

Treatment of Tunisian salt lakes using solubility phase diagrams*

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Abstract: The Tunisian salt lakes are considered as an important materials resource useful for industry and agriculture. They are called *sebkhat* or *chott*, and they cover a large part of Tunisian land. Their brines correspond to the quinary system: Na^+ , K^+ , Mg^{2+} / Cl^- , SO_4^{2-} - H_2O . In the first part of this paper, a short description and abstracted geochemical and economical data about some Tunisian salt lakes are given. In the second part, the fitting equations used for modeling the quinary system are established and applied to the subsystems $\text{NaCl-KCl-H}_2\text{O}$, $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$, $\text{KCl-MgCl}_2\text{-H}_2\text{O}$, and to $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{KCl-K}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$. The coherence between the calculated and the experimental diagrams is discussed.

INTRODUCTION

An important area of Tunisia is covered by salt lakes called *sebkhat* or *chott*. They are located all over the country. Meanwhile, they are more concentrated in the south (Fig. 1).

The most famous Tunisian salt lakes are: Chott el Jerid, in the south, appearing as the biggest one, Sebkhath el Melah of Zarsis and Sebkhath el Adhibate in the south east, and Sebkhath Om el Khialate in the Saharan part of the country.

The Tunisian sebkhats 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 20 times more important than in sea water and varies between 250 and 330 g/l. They can be a significant resource of useful salts.

The major elements contained in a sebkhat or a chott 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.

GEOCHEMICAL CHARACTERISTICS OF SOME TUNISIAN SALT LAKES [1]

Chott el Jerid covers 5000 km². Recent geological studies proved that this chott is not the vestige of a previous Saharan sea as presented by some geologists of the beginning of the 20th century. Recent studies have shown that its solid salts and brine come from the geological formations of the surrounding mountains. It contains a total stock of brine estimated to be 5 billion m³. Its salinity average is 330 g/l (Table 1), but its composition is heterogeneous. It is more sulfated on the east side and more concen-

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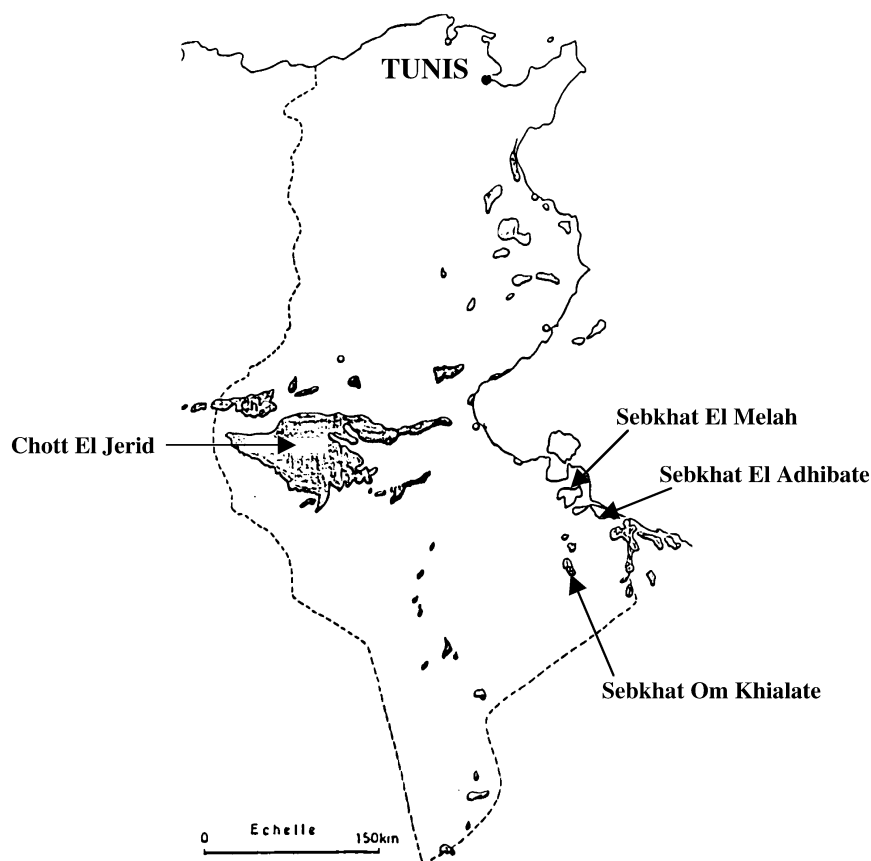


Fig. 1 Location of some salt lakes on the map of Tunisia.

trated in potassium on the west side. Chott el Jerid seems to be interesting because of its potassium sulfate content.

Sebkhat el Melah of Zarzis has the aspect of a large plain (150 km²) covered with salt and separated from the sea by a small offshore bar. 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 of 6 to 8 m deep. The brine of this sebkhat is homogeneous. It contains more magnesium, potassium, and chloride than brine from the other sebkhats (Table 1).

Sebkhat el Adhibate is located at the south east of the country; it covers 125 km². It is separated from the sea by a big depression and it is at the level -1 m. This sebkhat isn't as saturated as the others. Its major element is sodium (Table 1).

Sebkhat om Khialate is in the south east of Tunisia, in the desert region. Its area is 75 km². It is covered by a thin crust a few decimeters thick containing a mixture of halite, gypsum, and thenardite (Na₂SO₄) (Table 1). In the higher levels of the sebkhat the thenardite precipitates alone.

Table 1 shows that the salt lakes cited can be an important resource for interesting salts and that the concentration of the major ions varies from one brine to another.

Table 1 Average composition, g/l of Tunisian sebkhat and chott brines.

Ions	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻
Chott el Jerid	100	9.0	0.7	12	197	12
Sebkhat el Melah	45	7.7	0.2	50	200	28
Sebkhat el Adhibate	88	3.6	1.0	12.6	150	37
Sebkhat om Khialate	43	0.8	0.4	3.3	24	74

BIBLIOGRAPHICAL DATA

Since the beginning of the 19th century the sebkhats have caught the attention of scientists and economists. The geological and economical studies began early in the 20th century. The main questions were:

- How were these brines formed?
- Do they communicate with the sea?
- What is their composition?
- Do they contain important salts?
- How could these be extracted?

The first work was done on the Sebkhat el Melah of Zarzis [2–6,8,9,14–18]. Then, several Tunisian researchers began to work on Tunisian brines other than that of Sebkhat el Melah. Their studies did not only concern geological aspects but were extended to the study of phase diagrams related to the system representing the brines [18–24].

Many present studies involve modeling of phase diagrams [1,26,27,30,33,34] and extraction of interesting salts [28,29,31,32].

The preceding data show that the Tunisian salt lakes brines still interest many scientists. This can be explained by the economical value of the salts contained in these brines, for example: potassium sulfate and chloride for agriculture, sodium sulfate for glass and detergents industries, magnesium chloride for fireproof materials and pharmaceutical products, sodium chloride for food and for other industries.

Therefore, the chotts and sebkhats containing big deposits of salts are expected to play an important role in the economic sector of Tunisia.

However, the extraction of salts remains difficult, because of the lack of reliable models of the brines and of literature describing the methods which should be adapted in each case.

COMPILATIONS RELEVANT TO THE QUINARY SYSTEM REPRESENTING THE BRINES

The best way to find how to extract particular salts is to define their precipitation fields in the phase diagram representing the system containing the major elements of the brines: Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, CO₃²⁻, H₂O. This system contains seven elements plus water. It is so complicated that it has to be simplified. As the element calcium is in the presence of sulfate and carbonate, its concentration in the solution is low, so it can be considered as a minor element. As the solvent is water, in well-defined conditions, at each temperature, the system can be considered as a reciprocal quinary one with sodium, potassium, magnesium, chloride, and sulfate in water.

Representing this system is so complicated that many authors considered only the subsystem where the solutions are saturated with respect to sodium chloride. But if the industrial process has to eliminate sodium chloride from the final product the equilibria between all phases of the whole system must be known.

Compilations related to quinary systems date from the beginning of the 20th century: Van't Hoff and Meyerhoffer [10], d'Ans [7], Landolt–Börnstein [11], Stephen and Stephen [12] and Linke [13].

But these compilations are not easy to use, the representation of a quinary system diagram is very specific, and the data are widely scattered and are given in different units. At present, many organizations are looking for a solution. IUPAC, for example, especially Commission V.8, is preparing volumes containing evaluated data on the sea water systems [25]. The COPERNICUS project will lead to publishing of evaluated data on the Black Sea system. A book dealing with the extraction of salts from Tunisian brines will also soon be published.

MODELING OF PHASE DIAGRAMS APPLIED TO THE QUINARY SYSTEM

A rational exploitation of the system Na⁺, K⁺, Mg²⁺, Cl⁻, SO₄²⁻, H₂O, for industrial or fundamental application, requires reliable solubility data and the determination of the sequence of crystallization during evaporation or cooling of a brine, the calculation of yield, recycling rate, etc. It is based on convenient fitting equation allowing the calculation of solubility in a large range of temperature and composition.

The water–salt binary systems involving stoichiometric solid phases can be fully described with a semiempirical model derived from the thermodynamic conditions of equilibrium. The model complies with all thermodynamic constraints of the system and requires a small number of adjustable coefficients.

The same procedure can be used for the calculation of a complex system.

The solubility of a salt in saturated solution is described in terms of heterogeneous reaction between solid and liquid. An equation of the solubility field is established for each solid and each limiting or intermediate phase of a multicomponent aqueous salt system.

The model supposes that solid phases are stoichiometric and that the solution is a strong electrolyte. It includes all subsystems.

The equation of solubility surface of stoichiometric solid phases can be written as follows:

$$U - U^0 = A(\sigma) / T + B(\sigma)\ln T + C(\sigma) + D(\sigma)T + \dots$$

U represents the logarithm of solubility product of the species in equilibrium with liquid and U^0 is the same quantity considered at stoichiometry:

$$U = \sum_i v_i \ln x_i \quad U^0 = \sum_i v_i \ln x_i^0 \quad \text{with} \quad x_i^0 = v_i / \sum_j v_j$$

It is reduced to $\ln(x_i/x_i^0)$ if the solubility surface concerns a molecular compound (water).

When the order of a system is more than 2 the coefficients A, B, C,... are no longer independent of composition and several empirical expressions have been tried out and compared. Actually, two polynomial series that fill almost all criteria of selection are proposed.

The first equation has been tested on simple systems such as NaCl–KCl–H₂O, NaCl–MgCl₂–H₂O, and KCl–MgCl₂–H₂O. The coefficients along the solubility domain of a compound are:

$$A = \sum \left[\frac{v_i}{1-x_i} \sum_j a_{ij} x_j + \left(\frac{v_i}{1-x_i} \right)^2 \sum_j \sum_k a_{ijk} x_j x_k + \dots \right]$$

v_i , x_i are respectively the stoichiometric coefficient and the mole fraction of constituent i (salt or water) in the compound under consideration, a_{ij} , a_{ijk} ,... are adjustable coefficients; j , k , ... are assumed to be different from i .

Figure 2 representing the calculated diagram of the system NaCl–KCl–H₂O in the temperature range –30 to 140 °C, shows that the calculated mono-variant line separating the fields of KCl and NaCl is in very good agreement with the experimental data.

For the system NaCl–MgCl₂–H₂O (Fig. 3), only the curve separating the domains of NaCl and MgCl₂.6H₂O has been calculated in the range of temperature 0 to 115 °C. It represents an average between the scattered experimental points.

The experimental data and the calculated curves (Fig. 4) of the system KCl–MgCl₂–H₂O show a good agreement between the experimental data and the calculated curve separating the fields of KCl and KCl MgCl₂.6H₂O from 0 to 125 °C.

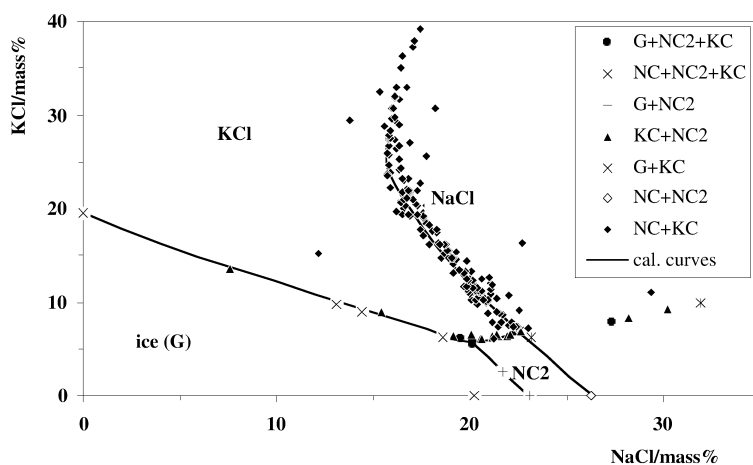


Fig. 2* System NaCl–KCl–H₂O.

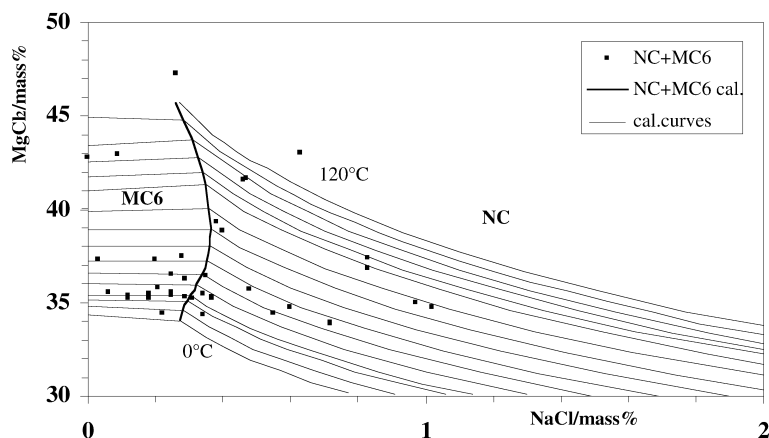


Fig. 3* System NaCl–MgCl₂–H₂O.

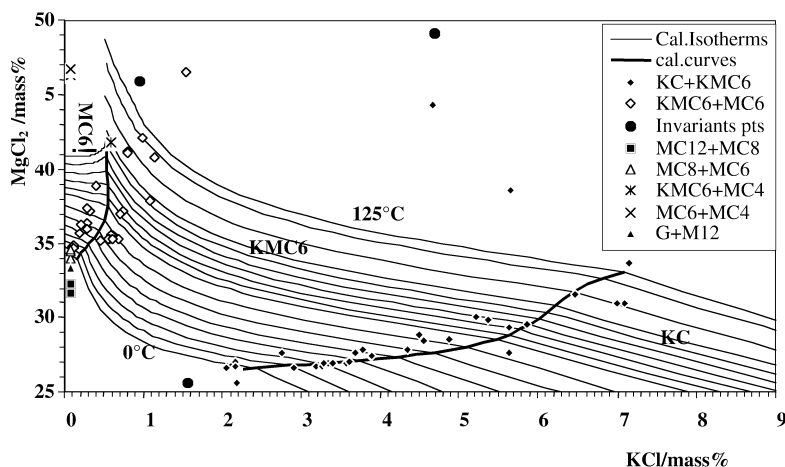


Fig. 4* System KCl–MgCl₂–H₂O (mass %).

The application of the first equation to reciprocal systems and to the solubility range of ternary or more complex salts is not easy. However, the second equation is more convenient. The ions are separated in cations N (Na⁺), K (K⁺), M (Mg²⁺), and anions C (Cl⁻), S (SO₄²⁻). The general equation of the solubility field of a compound in the quinary system is written as follows

$$A(\sigma) = \sum_i \sum_j X_i Y_j \left(a^{ij}(\sigma) + \sum_n \sum_k U_k^n \left(a_n^{ijk}(\sigma) + \sum_p \sum_l V_l^p \left(a_{np}^{ijkl}(\sigma) + \sum_q W_m^q a_{npq}^{ijklm}(\sigma) \right) \right) \right)$$

where $A(\sigma)$ is an adjustable coefficient of the solid-phase solubility field

The former relation includes the solubility fields of all subsystems. $a^{ij}(\sigma)$ is the coefficient of species σ in the binary system (i, j) -H₂O. $a^{ij}(\sigma) = 0$ when i and j are not constituents of σ , except for the solubility field of ice where $a^{ij}(\text{H}) \neq 0$ for all binary subsystems. $a_n^{ijk}(\sigma)$ is the coefficient of U_k^n in the ternary system (i, j, k) -H₂O, etc. The obtained analytical expression has been tested on several systems. The model gives a good description of the solubility surfaces of most of the solid phases in the two kinds of systems simple and reciprocal.

Three examples of calculated ternary systems belonging to the reciprocal quaternary diagram Na⁺, K⁺ / Cl⁻, SO₄²⁻-H₂O are presented in this paper:

The first one, NaCl–Na₂SO₄–H₂O (Fig. 5), treated between 10 and 150 °C contains only three domains easy to exploit and presents three mono-variant lines. In this diagram, the experimental data and the calculated curves are in good agreement.

The second system is KCl–K₂SO₄–H₂O (Fig. 6). It is calculated in the temperature range 0 to 100 °C. It has only one mono-variant line separating the domains of KCl and K₂SO₄. The calculated curve is coherent with the experimental data.

The last one is Na₂SO₄–K₂SO₄–H₂O (Fig. 7). It has been studied between 0 and 150 °C. The salts K₂SO₄, Na₂SO₄·3K₂SO₄, and Na₂SO₄·10H₂O have well-defined domains, and their calculated intersecting curves are in agreement with those of the literature. But the mono-variant line separating the fields of Na₂SO₄ and Na₂SO₄·3K₂SO₄ is not well defined probably because of the retrograde solubility exhibited by Na₂SO₄.

Other diagrams belonging to the quinary system calculated by the first or the second equation are presented in the Table 2.

For some other systems, solubility fields could not be evaluated due to the small number and low quality of the data available.

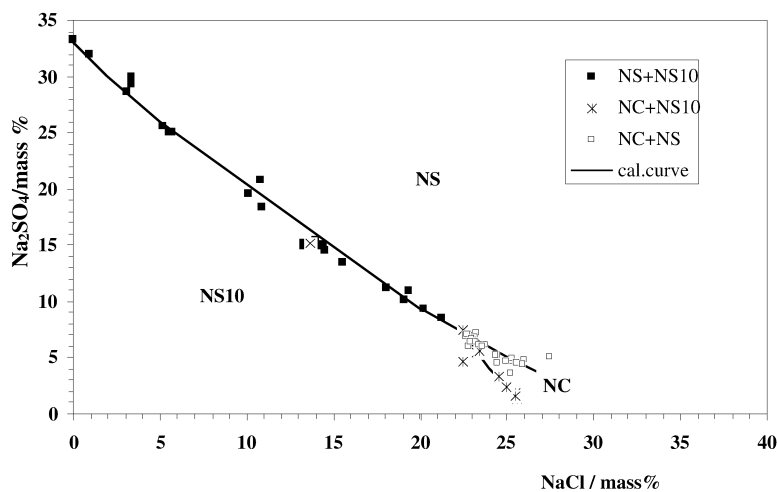


Fig. 5* System NaCl–Na₂SO₄–H₂O.

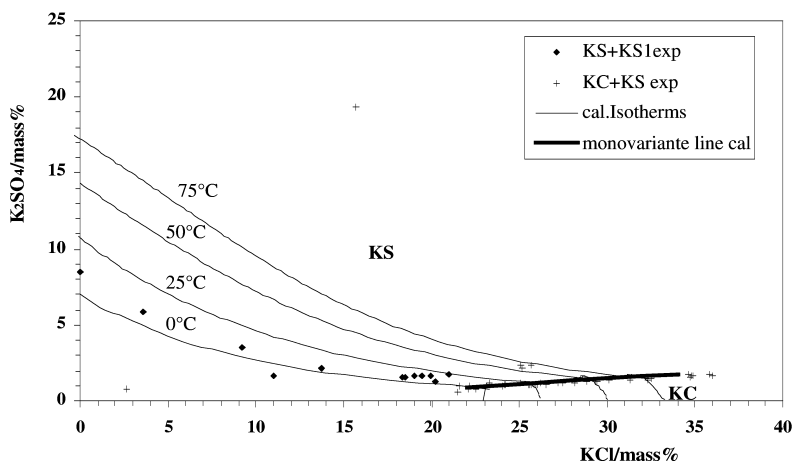


Fig. 6* System KCl–K₂SO₄–H₂O (mass %).

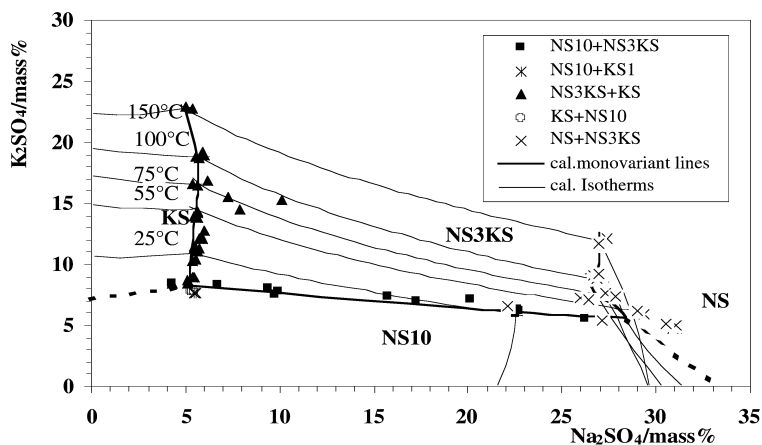


Fig. 7* Na₂SO₄–K₂SO₄–H₂O.

When the experimental solubility data are sufficiently well defined, the second analytical expression allows a critical evaluation of the data collected from various sources. It also confirms the nature of the solid phases determined by different methods.

The conclusion of this study is that a good knowledge of the solubility diagrams related to the quinary system Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , H_2O , could help in the treatment of the Tunisian salt lakes brines for extraction of useful salts. A lot of works have been carried out on the sebkhs and chotts, but there is still a lot to do for their valorization.

Table 2 Calculated solubility curves in the quinary diagram representing the brines.

Systems	Calculated curves	Calculated and experimental curves
$\text{NaCl-H}_2\text{O}$ [24]	H_2O ; NaCl ; $\text{NaCl}\cdot 2\text{H}_2\text{O}$	Coherent
$\text{KCl-H}_2\text{O}$ [24]	H_2O ; KCl	Coherent
$\text{MgCl}_2\text{-H}_2\text{O}$ [21]	H_2O ;	Coherent
	$\text{MgCl}_2\cdot 1_2\text{H}_2\text{O}$;	"
	$\text{MgCl}_2\cdot 8\text{H}_2\text{O}$;	"
	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$;	"
	$\text{MgCl}_2\cdot 4\text{H}_2\text{O}$;	"
$\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ [21]	$\text{MgCl}_2\cdot 2\text{H}_2\text{O}$	"
	H_2O ;	Coherent
	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$;	Coherent when
	$\text{Na}_2\text{SO}_4\cdot 7\text{H}_2\text{O}$;	$T < 100^\circ\text{C}$
$\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ [21]	Na_2SO_4 ;	"
	H_2O ; $\text{K}_2\text{SO}_4\cdot \text{H}_2\text{O}$;	Coherent when
	K_2SO_4	$T < 100^\circ\text{C}$
$\text{MgSO}_4\text{-H}_2\text{O}$ [21]	H_2O ;	Coherent
	$\text{Mg}_2\text{SO}_4\cdot 7\text{H}_2\text{O}$;	Coherent when
	$\text{MgSO}_4\cdot 6\text{H}_2\text{O}$;	$T < 100^\circ\text{C}$
	$\text{MgSO}_4\cdot 4\text{H}_2\text{O}$;	"
	$\text{MgSO}_4\cdot \text{H}_2\text{O}$	"
$\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ [33]	Na_2SO_4 ;	Partial coherent
	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$;	"
	$\text{MgSO}_4\cdot 7\text{H}_2\text{O}$;	"
	$\text{Na}_2\text{SO}_4\cdot \text{MgSO}_4\cdot 4\text{H}_2\text{O}$	"
$\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ [25]	NaCl ; KCl	Coherent

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***Symbols used in Figs. 2 to 7:**

G = H₂O; NC = NaCl; KC = KCl; MC = MgCl₂; NS = Na₂SO₄; KS = K₂SO₄; MS = MgSO₄; NC2= NaCl.2H₂O;
MC6 = MgCl₂.6H₂O; KMC6 = KCIMgCl₂.6H₂O; NS10 = Na₂SO₄.10H₂O; KS1= K₂SO₄.H₂O; NS3KS = Na₂SO₄.3K₂SO₄