# The Messinian salt of the Mediterranean : geochemical study of the salt from the Central Sicily Basin and comparison with the Lorca Basin (Spain)

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*Key words.* – Messinian, Evaporite, Salt, Halite, Bromine, Fluid inclusions, Sicily, Lorca, Spain.

*Abstract.* – A geochemical study has been performed on Messinian halite deposits from the Central Sicily Basin and the results compared with those published for the Lorca Basin (Spain), in order to provide a depositional model for these marine salt formations and to improve our understanding of the Messinian evaporitic event.

Halite samples from boreholes and mine galleries from the Salt Member of the Gessoso Solfifera Formation of the Caltanissetta Basin (Sicily) were studied petrographically and geochemically.

The bromine content of halite increases from the base of the Salt Member to the horizons containing kainite (layer B) up to 150 ppm. Upwards, the bromine content decreases and at the top of the member it drops down below 13 ppm, thus reflecting a marked dilution of the mother brine, which resulted in the precipitation of almost bromine-free salt. This dilution has been attributed to the inflow of continental waters in the literature. Fluid inclusion compositions at the top of the unit demonstrate the $SO_4$-rich character of the brine, which is only slightly depleted in $SO_4$ with respect to normal evaporated seawater and shows a significant Mg and K content, indicating the marine origin of the brine which controlled the final precipitation. This is in agreement with the petrographically well-established primary origin of kainite.

In the case of the Saline Unit from the Lorca Basin (SE Spain), bromine profiles are essentially similar to those described above, whereas fluid inclusion compositions at the top of the unit reveal the Mg, K and $SO_4$-poor character of the brine and reflect an inflow of continental waters into the basin which were responsible for final dilution and bromine-free salt precipitation.

Thus, in the Lorca basin, which occupied a marginal position in the Mediterranean Basin, dilution and salt reprecipitation at the top of the salt unit occurred when the basin was cut off from the sea and became completely isolated and desiccated. In the Caltanissetta basin, which occupied a relatively more central position, similar saline sediments were formed at the top of the Salt Member as a result of fresh marine waters inputs. Accordingly, in the Sicilian basin, the existing unconformity at the top of the Lower Evaporite Unit does not imply subaerial exposure or complete desiccation of the marine basin. Local tectonism probably controlled the different hydrochemical evolutions of these basins.

## Le sel messinien de la Méditerranée : étude géochimique de la formation saline du bassin central sicilien et comparaison avec le bassin de Lorca (Espagne)

*Mots-clés.* – Messinien, Evaporite, Sel, Halite, Brome, Inclusions fluides, Sicile, Lorca, Espagne.

*Résumé.* – Une étude géochimique a été réalisée sur les dépôts halitiques messiniens du bassin central sicilien et les résultats comparés avec ceux publiés sur le bassin de Lorca (Espagne), dans le but de proposer un modèle de dépôt pour ces formations salifères marines et d'améliorer notre connaissance de l'événement évaporitique messinien.

En Sicile, les échantillons de halite qui proviennent de sondages et de galeries de mines appartiennent au membre salifère de la formation Gessoso-Solfifera du bassin de Caltanissetta. Ils ont fait l'objet d'une étude pétrographique et géochimique.

Les teneurs en brome augmentent entre la base du membre salifère et le niveau contenant la kainite, pour atteindre 150 ppm. Plus haut, ces teneurs décroissent jusqu'à des valeurs inférieures à 13 ppm au toit du membre salifère, ce qui indique une dilution marquée des saumures-mères, dilution responsable de la précipitation d'un sel presque dépourvu de brome. Dans la littérature, cette dilution a été attribuée à un apport d'eaux continentales. Les compositions des inclusions fluides, au toit de cette unité, démontrent néanmoins l'origine toujours marine des saumures à partir desquelles ont précipité ces halites. Elles sont en effet riches en K et Mg et confirment que les saumures étaient riches en $SO_4$ qui n'apparaît que très faiblement appauvri par rapport à l'eau de mer normale évaporée. Ces données sont en accord avec l'origine primaire de la kainite qui a pu être établie à partir de l'étude pétrographique.

Dans le cas de l'Unité Saline du bassin de Lorca (SE de l'Espagne), les profils de brome sont identiques à ceux obtenus sur le sel de Sicile, mais les compositions des inclusions fluides au sommet de l'unité sont pauvres en K, Mg et $SO_4$ et reflètent nettement un apport d'eaux continentales responsables de la dilution finale et de la précipitation de sel dépourvu de brome.

Ainsi, dans le bassin de Lorca qui occupait une position marginale, la dilution et la reprécipitation du sel au sommet de l'Unité Saline sont intervenues après l'isolement complet du bassin marin et sa dessication. Au contraire, dans le bassin de Caltanissetta qui occupait une position plus centrale dans le bassin méditerranéen, les mêmes dépôts salins se sont formés au toit du membre salifère en relation avec de nouvelles entrées d'eaux marines dans le bassin. La tectonique locale a pu contrôler les évolutions hydrochimiques différentes dans ces deux bassins.

La discontinuité existant, dans le bassin central sicilien, au toit du membre salifère et à la base de l'Unité évaporitique supérieure n'implique pas nécessairement une dessication du bassin marin.

### VERSION FRANÇAISE ABRÉGÉE

La série du bassin de Caltanissetta (Sicile) fournit un équivalent des séries évaporitiques messiniennes épaisses connues dans les dépressions centrales méditerranéennes, où seule la partie superficielle de la formation saline a été atteinte par quelques sondages. Le bassin de Lorca (SE Espagne) comporte une série évaporitique réduite caractéristique d'un domaine plus marginal. A partir d'une étude géochimique des évaporites du bassin sicilien et d'une comparaison avec les données déjà acquises sur celui de Lorca, il est proposé un modèle de dépôt des séries salines et une connaissance plus approfondie de l'événement évaporitique messinien.

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*1) Les bassins néogènes de Sicile centrale et de Lorca.* La série "Gessoso-Solfifera" (Fig. 2, 3) du bassin sicilien central comporte deux unités évaporitiques qui recouvrent le Tripoli par l'intermédiaire du "Calcare di Base" à caractère évaporitique marqué. L'unité inférieure comprend les Gypses de Cattolica et la Formation saline (600m d'épaisseur), à intercalations de bancs de kainite, qui est équivalente de la formation salifère des dépressions méditerranéennes. L'unité supérieure (Gypses de Pasquasia, 300 m) est recouvert par les dépôts clastiques de l'Arenazzolo, puis par le Pliocène inférieur marin.

Dans le bassin de Lorca, l'unité saline qui succède aux dépôts préévaporitiques (marnes et diatomites), mesure 235 m d'épaisseur dans le sondage S4 et 49 m dans le sondage S5; elle est recouverte par les Gypses de La Serrata (60 m), encore marins, puis par des dépôts continentaux d'âge messinien à pliocène.

*2) Le sel messinien de Caltanissetta.* Les profils de brome (tab. I, fig. 4) permettent de différencier une unité inférieure, incluant les bancs de kainite, caractérisée par une augmentation régulière des valeurs de 13 ppm à l'extrême base à 150 ppm, et une unité supérieure avec des teneurs qui décroissent vers le haut jusqu'à des valeurs inférieures à 13 ppm (généralement inférieures à 70 ppm) caractéristiques d'un recyclage par des eaux marines normales ou faiblement concentrées. L'étude géochimique de la halite comme l'analyse isotopique ($^{34}$S) des sulfates associés indique l'origine marine des saumures-mères et l'évaporation d'un apport d'eau de mer faiblement modifiée. La microanalyse des inclusions fluides montre que le recyclage de sel qui est intervenu dans la partie supérieure est dû à des apports d'eau marine et non météorique, comme précédemment envisagé. Les modèles d'évolution chimique qui reproduisent le mieux les séquences sédimentaires et la composition des inclusions fluides sont : 1) pour l'unité inférieure, une évaporation d'eau marine sans précipitation de polyhalite, de faibles quantités de saumures à $CaCl_2$ remplaçant un volume équivalent d'apport d'eau de mer; l'inhibition de la cristallisation de polyhalite primaire joue alors un rôle dans la formation des dépôts économiques de kainite ; 2) pour l'unité supérieure, l'évaporation d'un apport d'eau de mer saturée en halite, par recyclage de sel déjà formé, et marqué également par un léger enrichissement en Ca.

*3) Comparaison avec le sel de Lorca.* Les profils de brome déjà publiés montrent aussi une phase de dissolution-précipitation au sommet de la formation halitique (tab. I et IV). Cependant, l'étude des inclusions fluides (tab. III et V) montre clairement, à ce niveau, que les saumures sont appauvries en Mg, K et SO4 par rapport à la composition de l'eau de mer normale en raison d'un apport d'eaux d'origine météorique, dans un bassin isolé du domaine marin, ce qui le différencie du bassin sicilien.

*4) Conclusions.* La différence dans l'évolution des deux bassins, notamment dans la partie supérieure des formations salines, illustre les différences de position dans le bassin méditerranéen. Le bassin sicilien, situé en position centrale, a conservé des apports d'origine marine tout au long de la sédimentation saline tandis que le bassin marginal de Lorca a évolué vers la dessication et a été soumis à l'influence des eaux météoriques.

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## I. – INTRODUCTION

Since the publication of the preliminary results of Legs 13 and 42a of the DSDP in the 1970s, the origin of the thick saline deposits of Messinian age (uppermost Miocene) under the floor of the present abyssal plains in the Mediterranean Sea has been the subject of debate [Hsü et al., 1973; Hsü et al., 1978; Rouchy, 1982; Busson,1990]. The evaporitic deposits containing these chlorides extend by more than $2 \times 10^6$ km², and are widely distributed throughout a mosaic of sedimentary basins of various sizes.

Most literature on these evaporites concerns surface studies carried out in the uplifted marginal Neogene basins located in several countries around the Mediterranean : Spain; Algeria, Italy, Cyprus, Greece and Israel [Ogniben, 1957; Decima and Wezel, 1973; Richter-Bernburg, 1973; Shearman and Orti-Cabo, 1976; Schreiber et al., 1976; Pierre, 1982; Rouchy, 1982; Dronkert, 1985]. All these basins are characterized by gypsiferous deposits while chloride bodies are scarce (Sicily, Lorca, Tuscany, Calabria, Cyprus). In contrast, deep seismic oceanographic profiles studied across the various Mediterranean central depressions reveal the existence of a thick saline formation that locally attains a thickness of up to 3000 m [Ryan, 1973; Montadert et al., 1978; Hsü et al., 1978; etc.].

Of more than 20 boreholes drilled during the DSDP surveys in the Mediterranean, and more recently during the ODP (Leg 107) in the Tyrrhenian sea [Kastens and Mascle, 1990] only a few have penetrated the top of this chloride formation : drillhole 134 in Leg 13, 374 and 376 in Leg 42a. All major Messinian salt bodies remain geographically confined to the abyssal plains. One exception is the salt-rich Caltanissetta basin in the central part of Sicily. By contrast, the Lorca basin (SE Spain) shows a thinner salt formation deposited in a marginal area (fig. 1).

## II. – EVAPORITES OF THE WESTERN MEDITERRANEAN BASIN

In the western Mediterranean Basin deep boreholes and seismic profiles have contributed to an improved understanding of the three major stratigraphic units forming the Messinian Evaporite Formation [Biju-Duval et al., 1976; Montadert et al., 1978] :

A) "Lower Evaporites" : bedded member composed of sulphates and laminated deposits equivalent to diatomitic marls of the marginal basins;

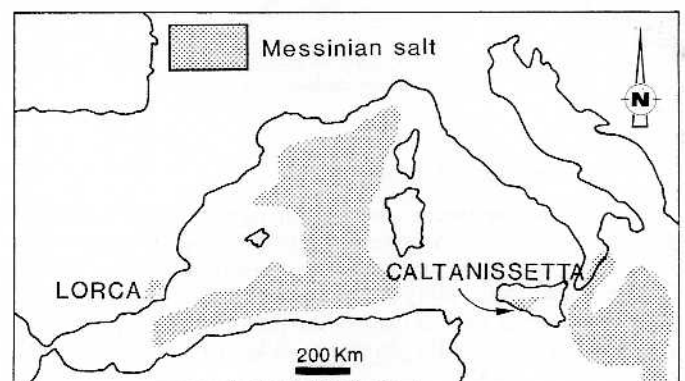B) "Salt Layer" : intermediate member developed in the main depressions;



FIG. 1. – Location of Caltanissetta (Sicily) and Lorca (SE, Spain) basins in the western Mediterranean Sea.

FIG. 1. – *Localisation des bassins de Caltanissetta (Sicile) et Lorca (Espagne) en Méditerranée occidentale.*

C) "Upper Evaporites" : mainly constituted by alternations of Ca-sulphates, marls and locally also salt lenses.

The interpretation of deep seismic profiles has also demonstrated the existence in the central part of the basin of an unconformity between the top of the Salt Layer and the base of the Upper Evaporites. This unconformity is connected to an erosional surface towards the margin of the basin.

## A) Neogene basin of Central Sicily

Evaporitic sediments of Messinian age in Central Sicily are known as the "Gessoso Solfifera Formation". They are distributed in several basins, the largest of which is the "Caltanissetta Trough" or "Central Sicily Basin" [Decima and Wezel, 1973] (fig. 2). The most subsident part of this basin was uplifted whereas its western marginal sector remained below the Mediterranean sea floor [Schmidt di Frieberg, 1962].

In the past decades the Messinian evaporites of Sicily have been the subject of sedimentological [Ogniben, 1957; Decima and Wezel, 1973; Richter-Bernburg, 1973; Schreiber, 1974; Schreiber et al., 1976; Rouchy, 1982; etc.] and geochemical [Longinelli, 1979/80; Pierre, 1982; Bellanca and Neri, 1986; McKenzie, 1985; etc.] studies, although little has been published concerning the Salt Layer excepted for a first study of the bromine content of the halite by Decima [1976].

The generalized sedimentary sequence of the Gessoso Solfifera Fm. (fig. 3) comprises the following marine units [Ogniben, 1957; Decima and Wezel, 1973; Hardie and Eugster, 1971] :

1) a pre-evaporitic unit (the Tripoli Member) mainly composed of marlstones interbedded with diatomitic deposits;

2) an extensive carbonate unit (the Calcare di Base Mb) with a marked evaporitic character [Ogniben, 1957; Decima et al., 1988; McKenzie et al., 1979];

3) a lower gypsiferous/anhydritic unit (the Cattolica Gypsum Member) characterized by a thick (a few hundreds of metres) sequence of cyclic selenitic gypsum;

4) a Salt Member that reaches a thickness of about 600m and develops along the axis of the basin. The salt is generally massive and includes kainite beds in the middle part of the stratigraphic section, which are the subject of mining extraction. Drilling data show that the saline member locally overlies a thin anhydrite layer (only a few meters thick), which in its turn covers directly the Tortonian-Messinian marls. The fact that the Cattolica Gypsum Mb. is usually absent below the Salt Mb. suggests that the stratigraphic scheme proposed by Decima and Wezel [1973] and Decima et al. [1988] should be modified, in such a way that the Cattolica Gypsum Mb. represents a lateral equivalent of the central salt body, the former being developed only at the margins of the basin (fig. 3), as proposed by Catalano and Esteban [1978], Catalano [1979], Catalano and D'Argenio [1982] and Rouchy [1982];

5) an upper gypsiferous unit (the Pasquasia Gypsum Member) which reaches a thickness of 300 m. This unit is mainly composed of a marly succession that contains up to six cyclic gypsum beds (laminated and selenitic) that define marl/gypsum sequences ranging from 5 to 80 m in thickness. This sequences are well exposed in the Eraclea Minoa section and widely distributed in the basin [Decima and Wezel, 1973; Rouchy, 1976];

6) a detrital unit (the Arenazzolo Member), deposited in brackish waters or in terrestrial environments. The upper
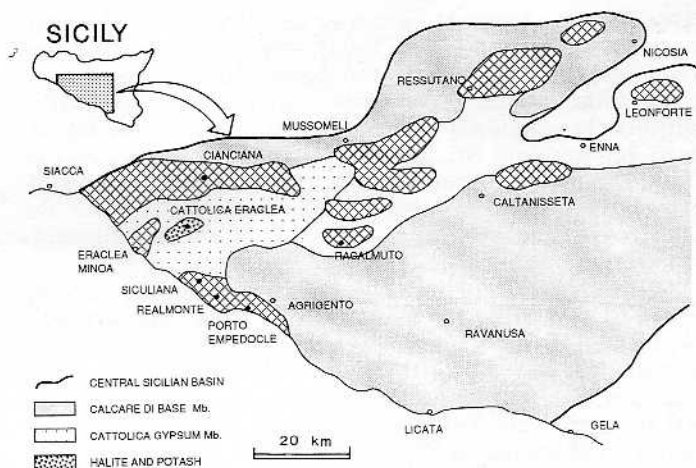


FIG. 2. – Distribution of Messinian facies in the Caltanissetta basin, central Sicily [after Decima & Wezel, 1973].

FIG. 2. – *Répartition des faciès messiniens dans le bassin de Caltanissetta en Sicile centrale [d'après Decima et Wezel, 1973].*
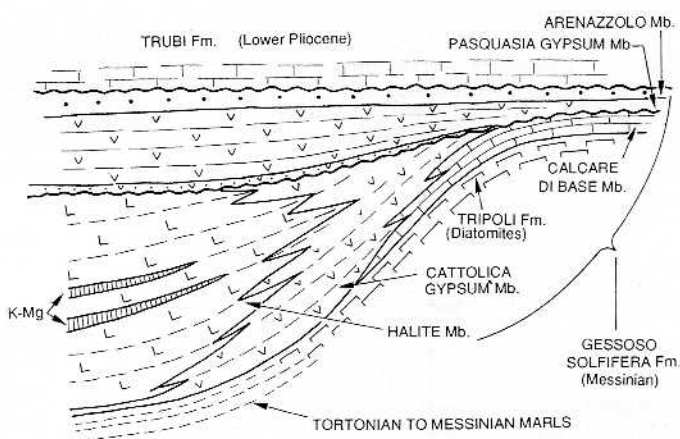


FIG. 3. – Representative section of Messinian sediments in the Caltanissetta basin [modified from : Decima and Wezel, 1973; Catalano, 1979; Catalano and D'Argenio, 1982; Rouchy, 1982].

FIG. 3. – *Agencement des sédiments messiniens dans le bassin de Caltanissetta [d'après Decima & Wezel, 1973; Catalano, 1979; Catalano and D'Argenio, 1982; Rouchy, 1982].*

stratigraphic contact of the Arenazzolo Mb. with the pelagic early Pliocene Trubi Fm marks the flooding of the Mediterranean by the Atlantic waters [Cita, 1975];

The base of the Pasquasia Gypsum Mb. corresponds to a regional unconformity which may be correlated with the one separating the Upper Evaporites and the Salt Layer in the present abyssal plains of the Mediterranean Sea. Thus, the similarity in the stratigraphic succession between the Gessoso-Solfifera Fm. and the seismic profiles of the deep Mediterranean depressions has led many authors to consider the Central Basin of Sicily to be the best example of the "deep basin" during Messinian times.

## B) Evaporites of the Lorca Basin

The Neogene tectonism created a number of intramontane basins [Montenat et al., 1987] in the eastern domain of the Betic Chain (south of Spain). The Lorca Basin whose Neogene stratigraphy was studied by several authors [Geel,

1976; Rouchy, 1982; Montenat *et al.*, 1990; Pérez Lorente *et al.*,1992; Dittert *et al.*, 1994], contains evaporitic deposits of Messinian age. In this basin, the Messinian sediments form three marine units : (a) basal pre-evaporitic unit, mainly composed of marls including diatomitic layers, up to 100 m thick; (b) saline unit, attaining a thickness of 235m, located in the centre of the basin; (c) laminated gypsiferous unit, up to 60 m thick (Serrata Gypsum Mb.); the latter is overlain by a thick sequence of clastic sediments of terrestrial origin (Messinian to Pliocene).

The saline unit of the Lorca Basin is known only by means of two drills for mining prospection : the borehole S4, located in the centralmost part, and the borehole S5, located close to the former (about 2 km) but in a more marginal position. The respective thicknesses of the salt in the two boreholes are 235 and 49 m indicating a strong differential subsidence in the central trough of the basin. García-Veigas *et al.* [1994] correlated the thin salt record of borehole S5 with the base of the saline unit of borehole S4.

## III. – MATERIALS AND METHODS

The aim of this work is to discuss the results of a geochemical study performed on the Central Sicily Basin (Caltanissetta) which has a central position in the Medi-

terranean, and to compare them with the findings published for the Lorca basin (Spain) which is located in a marginal position. This would provide a depositional model of chlorides and would improve the understanding of the Messinian evaporitic event.

Several studies on evaporitic samples of the Salt Member of the Gessoso Solfifera Fm. of Sicily were carried out : petrography, bromine determinations, microanalysis of fluid inclusions in halite and isotopical composition determinations of accompanying sulphates.

The geochemical study was done on samples obtained from several boreholes drilled decades ago by the Ente Minerario Siciliano in the western part of the basin : Ciancianna 2, Cattolica 5, Siculiana 1 and Porto Empedocle 38 (fig. 4). Some of these samples were initially analyzed for bromine content by Rouchy [1982]. The boreholes Racalmuto 4 and Petralia 3 previously studied by Rouchy [1982] were not retained because of their incomplete stratigraphic record (the lower part of the evaporite section is probably absent).

Additional sampling was carried out in the galleries of the Realmonte Mine, whose stratigraphical position is indicated in figure 5 which offers a correlation between the saline layers in two mining boreholes of this sector and includes the terminology used originally by Decima [1976] to subdivide the chloride body into several units (layers A to D).
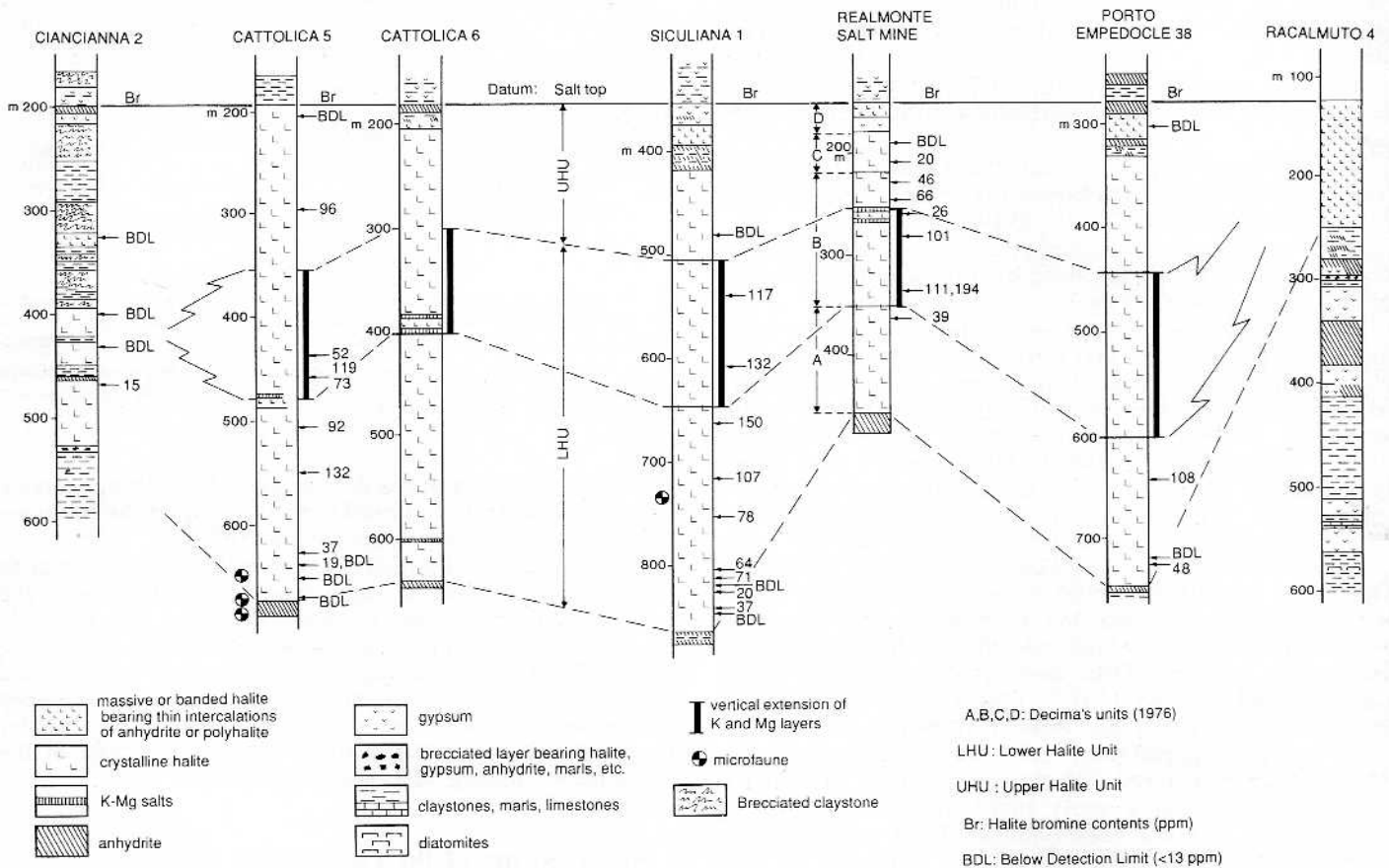


FIG. 4. – Correlation of Messinian Salt Layer in boreholes in Caltanissetta basin [based on Rouchy, 1982]. Bromine contents in halite samples (in ppm) are indicated.

FIG. 4. – *Corrélation des niveaux de sel dans les sondages du bassin de Caltanissetta [d'après Rouchy, 1982]. Les teneurs en brome (exprimées en ppm) des échantillons de halite sont indiquées sur les profils.*
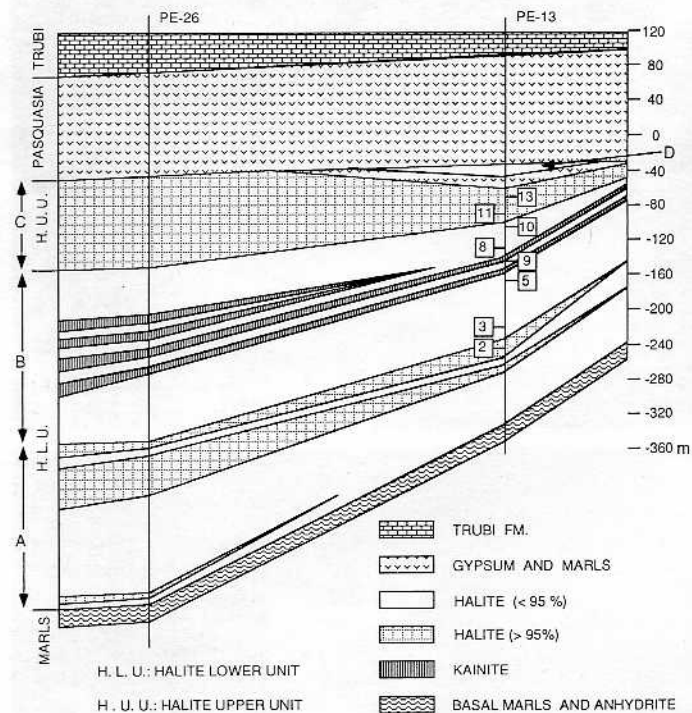
## REALMONTE SALT MINE

FIG. 5. – Correlation between two boreholes in Realmonte Mine (PE : Porto Empedocle) indicating the terminology used by Decima and Wezel [1973]. The sampling carried out in the Realmonte Mine for this paper is indicated in PE-13 section.

FIG. 5. – *Corrélation entre deux sondages de la mine de Realmonte (PE : Porto Empedocle) indiquant la terminologie utilisée par Decima et Wezel [1973]. L'échantillonnage réalisé pour cette étude dans la mine de Realmonte est indiqué sur le profil PE-13.*

## IV. – THE MESSINIAN SALT OF THE CALTANISSETTA BASIN

### A) Petrography

Thirty-five thin sections representative of the Realmonte Mine from salt layers B and C, and also from the kainite beds intercalated in layer B (fig. 5) were studied petrographically.

Rectangular-shaped and flattened halite plates lying horizontally are common in layer B, whereas layer C contains randomly oriented hopper crystals (pl. I 1). Both fabrics display a well developed fluid inclusion zonation and may represent cumulates composed of halite crystals growing at the air-water interface (plates) and at the bottom of the basin (hoppers).

Anhydrite occurs commonly in layer C and rarely in layer B, either as isolated small-sized laths or as granular aggregates of equant crystals commonly replaced by polyhalite. Polyhalite occurs in layers B and C, where it may form millimeter to centimeter-thick discrete laminae, and locally within the kainite beds intercalated in layer B. The most common habit is represented by length-fast fibers [Ortí and Pueyo, 1980], but microcrystalline aggregates and isolated, rarely twinned, prisms have been observed. The fibrous polyhalite displays the following fabrics : (A) ellipsoidal-shaped radial spherulites commonly showing several concentric layers (pl. I : 2 and 4); (B) cross-shaped aggregates of parallel fibers crossed at a straight angle; and (C) rectangular and pseudohexagonal-shaped radial aggregates of polyhalite that have apparently grown within the pelitic intercalations and around the halite crystals;

cubic halite crystals may be replaced by randomly oriented polyhalite fibers (pl. I : 3 and 4). Kainite crystals appear to be partially replaced by polyhalite.

Kainite forms discrete laminae and beds ranging from a thickness of few mm to a maximum of 2 m intercalated in salt layer B. It may also be found as small sized isometric crystals scattered within halite rocks. Textures consist of densely-packed equant granular mosaics which show pressure-dissolution features. Three main kainite lithofacies were identified in the beds and laminae closely stratified in halite, which were formerly differentiated by Berry and Ribacchi (1976) :

1) fine-grained kainite-rock composed of small crystals (averaging 200 µm) with unoriented idiomorphic habits varying from rhombohedral to almost rectangular in shape. In a few laminae the intercrystalline spaces are occupied by insoluble materials such as clay, organic matter, Fe oxides and/or hydroxides (pl. I 5). This lithofacies normally contains halite crystals;

2) medium-grained kainite rocks made up of millimetric crystals forming transparent laminae. The texture is granular with a relative tendency to graded bedding. In some cases, large kainite crystals (> 400 µm in size) are present within the medium grained matrix forming a bimodal fabric. Transparent halite crystals are also included within the kainite matrix;

3) Coarse-grained laminae composed of flattened kainite crystals parallel to bedding ranging from 0.5 to 1.5 mm in length (pl. I 6). This lithofacies includes millimetric hopper crystals partly replaced by kainite. A gradual transition from these coarse-grained laminae to halite-dominated ones is common. The coarse-grained kainite is commonly associated, in millimetric to centimetric alternations, with fine-grained kainite beds.

### B) Bromine contents in salt

Determination of bromine contents were performed using X-ray fluorescence spectroscopy. Halite samples contained a negligible proportion of associated minerals (sulphates, clays, etc.) and were ground in dryness. The standards ranged from 13 to 690 ppm and yielded a linear regression. Despite the fact that the samples studied are not homogeneously distributed in the profiles and that they are scarce in some parts of the profiles, the results obtained (tab. I, fig. 4) allow us to comment on the origin of the halite.

TABLE I. – Bromine average contents (ppm) in halite samples (dry powdered) from boreholes Ciancianna-2, Cattolica-5, Siculiana-1 and Porto-Empedocle-38 and from sampling taken in the Realmonte Salt Mine galeries. See stratigraphical position of samples in figures 4 and 5.

TABL. I. – *Teneurs moyennes en brome (ppm) des échantillons de halite (broyés à sec) des sondages Ciancianna-2, Cattolica-5, Siculiana-1 et Porto-Empedocle-38 et des échantillons prélevés dans les galeries de mine de Realmonte. La position stratigraphique des échantillons est indiquée dans les figures 4 et 5.*

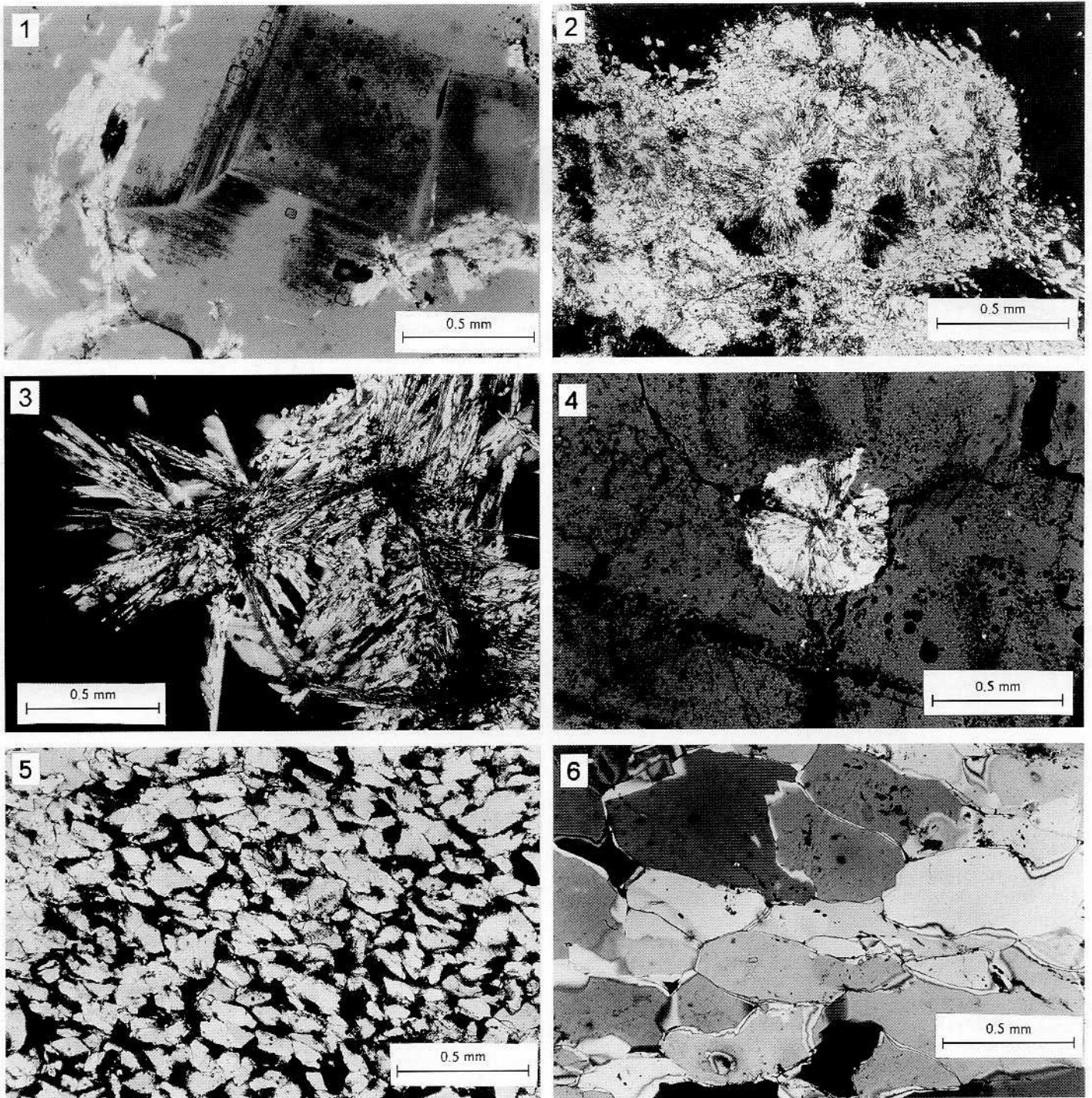| CIA-2 | Br | CAT-5 | Br | SIC-1 | Br | PE-38 | Br | RE-MI | Br |
|---|---|---|---|---|---|---|---|---|---|
| Upper Unit | | | | | | | | | |
| 326 | <13 | 206 | <13 | 479 | <13 | 305 | <13 | 13 | <13 |
| 396 | <13 | 296 | 96 | | | | | 11 | 20 |
| 430 | <13 | | | | | | | 10 | 46 |
| 470 | 15 | | | | | | | 8 | 66 |
| Lower Unit | | | | | | | | | |
| | | 436 | 52 | 538 | 117 | 642 | 108 | 9 | 26 |
| | | 457 | 119 | 613 | 132 | 721 | <13 | 5 | 101 |
| | | 462 | 73 | 666 | 150 | 726 | 48 | 3 | 194 |
| | | 508 | 92 | 720 | 107 | | | 3' | 111 |
| | | 550 | 132 | 755 | 78 | | | 2 | 39 |
| | | 627 | 37 | 804 | 64 | | | | |
| | | 638 | 19 | 820 | 71 | | | | |
| | | 639 | <13 | 832 | 20 | | | | |

PLATE I. – Petrography of the salt rocks from the Realmonte mine (Agrigento, Sicily). 1. – Photomicrograph of a salt rock composed of halite crystals (gray) showing a marked fluid inclusions zonation; the halite crystals are partially replaced by fibrous polyhalite located at the grain boundaries (bright areas); sample RP-10, top of salt layer C; partially crossed polars. 2. – Photomicrograph of radial spherulite aggregates composed of fibrous polyhalite within halite rock (black); salt layer C; crossed polars. 3. – Fibrous, prismatic polyhalite crystals that grew within a halite rock (black) partially replacing it; the replacement starts from grain boundaries. The shape of a former halite grain, now almost completely replaced by polyhalite, is still recognizable in the right side of the photomicrograph; sample RM-10, top of salt layer C; crossed polars. 4. – Radial spherulite composed of fibrous polyhalite (center of photomicrograph) that grew at the boundary among three halite grains (dark gray) partially replacing them; sample R-2, salt layer C; partially crossed polars. 5. – Fine-grained kainite rock; the dark material among the idiomorphic kainite crystals is composed of clay and organic matter; kainite bed in salt layer C; photomicrograph in natural light. 6. – Coarse-grained kainite from salt layer B displaying flattened crystals; photomicrograph, crossed polars.

PL. I. – *Pétrographie des roches salines de la mine de Realmonte (Agrigente, Sicile). 1. – Dépôt salin composé de cristaux de halite (gris) présentant une zonation marquée par des inclusions fluides; les cristaux de halite sont partiellement remplacés par de la polyhalite fibreuse le long des limites de grains (zones claires); échantillon RP-10, toit de l'horizon C, lumière polarisée. 2. – Agrégats sphérulithiques radiaires composés de polyhalite fibreuse dans la halite (noir); horizon C, lumière polarisée. 3. – Cristaux prismatiques de polyhalite fibreuse se développant dans le sédiment halitique (noir) en le remplaçant partiellement; le remplacement débute le long des limites cristallines. La morphologie antérieure de l'un des grains qui est maintenant presque intégralement remplacé par la polyhalite est encore reconnaissable sur le bord droit de la photo; échantillon RM-10, toit de l'horizon C, lumière polarisée. 4. – Agrégats sphérulithiques radiaires composés de polyhalite fibreuse (partie centrale de la photo) qui se développent aux limites entre les grains de halite (gris-clair), en les remplaçant partiellement; échantillon R-2, horizon C, lumière polarisée. 5. – Dépôt kainitique finement grenu; le matériel sombre présent parmi les cristaux automorphes de kainite est composé d'argiles et de matière organique; lit de kainite dans l'horizon C; lumière naturelle. 6. – Kainite à grain grossier de l'horizon B; montrant des cristaux aplatis; lumière polarisée.*

Other authors have provided some data on the bromine content in Messinian halite : on the salt from Realmonte [Decima, 1976], on boreholes samples from Sicily [Rouchy, 1982] and on DSDP drillings [Kühn and Hsü, 1975, 1978]. Significant differences appear between our results and those of Decima [1976], the latter attaining higher values. With regard to these differences probably due to analytical methodology, we have to point out that our data have been checked by analyzing several mineral samples (whose composition was known) as well as synthetic samples.

The results can be separated in two groups (tab. I) : the lower unit corresponds to the lower part of the formation which includes the potash (kainite) beds, and the upper unit comprises halite overlying the potash beds. Comparing with the units reported by Decima [1976] in the Realmonte Mine, the lower unit coincides with unit A and the lower part of unit B whereas the upper unit includes the upper part of unit B together with units C and D.

In the lower unit, the basal halite samples show bromine contents always below 75 ppm, some of them being below the standard of the lowest concentration (13 ppm). The bromine content of the other samples of this unit increases towards the potash zone, reaching a maximum of 150 ppm in the Siculiana 1 profile, except for a sample close to the potash zone from Realmonte. In unit A from Realmonte, Decima [1976] obtained much higher values, up to 400 ppm. The halite samples from the potash zone contain between 52 and 194 ppm of bromine. In Realmonte, a very low value (26 ppm) is found in the salt below the second kainite bed. Values obtained by Decima in this zone corresponding to the lower part of unit B were between 200 and 250 ppm.

In the upper unit of the Realmonte Mine, bromine contents decrease from 66 to less than 13 ppm to the top of the unit. In the other profiles most values also lie below 13 ppm. In this upper halite unit, Decima [1976] also obtained very low values ("undeterminable traces").

Many halite deposits have a bromine content in the range of 30-80 ppm, below the values of 75 ppm predicted for the first halite precipitated from evaporated sea water [Holser, 1966]. These values have been interpreted as a result of halite recycling by dissolution and recrystallization either in non marine inflow [Lowenstein, 1988] or in normal to slightly concentrated sea water [Holser et al., 1972]. Holser et al. [1972] have calculated that a marine halite, recycled by sea water, would contain 10 ppm of Br, on the assumption that the parent halite had 75 ppm, and that subsequent recycling could not produce a reduction below 7 ppm, due to the amount of bromine in sea water.

For the salt of Sicily, Decima [1976] interpreted the marked decrease in bromine content of the upper halite as due to basin desiccation and recycling of the previously precipitated salts by meteoric and continental waters.

In our opinion, halite recycling could explain the low bromine contents in the basal samples and in the upper group. However, the origin of the fluids responsible of the dissolution and reprecipitation of the salts cannot be established from bromine data exclusively. It is necessary to use the data from fluid inclusion microanalysis.

The marine origin of the sulphate minerals accompanying chlorides in the Salt Member was confirmed by the isotopic study in some samples from the galleries in the Realmonte Mine. In these samples the sulphate fraction was recovered after dissolving the dominant halite fraction and the mineralogy was controlled by XRD. Kainite predominates over halite only in one sample from the K-Mg intercalations in layer B (RM-4). Values of $\delta^{34}S$ (tab. II) are in good agreement with those found for Messinian sulphates

TABLE II. – Isotope composition (in ‰) of sulphates present in halite and kainite samples from Realmonte Salt Mine galeries. See stratigraphical position of samples in figure 5.

TABL. II. – *Composition isotopique (en ‰) des sulfates présents dans la halite et la kainite des échantillons prélevés dans les galeries de mine de Realmonte.*

| Sample | Layer | Mineralogy | $\delta^{18}O$ SMOW | $\delta^{34}S$ CDT |
|---|---|---|---|---|
| RM-11 | C | Polyhalite Anhydrite (+Halite) | 15.9 | 21.2 |
| RM-10 | B(top) | Anhydrite Polyhalite (+Halite) | 12.8 | 22.7 |
| RM-4 | B(potash) | Kainite (+Halite) | 9.8 | 24.3 |
| RM-5 | B(potash) | Kainite (+Halite) | 14.7 | 22.2 |

in the literature [Ricchiuto and McKenzie, 1978; Pierre and Fontes, 1978; Pierre, 1982; among others] and they reflect their marine origin, according to the curves presented by Claypool et al. [1980]. No significant differences in $\delta^{34}S$ between the various sulphate (polyhalite, anhydrite) or sulphate-bearing minerals (kainite) were found. The $\delta^{18}O$ values display a range that is slightly wider than the one offered in the literature, the lowest one (nearly 10‰) corresponding to the kainite-rich sample.

## C) Composition of fluid inclusions in salt

Halite samples from Porto-Empedocle 38, Cattolica 5, and Siculiana 1 boreholes (fig. 4), and from the Realmonte Mine galleries were analyzed. Hopper textures and zonation of primary fluid inclusions were noticeable in all cases. The chemical composition of fluid inclusions was studied with the Cryo-SEM-EDS technique [Ayora and Fontarnau, 1990; García-Veigas, 1993; Ayora et al., 1994a,b] which consists of analyzing frozen fluid inclusions in a Scanning Electron Microscope (SEM) with an Energy Dispersive System (EDS) and with a cryogenic device which allows us to maintain the sample and the standard brines at a constant temperature below – 190°C.

The Na, Mg, K, Cl and S (expressed as $SO_4$) contents were measured in individual fluid inclusions. The Ca content was always under the detection limit (0.01 mol/kg $H_2O$). The consistency of each analysis was checked for charge-balances and for the NaCl saturation index [Ayora et al., 1994a,b]. More than 90 % of individual determinations were considered as valid.

Although the fluid inclusions show a wide compositional range they can be divided into two groups (tabl. III). The first group corresponds to concentrated brines with high Mg and low Na contents which characterize the lower part of the salt formation (samples SIC-647, 675, 745, PE-647, RM-3'). The second group of fluid inclusions has contents lower in Mg and higher in Na and belongs to the upper part of the salt formation (samples CAT-194, PE-298, 340 and RM-11,11',13). The boundary between the two units coincides with the one recorded for bromine profiles (fig. 4).

A computer program based on a hydrologically open basin model [Sanford and Wood, 1991] and the thermodynamic modelling of the solubility of evaporite minerals [Harvie et al., 1984] were used to simulate different scenarios of evaporation paths. The comparison of predicted

TABLEAU III. – Average composition (mol/kg water) of fluid inclusions in halite samples from boreholes and Realmonte Mine samples. Sample location is indicated in figures 4 and 5 (n: number of analyses).

TABL. III. – *Composition moyenne (moles/kg $H_2O$) des inclusions fluides de la halite provenant des sondages et de la mine de Realmonte. La localisation des échantillons est indiquée dans les figures 4 et 5 (n: nombre d'analyses).*

| Sample | n | Na | Mg | K | Cl | SO$_4$ |
|---|---|---|---|---|---|---|
| CATTOLICA-5 | | | | | | |
| 194 | 7 | 5.43 | 0.51 | 0.06 | 5.87 | 0.13 |
| SICULIANA-1 | | | | | | |
| 647 | 4 | 1.36 | 3.25 | 0.61 | 5.94 | 0.72 |
| 675 | 4 | 2.20 | 2.50 | 0.47 | 5.54 | 0.59 |
| 745 | 5 | 2.62 | 2.48 | 0.46 | 5.76 | 0.58 |
| PORTO-EMPEDOCLE-38 | | | | | | |
| 298 | 7 | 4.60 | 0.72 | 0.04 | 6.35 | 0.04 |
| 340 | 7 | 4.42 | 0.80 | 0.23 | 5.53 | 0.23 |
| 647 | 7 | 2.47 | 2.15 | 0.52 | 5.57 | 0.55 |
| REALMONTE | | | | | | |
| 13 | 7 | 4.21 | 1.13 | 0.25 | 6.55 | 0.31 |
| 11 | 6 | 4.73 | 0.44 | 0.04 | 5.86 | 0.14 |
| 11' | 8 | 5.10 | 0.76 | 0.08 | 6.03 | 0.19 |
| 3' | 7 | 2.43 | 2.21 | 0.46 | 5.72 | 0.54 |

results with the observed mineral thickness, the depositional sequence, and the major solute composition of fluid inclusions, enable us to constrain the hydrological and chemical evolution of a potash-forming evaporite basin. Details on the numerical modelling and methodology of interpretation are found in Ayora *et al.* [1994a,b]

### 1) Chemical evolution model for the lower halite unit

A simulated basin containing initial seawater was evaporated with seawater flowing into it in order to keep constan the total mass of water. The following mineral sequence was predicted : carbonates, anhydrite (gypsum), glauberite, halite, polyhalite, hexahydrite, and kieserite. The lower part of this mineralogical sequence is coincident with that found in the lower halite group, except for glauberite, which is absent. However, kainite instead of predicted Mg-sulphates is the mineral found in the lower part in the advanced stages of evaporation.

According to geochemical calculations the content of Mg increases regularly with the exception of a very small proportion depleted by the precipitation of polyhalite until the precipitation of Mg-sulphates. Therefore, the amount of Mg was considered to be quasi-conservative and an indicator of the degree of evaporation. Accordingly, the mean values of the solute contents found in fluid inclusions were plotted against Mg in figure 6A. It can be observed that the predicted values for Na and SO$_4$ match those analyzed in fluid inclusions. The measured values of Cl show the same trend although they are systematically lower by 0.4 mol/kg $H_2O$ than predicted, probably due to an analytical error. For Mg contents higher than 2.0 mol/kg $H_2O$, K is predicted to decrease due to polyhalite crystallization; however, the increase in K with Mg in the analyzed fluid inclusions is not consistent with polyhalite precipitation and suggests that it was inhibited.

Figure 6B illustrates the results of the calculation of the same evaporation model of seawater recharge without polyhalite precipitation. The trend of calculated K contents matches amounts analyzed in fluid inclusions. However, SO$_4$ is predicted to be present in amounts higher than those analyzed in fluid inclusions. Moreover, syngenite and hexanhydrite, which were not found in the paragenesis, are predicted to precipitate before and in higher amounts than kainite.

Calculations based on the described evaporation model were performed with a small amount (0.5 % in volume) of a hypothetical 1mol CaCl$_2$ brine replacing an equal volume
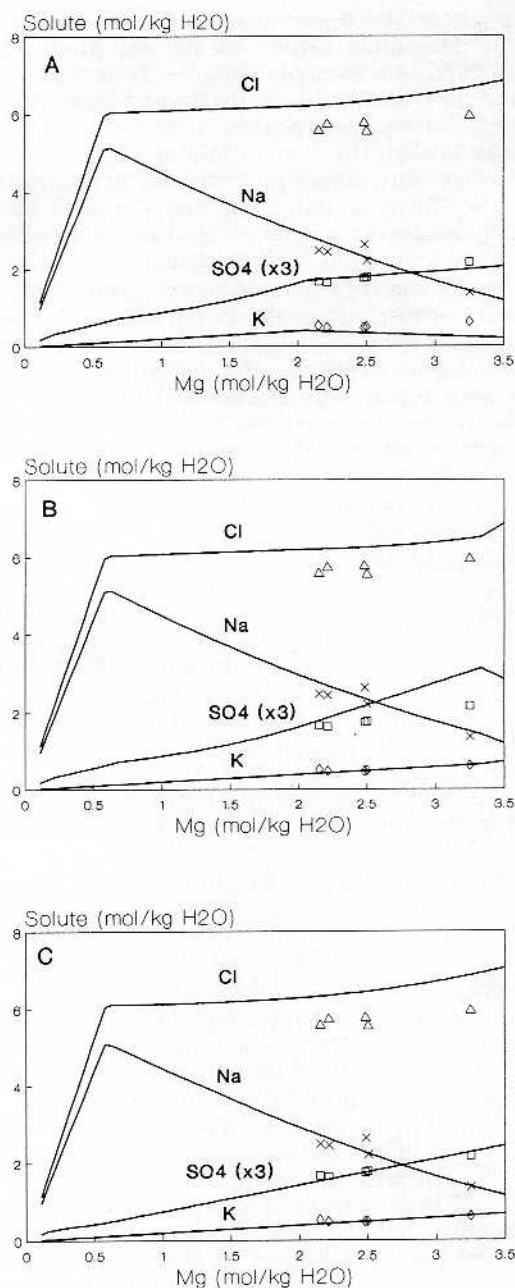


FIG. 6. – A. – Calculated evolution of the solute content with respect to Mg (mol/kg water) for the evaporation in a basin with seawater inflow at 25°C. B. – The same process as A, but polyhalite is not allowed to form. C. – The same process as B, with 0.5 % (in volume) of the inflow made up of a 1 mol CaCl$_2$ brine. The symbols correspond to the analyses of fluid inclusions in halite from the lower halite unit. Legend : triangle = Cl; cross = Na; square = SO$_4$ × 3; diamond = K.

FIG. 6. – A. – *Évolution calculée des saumures en fonction de la concentration en Mg (moles/kg $H_2O$) pendant l'évaporation dans un bassin soumis à un apport d'eau de mer à 25°C. B. – Même situation qu'en A, mais dans le cas où la polyhalite ne peut se former. C. – Même situation qu'en B, mais avec 0,5 % (en volume) d'apport de saumures riches en CaCl$_2$ équivalent à une couche d'eau de 1 mètre d'épaisseur. Légende : triangles = Cl; croix = Na; carrés = SO$_4$ × 3; losanges = K.*

of the seawater inflow. The possible origins of a Ca-enriched brine (dolomitization, deep diagenesis, hydrothermal) are discussed in Ayora *et al.* [1994a,b]. The predicted trends of solute evolution match the contents analyzed in fluid inclusions (fig. 6C)

As observed in other evaporite basins, an excess of Ca in the basinal brine may be responsible for the SO$_4$ deple-

tion observed in the fluid inclusion analyses [Ayora *et al.*, 1994a,b]. The predicted depletion of $SO_4$, in this model, is sufficient to prevent the formation of glauberite in the early stages of evaporation. The increase in K causes kainite, instead of Mg-sulphates, to precipitate in the advanced stages of evaporation, which is in agreement with the observed salt formation from Sicily.

Accordingly, (1) inhibition of polyhalite crystallization plays an important role in the formation of economic deposits of kainite. Indeed, polyhalite is never found as primary beds formed from the free brine. Moreover, its textures provide evidence of its diagenetic origin from interstitial brines, (2) Ca excess in the seawater inflow is necessary for an agreement between the predicted and observed evaporitic sequences and solute contents.

### 2) *Chemical evolution model for the upper halite unit*

The two evaporation models for the upper part of the salt formation are based on the evaporation of a residual brine (post-kainite) with a composition similar to the most concentrated fluid inclusions found in the lower group (SIC1-647), and with the inflow of, first, continental water and, secondly, marine water.

In the first case, the inflow of meteoric water saturated in halite (simulating salt recycling mechanism) replaced the water lost by evaporation. The Na, Cl, and K calculated trends are similar to those analyzed in the fluid inclusions of the upper halite unit. However, due to the relatively high $Ca/SO_4$ ratio of continental water with respect to the marine water, the predicted contents are lower than those found in fluid inclusions which have high $SO_4$ and low Ca ($< 0.01$ mol/kg $H_2O$) contents. These compositions as well as the lack of glauberite crystals or pseudomorphs in the natural paragenesis suggest that this hypothesis is not valid.

In the second case, the inflow of seawater saturated in halite (salt-recycling) is assumed to replace the evaporated water outflow. The calculated solute contents match well the analyzed fluid inclusions except for two samples (RM-11 and CAT-194) impoverished in Mg (fig. 7A). Calculations under a similar hydrological configuration were repeated considering the same Ca-enrichment in the marine water inflow proposed in figure 6C. The calculated solute trends match those found in the analyzed fluid inclusions (fig. 7B). Moreover, the predicted sulphate paragenesis by the latter calculations is coincident with that described for the upper group (anhydrite is present, glauberite and polyhalite are absent).

It follows that : (1) the salinity decrease found in the analysed fluid inclusions from the upper part of the salt formation reveals a significant change in the hydrologic configuration in the basin; (2) only the inflow of marine water slightly enriched in Ca, recycling already formed halite, is able to predict the mineral paragenesis of this group and the mother brine evolution reflected by the fluid inclusion composition throughout the upper part of the salt formation in Caltanissetta. Furthermore, the calculations performed with continental water inflow failed to reproduce the experimental data.

### V. – COMPARISON WITH THE SALT OF THE LORCA BASIN (SPAIN)

#### A) **Geochemical results in the salt of the Lorca Basin**

Several papers have been devoted to the petrography and geochemistry of this evaporitic formation [García-Veigas *et al.*, 1990; García-Veigas, 1993; García-Veigas *et al.*, 1994; Ayora *et al.*, 1994a; Rosell *et al.*, 1996]. Bromine profile
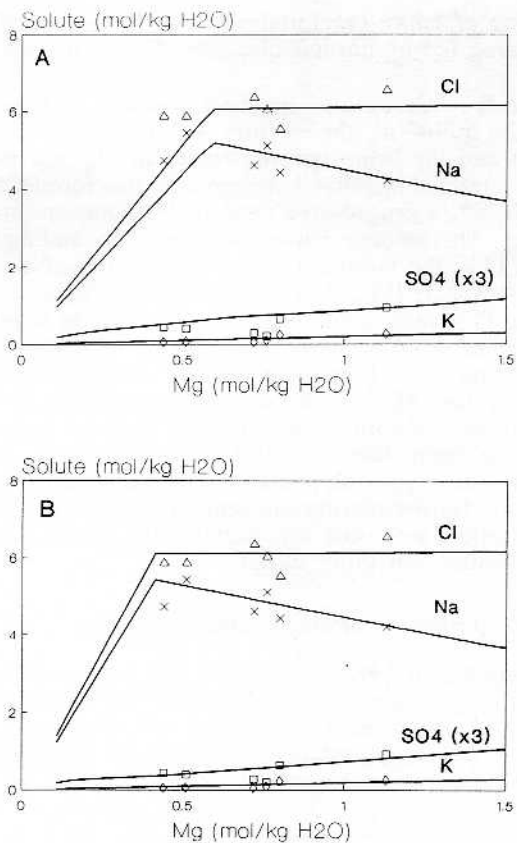


FIG. 7. – A. – Calculated evolution of the solute content with respect to Mg (mol/kg water) for the evaporation of a brine with similar composition of fluid inclusions in sample SIC1-647, with an inflow of seawater saturated in halite. B. – The same process as A, with 0.5 % (in volume) of the inflow made of 1mol $CaCl_2$ brine. The symbols correspond to the analyses of fluid inclusions in halite from the upper halite unit. Legend : triangle = Cl; cross = Na; square = $SO_4 \times 3$; diamond = K.

FIG. 7. – A. – *Evolution calculée des saumures en fonction de la concentration en Mg (moles/kg $H_2O$) pendant l'évaporation d'une saumure ayant une composition des inclusions fluides qui correspond à celle de l'échantillon SIC-647, mais avec un apport de saumures marines saturées en halite. B. – Même situation qu'en A, mais avec 0,5 % (en volume) d'apport de saumures riches en $CaCl_2$ équivalent à une couche d'eau de 1 mètre d'épaisseur. Les symboles correspondent aux analyses des inclusions fluides réalisées dans les halites de l'unité saline supérieure. Légende : triangles = Cl; croix = Na; carrés = $SO_4 \times 3$; losanges = K.*

of the borehole S4 may be separated in two parts at the depth of 139 m (tab. IV) : the lower unit is characterized by very homogeneous contents, which are slightly lower than in the first halite precipitated in coastal salinas; the upper unit has values that decreases progressively upwards, which is due to a final dilution of the brines. Bromine contents obtained in the central part of borehole S5 are also low (tab. IV), even lower than in the lower unit of borehole S4, thereby suggesting that the first halite crystals precipitated in the Lorca saline unit were significantly poor in bromine.

Modelling of the composition of fluid inclusions in samples from the two boreholes [Ayora *et al.*, 1994a; García-Veigas *et al.*, 1994] point to the existence of three main hydrological stages in the evolution of marine brines in this saline formation [tabl. V; and Fig. 3 of García-Veigas *et al.*, 1994] :

Stage A is represented by the salt of borehole S5; the salinity of brine was mainly of sodic nature and relatively high (300-335 g/l), similar to the salinity expected at the

beginning of halite precipitation in an hydrologically open basin being fed by normal seawater [Fig. 8 of Ayora et al., 1994a].

Stage B is represented by the lower unit of borehole S4 from 229 to 147 m; the salinity was relatively high (333-339 g/l) and the brine became richer in Mg and poorer in Na. In contrast to what happened in the former stage in borehole S5, a progressive drop in $SO_4$ concentration was recorded. This decrease was modellized by adding a small amount (1 % the volume of the total inflow) of a fluid enriched in $CaCl_2$ [Fig. 9 of Ayora et al., 1994a].

Stage C is represented by the upper unit of borehole S4 from 139 m to 76 m, where the salinity was relatively low (317-329 g/l) and brine was mainly constituted by NaCl with very low Mg and K contents. According to the proposed model [Ayora et al., 1994a; García-Veigas et al., 1994], the basin was cut off from the sea and only continental water was supplied. These meteoric waters dissolved the former marine salt and, after further evaporative concentration, new salt was precipitated in the depocenter of the central subsiding trough.

## B) Comparison of the bromine profiles

A parallelism between the two bromine profiles (tab. I and IV) may be observed. They begin with low Br contents, lower than expected for the first salt deposited from a marine brine in accordance with current literature. After this, they show an important Br enrichment up to 50-60 ppm in Lorca and 130 ppm in Caltanissetta. Finally, both sequences finish with a drastic drop. Such a parallelism demonstrates that both saline formations experienced similar salinity trends.

## C) Comparison of the composition of the fluid inclusions

The composition of fluid inclusions reveals differences which imply different hydrological systems for each basin (tab. III and V). In both cases the modelling assumes that the basins were hydrologically open and that marine waters were continuously supplied. The $SO_4$ content constitutes the first difference since the Lorca brines underwent a significant inflow of $CaCl_2$-rich fluids whereas the Caltanissetta brines remained essentially uncontaminated marine waters. A second discrepancy arises from the different composition of the brines at the top of both saline formations, which were of continental origin in Lorca and of marine origin in Caltanissetta. In both cases, however, a final transgressive episode caused sedimentation of Ca-sulphates directly upon the salt formation and onlapped the marginal facies (Serrata Gypsum Fm. in Lorca, Pasquasia Gypsum Mb. in Caltanissetta).

## VI. – CONCLUSIONS

On the basis of available subsurface data, and previous stratigraphic observations on the Gessoso Solfifera Formation (Messinian, Caltanissetta Basin, Sicily), the existence of a lateral facies change between the Saline Member and the Cattolica Member (Lower Gypsum Member) should be noted.

The petrographic study carried out on chloride and sulphate samples of the Saline Member from both mine galleries and boreholes reveals the primary origin of the halite and kainite beds and the diagenetic origin of the polyhalite occurrences.

TABLE IV. – Bromine average contents (ppm) in halite samples, dry (d) and alcohol (a) powdered, from Lorca basin: boreholes S4 and S5 (n: number of analyses).

TABL. IV. – Teneurs moyennes en brome (ppm) des échantillons de halite du bassin de Lorca (sondages S4 et S5), broyés à sec (d) et dans l'alcool (a) (n = nombre d'analyses).

| Sample(m) | n | Br(d) | Br(a) | Sample(m) | n | Br(d) | Br(a) |
|---|---|---|---|---|---|---|---|
| BOREHOLE S4 | | | | BOREHOLE S5 | | | |
| 78 | 2 | <13 | <13 | 126 | 1 | 45 | 33 |
| 102 | 1 | <13 | <13 | 127 | 1 | 46 | 31 |
| 108 | 2 | 32 | 22 | 129 | 3 | 52 | 31 |
| 111 | 2 | 20 | <13 | 130 | 1 | 58 | 25 |
| 112 | 2 | 26 | <13 | 131 | 1 | 44 | 22 |
| 139 | 2 | 48 | 32 | 132 | 1 | 63 | 57 |
| 140 | 2 | 55 | 38 | 133 | 1 | 57 | 40 |
| 147 | 2 | 59 | 41 | 134 | 1 | 61 | 52 |
| 182 | 2 | 61 | 37 | 135 | 1 | 45 | 33 |
| 193 | 2 | 57 | 31 | 136 | 3 | 53 | 35 |
| 212 | 2 | 59 | 40 | 137 | 1 | 34 | 16 |
| 226 | 2 | 49 | 35 | 139 | 1 | 41 | 20 |
| 227 | 4 | 48 | 39 | 140 | 1 | 37 | 15 |
| 229 | 2 | 50 | 38 | 142 | 1 | 38 | <13 |
| 244 | | 53 | 45 | 143 | 1 | 50 | 41 |
| | | | | 144 | 3 | 35 | 18 |
| | | | | 145 | 4 | 36 | 18 |
| | | | | 146 | 3 | 38 | 22 |

TABLE V. – Average composition (mol/kg water) of fluid inclusions in halite samples from Lorca basin in boreholes S4 and S5 (n = number of analyses).

TABL. V. – Composition moyenne (moles/kg $H_2O$) des inclusions fluides des échantillons de halite des sondages S4 et S5 du bassin de Lorca (n = nombre d'analyses).

| Sample (m) | n | Na | Mg | K | Cl | SO4 |
|---|---|---|---|---|---|---|
| LORCA S4 | | | | | | |
| Upper unit | | | | | | |
| 76 | 2 | 5.41 | | | 6.34 | 0.05 |
| 77 | 3 | 5.43 | | 0.09 | 6.33 | |
| 111 | 4 | 3.23 | 1.12 | 0.20 | 6.39 | 0.09 |
| 112 | 5 | 3.53 | 1.42 | 0.17 | 6.73 | 0.13 |
| 139 | 3 | 2.13 | 2.01 | 0.22 | 6.81 | 0.12 |
| Lower unit | | | | | | |
| 147 | 3 | 1.21 | 2.93 | 0.25 | 7.19 | 0.21 |
| 173 | 3 | 1.42 | 2.46 | 0.25 | 7.45 | 0.24 |
| 193 | 7 | 1.60 | 2.65 | 0.21 | 6.68 | 0.32 |
| 212 | 3 | 2.13 | 2.13 | 0.21 | 6.48 | 0.28 |
| 222 | 3 | 1.95 | 2.32 | 0.37 | 6.20 | 0.36 |
| 226 | 6 | 2.33 | 2.03 | 0.22 | 6.49 | 0.35 |
| 228 | 9 | 1.88 | 2.47 | 0.27 | 6.52 | 0.35 |
| 229 | 7 | 2.21 | 2.35 | 0.29 | 6.12 | 0.38 |
| LORCA S5 | | | | | | |
| 127 | 7 | 3.17 | 1.54 | 0.38 | 5.62 | 0.49 |
| 134 | 7 | 3.63 | 1.39 | 0.36 | 5.68 | 0.44 |
| 146 | 8 | 4.25 | 1.01 | 0.31 | 5.67 | 0.38 |

The bromine concentrations clearly differentiate two units in the Salt Member : in the lower unit including the kainite beds, the Br contents increase towards the potash zone up to a maximum of 150 ppm; in the upper unit, the Br contents decrease towards the top attaining values below 13 ppm. Values lower than 70 ppm suggest salt recycling by normal or only slightly concentrated seawater. The compositions of the fluid inclusion also record the same two saline units. The lower one is characterized by concentrated brines (high Mg, low Na contents), whereas the upper unit shows less concentrated brines (lower Mg, higher Na).

In the lower unit the chemical evolution model that best matches the contents analyzed in fluid inclusions is the evaporation of seawater recharge without polyhalite precipitation, in which a small amount of $CaCl_2$ brine replaces an equal volume of seawater inflow. It follows that polyhalite inhibition to crystallize as a primary mineral plays an important role in the formation of economic deposits of kainite.

In the upper unit the chemical evolution model that best reproduces the salinity decrease found in the fluid inclusions is the evaporation of seawater inflow saturated in halite (salt-recycling) in which also some Ca-enrichment is considered. Thus, the overall geochemical study of halite

samples confirms the marine origin of the mother brines and their relationship to the $SO_4$-normal evaporation trend with the inflow of seawater only slightly modified. The microanalysis of fluid inclusions demonstrates that the salt dissolution and reprecipitation at the top of the Saline Member in the Caltanissetta Basin was due to the inflow of normal sea water to the basin instead of a meteoric water influx as previously thought from Br data. Therefore, the very low bromine contents found at the top of the saline sequence do not really imply any significant contribution of continental waters. In conclusion, the elementary study of Br in the solid phase has proved to be less precise than the compositional study of the original brines in fluid inclusions.

The comparison with the marginal Lorca Basin (SE Spain), where locally a thick Saline Unit was deposited from marine waters in Messinian times, is of much interest. In this basin, the bromine analysis of the solid phase shows a similar event of salt dissolution-reprecipitation at the top of the halite sequence. However, in this case, the fluid inclusions reveal the Mg, K and $SO_4$-poor character of the brine with respect to normal marine waters at the top of the sequence, due to the meteoric origin of the inflow waters.

Thus, the two basins have recorded a similar evolution during most of the Messinian salt deposition, except for the uppermost part of the two formations. At this time, the Sicilian basin which was deeper and located in a more central position continued to receive inflow of marine waters till the end of the salt deposition while the marginal basin of Lorca was isolated from the sea, evolved to desiccation and was submitted to the influence of continental waters. Such diversified evaporitic records for both basins probably result from a differentiated structural history. This fact deserves to be taken into account when interpreting the significance of the sharp stratigraphic boundary recorded between the Upper Evaporite and the Salt Layer of the Messinian throughout the central parts of the Mediterranean Basin. For this interpretation it is not necessary to assume non-marine water inflow.

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