudie et al., 2002). As a result, the presence of these mixed sulfates was assessed by X-ray diffraction and SEM methodology, and the results are presented below. The waters samples were slightly undersaturated with syngenite or with epsomite. The formation of these magnesium sulfate minerals seems more difficult and should appear only occasionally.

Lastly, if part of the solutions are undersaturated with celestite, the thermodynamic equilibrium condition may be reached in several groundwater and soil solution samples (Figure 12). These new conditions in mineral/solution equilibria in soils derived from the Saharan desert zones should be confirmed by measurements with the SEM and X-ray diffraction methods.

**Mineralogical Study: X-ray Diffraction and SEM**

The results of X-ray diffraction analyses are given in Table 2. The signature of sulfate semihydrates (basanite) was frequently observed (Figure 13). Similarly, mixed sulfates such as glauberite and bloedite (Figure 14), were detected, as well as the eugsterite (Vergouwen, 1981) but the latter mineral was frequently absent. Hexahydrate was also identified (Table 2) but rarely present as compared to the previous minerals. Lastly, the diffractograms obtained from the fine fractions (<2 μm) showed existence of palygorskite, a fibrous clay characteristic of confined conditions.

However, it should be recognized that no specific minerals, including trace elements, were found by X-ray diffraction, but this technique does allow the detection of abundant compounds in an analyzed sample. Visual observations and
the microchemical probe analyses did not suffer from the same limitations as that of X-ray diffraction. Using the former technique, the presence of well-crystallized celestite was identified. It generally occurred on the periphery of gypsum crystals (Figure 15.1) or as an inclusion within the crystal (Figure 15.2). Glauberite (Figure 15.3), hexahydrate (Figure 15.4), thenardite (Figure 15.5) and the fibrous clays were observed, analyzed, and observed to be associated with the more frequent minerals calcite, gypsum and halite (Figure 15.6). Dissolution features of lenticular gypsum crystals could be also observed when this mineral was in contact with halite (Figure 15.7). The observation of soil samples using the optical microscope showed that the basanite, easily recognizable by its weak typical birefringence due to its dehydration, is mainly located on the periphery of the gypsum crystals (Figure 15.8). When a laboratory test for the dehydration process was performed on selected lenticular gypsum crystals at 40 and 80°C during a 24 h incubation period, a partial dehydration occurred affecting the periphery of gypsum crystals (Hamdi-Aïssa, 2001b).

**Discussion**

The results from this study show a unique mineralogical specificity of the hyperaridic zones compared those usually studied arid regions. The existence of various mineral forms characterized by hydration is a concept that is already known to occur in high salt environments. This is particularly true for the carbonated systems. However, very few field studies for sulfated/carbonated facies have been reported.
<table>
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<tr>
<th>Sample</th>
<th>Calcite</th>
<th>Gypsum</th>
<th>Basanite</th>
<th>Thenardite</th>
<th>Bloedite</th>
<th>Hexa-hydrite</th>
<th>Eugsterite</th>
<th>Glauberite</th>
<th>Halite</th>
<th>Quartz</th>
<th>Paly-gorskite</th>
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* + + + Dominant, + + Abundant, + Mean, + Minor.
* surface salt crusts and efflorescences.
** surface gypsic crusts.
FIGURE 13 X-ray diffractogram of surface polygonal gypsum crust. Crust is dominated by gypsum and basanite.
FIGURE 14 X-ray diffractogram of a surface salt efflorescence, showing salt minerals in association, include halite, gypsum, quartz and mixed minerals: bloedite and glauberite.
Dehydrated Forms of Calcium Sulfates

The transition temperature for the thermodynamic equilibrium between gypsum and anhydrite is close to 35°C in a diluted water solution (Innorta et al., 1980; Zen, 1965). The anhydrite layers are often explained by a diagenetic evolution (a rise in temperature within buried deposits) (Jauzein, 1974; MacDonald, 1953). However, this critical temperature of gypsum/anhydrite transition may drop in the case of brines, due to the low activity of water, which supports the formation of less hydrated minerals (Marshall & Slusher, 1966).

In the hyperarid soils there are two genesis pathways for the dehydrated forms of Ca-sulfate:

1. The first pathway is related to the partial evaporation of water molecules from gypsum. On desert soil surface, the temperature may reach 70 to 80°C (Cooke et al., 1993; Dubief, 1963; Goudie, 1997). During the day, part of the gypsum mineral may be dehydrated and converted into basanite and anhydrite when the temperatures exceed 45°C. This conversion is stimulated by the chlorinated salinity of the soil environment (Ostroff, 1964). During the night, the fall in temperature (modifying relative humidity) results in the partial dissolution of the two dehydrated minerals on the soil surfaces (i.e., basanite and anhydrite). Basanite and anhydrite are unstable minerals and are more soluble than the gypsum (Jauzein, 1974; Innorta et al., 1980; Zen, 1965), resulting in the rapid dissolution of dehydrated minerals followed by gypsum recrystallization during the colder period at night. The coalescent, microcrystalline crystals of gypsum observed on the surface soil millimeters in the polygonal gypsum crust, may be the best explanation for rapid recrystallization of gypsum (Chen, 1997; Hamdi-Aïssa, 2001a,b; Watson, 1988; Yair & Verrecchia, 2002).

2. A second pathway may be related to water activity. In the gypsum dissociation equation:

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O},
\]

where the ionic product \( \log Q = \log(\text{Ca}^{2+}) + \log(\text{SO}_4^{2-}) + 2\log(\text{H}_2\text{O}) \), and where ( ) indicate ionic activities.

For the above calculation, the water activity must also be taken into account. In diluted solutions, the \( \text{H}_2\text{O} \) phase is practically pure, and its activity is very close to 1. As solutions concentrate, the water activity decreases (Al-Droubi et al., 1976).

**FIGURE 15** 1. BESI micrograph of gypsum crystal exhibit peripheral acicular crystals of celestite (bar scale represent 200μm). 2. BESI micrograph of celestite in inclusions inside the gypsum crystal (bar scale represent 100μm). 3. BESI micrograph of halite crystals enclosing the tip of fibrous glauberite (bar scale represent 200μm). 4. SEM photo of mottled hydrated MgSO₄, presumably hexahydrate (bar scale represent 50μm). 5. SEM photo of needle shaped thenardite crystals (bar scale represent 50μm). 6. SEM photo of idiomorphic cube of halite (bar scale represent 50μm). 7. BESI micrograph of some lenticular gypsum crystals in direct contact with the halite (in white) exhibit inside dissolution features due probably to increasing solubility of gypsum under super concentration of NaCl (bar scale represent 200μm). 8. Photomicrograph (PPL) showing a porphyroblastic lenticular gypsum within a spongy groundmass, presumably gypsum-dehydrated microfabric. Anisotropic areas formed in the edges and within the lenticular crystal are zones of recent dehydration (bar scale represent 362μm).
As a result, the following reaction is favored to the right:

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 + 2\text{H}_2\text{O} \quad \text{or} \quad \text{CaSO}_4, 0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O}, \text{i.e.,}
\]

gypsum \rightleftharpoons \text{anhydrite or basanite + water.}

Indeed, in the saturation diagram for anhydrite (Figure 6), only the most concentrated solutions where ionic strengths are higher than 3 mol kg\(^{-1}\) of H\(_2\)O, and those with water activities lower than 0.9, are thermodynamically close to the equilibrium with anhydrite. The X-ray diffraction analysis (Table 2) clearly shows the presence of basanite which is an intermediate form between gypsum and anhydrite, even in the deeper waterlogged horizons.

**Mixed Sulfates**

The presence of mixed sulfates, such as glauberite, which may be frequent, appear to have a distinctive feature in these hyperarid soils (Mees, 1998) as compared to the neighboring arid regions. Studies by Braitsch (1971), Doner & Lynn (1977), Driessen & Schoorl (1973), Harvie & Weare (1980) and Vergouwen (1981) have shown that when temperature increases, the mixed sulfates are more stable than the simple sulfate association. Below 10°C, the formation of mixed sulfates is difficult, it becomes possible at 20°C and it is easily achieved above 47°C. Thus, the extremely high temperatures that were recorded on the surface of these soils are most likely to be responsible for the frequent presence of mixed sulfates.

**Coprecipitation of Strontium with Gypsum**

Another sulfate mineral that has a low solubility is celestite (SrSO\(_4\)). The concentration of Sr\(^{2+}\) in the sampled solutions was low, limited by the solubility of SrSO\(_4\) and the number of Sr\(^{2+}\) ions coprecipitating with gypsum, which is comparable with the amount of Sr\(^{2+}\) in association with the brine. When gypsum crystallizes, the concentration of Sr\(^{2+}\) in the brine decreases substantially. The distribution of Sr\(^{2+}\) between gypsum and aqueous solutions was studied experimentally by Yamamoto and Uneki (1978). They reported that the distribution coefficient value decreases with an initial decreasing CaCl\(_2\) concentration and an increasing initial Na\(_2\)SO\(_4\) concentration. Butler (1973) and Kushnir (1980) showed that the kinetic effect in the coprecipitation of Sr\(^{2+}\) with gypsum occurred with a negative correlation between the size of the crystal and coprecipitated ion concentration. In this present study, the samples of Ouargla soils showed gypsum crystals exhibiting celestite inclusions which were generally <500\(\mu\)m in size. As shown in Figures 15.1 and 15.2, celestite crystals occur in the periphery or as pockets inside the lenticular gypsum crystals, and are generally a discrete component. Although its coprecipitation with gypsum in soils has been reported by many authors (Butler, 1973; Barzanji & Stoops, 1974; Kushnir, 1980; Watson, 1985), its genesis and properties have not been evaluated. Butler (1973) has previously demonstrated the complexity of Sr\(^{2+}\) diagenesis in sedimentary gypsum and anhydrite in several highly evaporative environments.

**Temporality of the Mineralogical Evolution**

The strong seasonal and daily thermal amplitudes of the desert environment determine the precipitation patterns into the mirabilite/thendarite or into the mirabilite/halite paragenesis. According to Hamdi-Aissa et al. (1997) the powdery efflorescences are characterized by Na-sulfate salinity during the winter and Na-chloride during the summer. In winter, low nocturnal temperature (close to 0°C) causes water
to reach thermodynamic equilibrium with respect to mirabilite and several other sulfated minerals (bloedite, eugsterite, glauberite, epsomite, and others). The idiomorphic crystals of mirabilite will then concentrate on mineral surfaces. During the day, the solar radiation raises the temperature rapidly and the translucent, well-crystallized mirabilite transforms into white powdery thenardite (Driessen & Schoorl, 1973; Shahid & Jenkins, 1994). This transformation is the fastest pedogenic process observed in this area (Hamdi-Aissa et al., 1997, 1998). In pure water, the transition temperature between the two phases of mirabilite and thenardite, in the Na₂SO₄·H₂O system, is fixed within the range of 32–38°C (Braitsch, 1971; Cooke, 1981; Timpson et al., 1986). In saturated solutions of NaCl this point of transition is lowered to 17.9°C (Mees & Stoops, 1991; Obika et al., 1989).

The temperature influence on the mineralogical transformation of gypsum may affect its mobilization. In the surface, the salt crust of playa, the process of dissolution/precipitation of gypsum is a continuous cycle. Halite dissolution accelerates the solubility of gypsum (Arslan & Dutt, 1993; Marshall & Slusher, 1966) while the dissolution of mirabilite inhibits gypsum solubility by the common ion effect (Doner & Lynn, 1977; Tanji, 1969). Such transformations appear on a seasonal scale (Hamdi-Aissa et al., 1997). Indeed, the strongly corroded porphyritic gypsum crystals are frequently identified in the salt crust (Figure 15.7), and may be allotted to the dissolution of gypsum in a saturated NaCl solution (Hamdi-Aissa, 2001a,b).

Moreover, according to Pouget (1968) and Watson (1985) the gypsum microrosettes observed in salt crust, result from gypsum crystallization associated with a strong fluctuation in NaCl concentration.

**Conclusion**

The precipitation sequence of calcite → gypsum → mirabilite → halite, usually found in the Mediterranean and sub-Saharan arid areas, must be supplemented by semihydrates of Ca-sulfate, such as basanite, hexahydrite, and mixed sulfates (glauberite, bloedite, eugsterite) for the soils of hyperarid desert. The presence of these minerals as observed by X-ray diffraction and SEM, parallels the geochemical calculations on the solution chemistry if consideration is given to the high levels salinity, which cause difficulties in predicting thermodynamic ionic activities. The analyses of the data suggest that the dehydration status of Ca-sulfate is influenced by high surface temperature and salinity as related to the extreme aridity, and that the transformations between hydrated and partially dehydrated species are interchangeable.

In spite of the low availability of water, this hyperarid environment has a remarkable chemical and mineralogical reactivity. This is due to the high solubility of minerals and to the flux in hydration status of a number of minerals. The first reaction step allows for the mobilization of significant chemical species that are associated with a weak variation of the water content. The second reaction step supports the frequent dissolution and precipitation of gypsum and is related to the change in hydration state. However, the dehydrated form of Ca-sulfate on the soil surface may be proposed as a pedological criterion for differentiation of hyperarid and arid ecosystems.

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