

Response to reviewers and list of changes made in the manuscript

Response to Dr. Bourquin, Referee #1

Referee Suggestions:

- Maybe a sedimentological section could be added
- Fig. 1D for example, to illustrate the four main units and the ages (lines 14-15).
- Middle unit, in figs 1, 2, has been name Intermediate unit line 14: so added "Intermediate or Middle Unit" line 14.

Authors:

We have included a more detailed sedimentological description and interpretation of the sequence in order to give readers a better understanding of the basin evolution.

We have modified, as proposed by Dr. Bourquin, line 14 into "Intermediate or Middle Unit" in order to avoid confusion with units names.

Response to Dr. Monnin, Referee #2

- *Referee Suggestion: In the introduction, I may be wrong, but the use of calling all salt formations evaporites is not adequate. The authors themselves describe mechanisms of salt formation that do not call for evaporation. They also recall (l. 25) that “a few of these deposits are not really evaporites”. To me the first sentence (l. 18) should read “salt formations are natural deposits that have . . .”. Then in line 20 “. . .most salt deposits are formed by evaporation under arid environmental conditions. . .”. This may look petty, but it orients the discussion of salt formation, an important point of the manuscript.*

Authors: We do agree with this comment. This is one of the main points of this work: salts found in nature are not always evaporites. We have made changes in the text in relation to the referee suggestions in order to avoid confusion.

- *Referee Suggestion: In section 5.2 (page 3232), the authors distinguish “two different pathways of salt formation”: evaporative concentration and frigid concentration. They describe these two main mechanisms in detail in this section. The authors nevertheless distinguish two mechanisms in the frigid concentration pathway, namely cooling and freezing. I think these mechanisms can be described in a different way. Starting from a given aqueous solution (what the authors call the “mother brine”), that is undersaturated with respect to a given mineral, formation of this mineral can be achieved in three ways (and not two): 1) removal of the solvent (water) at more or less constant temperature by evaporation, 2) removal of water at constant salinity by freezing, 3) change in temperature at constant salinity (or total concentration). The first two mechanisms increase the concentration of all the dissolved species at the same time leading to a so-called brine (a high salinity solution). The third one relates to the change in mineral solubility with temperature, that the authors describe in an awkward sentence in line 24 page 3226 (“sodium sulphate minerals appear to be highly dependent on temperature range”). This third mechanism only modifies the concentration of the dissolved species constituent of the mineral. The second mechanism (freezing) compulsorily implies the third one (solubility change with T). Note that in general mineral solubility increases with temperature, but there are cases where it decreases (this is the case of Ca carbonates). Even worse the change in solubility with temperature is also related to the change in solution composition (all this is taken into account by the interplay between non-ideality and common ion effects). A mineral can see its solubility in pure water increasing with temperature, while it may behave in a totally different manner in highly concentrated solutions due to changes in the activity coefficient of the dissolved species.*

Authors: We have made the description of the third precipitation pathway (reduction of the solubility with temperature decrease) and we have explained the inter relation between this pathway and the solvent freezing pathway.

- *Referee Suggestion: I have not read the Zheng et al (2000) paper but a classification of evaporitic minerals according to their temperature of formation can only be related to the environmental and geological conditions of the salt deposit and cannot be an intrinsic*

property of such minerals. As such their temperature of formation may change from one setting to another.

Authors: We fully agree with Dr. Monnin in this point, nevertheless we wanted to cite this reference because we find it interesting as it is the first attempt to classify evaporites by their temperatures of formation. Certainly, salts precipitation is a complex process and obviously temperatures are just one of the factors, and this is the reason why we have included it in the last version of the manuscript.

- Referee Suggestion: The references on seawater evaporation are somewhat outdated. While the citation of Marion's work on seawater freezing is adequate, the authors should cite the papers of Harvie, Weare, Eugster and others who calculated the mineral sequences forming during the evaporation of seawater and who provided evaporation pathways resembling and updating those mentioned in Fig. 4. May be these references are included in Orti's papers (not available to me).

Dr. Monnin is right: Most of the relevant works about precipitation sequences from seawater evaporation appear referenced in Orti (2010), including those of Harvie, Weare, Hardie, Eugster etc. In any case, we have completed the revised manuscript with additional key references dealing with the precipitation sequences produced as a result of seawater evaporation.

- Referee Suggestion: In the discussion of the formation of salt deposits (like any sediment in fact), there are two things to distinguish (as the authors indicate in page 3234 line 5 et seq.): how the deposit itself has formed and how it has evolved afterwards. I think the paper could benefit from a description of the way the salt deposit has formed, i.e. expand section 2 "Study site", as far as there is any extensive study of the génesis of this deposit. For example, was the original environment marine? What is the subsequent role of continental waters? Etc.

We have completed the facies description and environmental interpretations in the revised version as both reviewers have suggested. We consider that this way there is a more detail information about the sedimentary system and environmental conditions where the salts were formed.

- Referee Suggestion: Do we have any idea of the composition of what the authors call the "mother brine"? The authors do describe the formation of salt deposits in other parts of the world in section 5, but it is a general point of view.

The precise composition of the mother brine from which sodium sulphate formed has been impossible to obtain as there is a diagenetic transformation of this mineral phase into thenardite. Ayllon-Quevedo et al. (2007), cited in the text, obtained the brine composition from the analysis of primary fluid inclusions of the gypsum deposits from the Intermediate Unit, higher up in the sequence, being a $\text{SO}_4\text{-Ca-(Na)-(Cl)}$ brine, with $\text{HCO}_3^- \ll \text{Ca}^{2+} + \text{Mg}^{2+}$. This brine composition is coherent with the recycling of Triassic and Cretaceous gypsum and halite deposits that crop out in the borders of basin.

1 Thenardite after mirabilite deposits as a cool climate indicator 2 in the geological record: lower Miocene of Central Spain.

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8 ABSTRACT

9 **Evaporites****Salt deposits** are commonly used as indicators of different paleoclimates
10 and sedimentary environments, as well as being geological resources of great economic
11 interest. Ordinarily the presence of **evaporites****salt deposits** is related to warm and arid
12 environmental conditions, but there are **evaporitic minerals****salts**, like mirabilite, that form by
13 cooling and a concentration mechanism based on cooling and/or freezing. The diagenetic
14 transformation of mirabilite into thenardite in the upper part of the lower Miocene unit of the
15 Tajo basin (Spain) resulted in the largest reserves of this important industrial mineral in
16 Europe. This unit was formed in a time period (~18.4 Ma) that, in other basins of the Iberian
17 Peninsula, is characterized by the existence of particular mammal assemblages appropriate to
18 a relatively cool and arid climate. Determining the origin of the thenardite deposits as related
19 to the diagenetic alteration of a pre-existing mirabilite permits the establishment and
20 characterization of the sedimentary environment where it was formed and also suggests use
21 as a possible analogue with comparable deposits from extreme conditions such as Antarctica
22 or Mars.

23 1.- Introduction

24 **Evaporites****Salt deposits** are natural chemical deposits that have significant economic,
25 scientific and social implications (Herrero et al., 2013; Warren, 2006). They constitute or
26 contain valuable geological resources such as industrial minerals and building materials, and
27 they are both source and cap-rock of hydrocarbons, etc. (Warren, 2010). It is commonly
28 accepted that most **evaporites****salt deposits** are formed under arid environmental conditions,
29 being that most salts are produced in hot arid climates. For some saline deposits this is the
30 case, but there are many examples in current settings being produced under arid but cool
31 conditions (Dort and Dort, 1970; Last, 1994; Socki et al., 2012; Stankevich et al., 1990; Zheng et
32 al., 2000) and a few are not really evaporites, although they may appear so, superficially, but
33 are pressure and thermal hydrothermal release precipitates (Chaboureau et al., 2012; Hovland
34 et al., 2006).

35 **Evaporites****Saline deposits** have proved to be very useful in the study of
36 paleoclimatology and sedimentology (Babel and Schreiber, 2014; Escavy et al., 2012; Fan-Wei
37 et al., 2013; Kendall, 1992; Lowenstein et al., 1999; Minghui et al., 2010; Rouchy and Blanc-
38 Valleron, 2009; Schreiber and El Tabakh, 2000; Warren, 2010). These studies are focused on
39 the relationship between the main periods of the Earth history with **evaporites****salt deposits**

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1 formation and climate, which is one of the key factors involved in their deposition. Particularly,
 2 continental deposits in arid closed basins may record very accurately the changes in
 3 paleoclimate, these being the most important factors the water inflow-outflow ratios,
 4 temperatures, wind patterns, storm records, and evaporation rates (Lowenstein et al., 1999).
 5 Comparison of evaporitesalt deposits from lake with marine records permits to develop land-
 6 sea correlations in the perspective of global reconstructions of environmental and climatic
 7 changes (Magny and Combourieu Nebout, 2013).

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8 Most studies point to evaporative concentration as the main mechanism controlling
 9 precipitation of salts. Evaporitic salts precipitate after salt saturation of brines, and indicate
 10 hydrological systems in which evaporative water loss is greater than water gain. An alternative
 11 way to concentrate brine is by cooling-freezing processes that removes water from it through
 12 ice formation. These two concentration mechanisms lead to two different salt formation
 13 pathways: evaporative and 'frigid' concentration (Strakhov, 1970). In addition, precipitation of
 14 certain salts occurs due to their reduction in solubility with temperature decrease (positive
 15 temperature coefficient of solution). The resultant minerals, like epsomite, sylvite and
 16 hexahydrate, are called cryophile salts (Stewart, 1963) or cryophilic salts (Sánchez-Moral et al.,
 17 2002). The main difference between evaporitesalt deposits formed under cool or hot
 18 temperatures is the resulting mineral assemblage (Zheng et al., 2000), indicating the high
 19 dependence of the resultant mineralogy on the mechanism of brine concentration.

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20 Sodium sulphate minerals appear to be highly dependent on temperature range (Dort
 21 and Dort, 1970) being the most common the anhydrous phase, Na_2SO_4 (thenardite), and two
 22 hydrated forms, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (sodium sulphate heptahydrate) and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite).
 23 Both thenardite and mirabilite occur extensively in nature, while the heptahydrate is
 24 metastable and does not form or become preserved as natural deposits (Dort and Dort, 1970).
 25 Attempts to classify evaporitic minerals by their temperature of formation was proposed by
 26 Zheng et al. (2000), with mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) being the typical product of cool periods,
 27 bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) for slightly warm phases, and thenardite (Na_2SO_4) being formed
 28 under warm conditions. This work has been the first attempt to classify minerals by their
 29 temperature of formation, but the precipitation of saline minerals should always be related to
 30 the environmental and geological conditions of the salt deposit because their temperature of
 31 formation may vary from one setting to another.

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32 Mirabilite, therefore, is the most common evaporitic mineral crystallizing under cool
 33 temperatures (Nai'ang et al., 2012; Wang et al., 2003; Zheng et al., 2000). An example is the
 34 mirabilite layers from the Huahai lake (China), were they precipitated under mean
 35 temperatures around 11 °C lower than current ones, during the Quaternary Younger Dryas
 36 event (Nai'ang et al., 2012). Thenardite, however, is the most common sodium sulphate found
 37 in ancient deposits (GarretGarrett, 2001), occurring mostly in Neogene continental endorheic
 38 settings (Warren, 2010). As a primary mineral, it forms either by direct precipitation from
 39 warm brines in shallow lakes (Last, 1994), either in/or near the surface of playas as capillary
 40 efflorescent crusts by evaporative concentration (Jones, 1965). It commonly occurs as thin
 41 layers interbedded with other evaporitic minerals forming salts assemblages (GarretGarrett,
 42 2001). In Lake Beida (Egypt), thenardite occurs as a 50 cm thick crust together with halite
 43 (NaCl), trona ($\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2(\text{H}_2\text{O})$) and burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$) (Shortland, 2004).

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1 Therefore, both mirabilite and thenardite precipitate in modern lacustrine systems
 2 whereas only thenardite appears as the prevalent sodium phase in the geological record (Ortí
 3 et al., 2002). Mirabilite is a very reactive mineral due to its low melting point and high
 4 solubility (GarretGarrett, 2001), being this the main reason of the lack of this mineral in
 5 ancient deposits. When the conditions where mirabilite has accumulated change (increase of
 6 temperature, evaporation rate, burial, interaction with concentrated salt solutions, etc.) it
 7 melts, dissolves, or is transformed into more stable minerals such as thenardite, astrakanite
 8 (bloedite), glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) or burkeite (GarretGarrett, 2001).

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9 The Oligocene-lower Miocene sequence of the Tajo basin contains a 100 to 650 meters
 10 thick succession of evaporitic materials (Calvo et al., 1989) that include one of the major
 11 thenardite deposits of the world (GarretGarrett, 2001). This paper presents the results of the
 12 analysis of this thenardite deposit and establishes its secondary origin as a transformation
 13 phase after mirabilite. As a result, we postulate that the thenardite level within the lower
 14 Miocene lacustrine sequence is a cool paleotemperature indicator. Therefore, we have been
 15 able to identify a decrease in temperature and precipitation regime in the Lower Miocene
 16 geological record of the Iberian Peninsula during which there also was a significant change in
 17 faunal diversity, coincident with the Mi-1a event of Miller et al., (1991) that took place 18.4 Ma
 18 that is well documented on a worldwide scale (Zachos et al., 2001).

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19 2. - Study site.

20 The Tajo basin, located in the central part of the Iberian Peninsula (Fig. 1), was formed
 21 during the Cenozoic by several basement uplifts (De Vicente et al., 1996). Growth strata
 22 related to syntectonic alluvial deposits appear in the margins of the basin and pass into
 23 lacustrine and palustrine deposits towards the centre (Calvo et al., 1989). Ordoñez and García
 24 del Cura (1994) defined four main units in the Neogene of the Tajo Basin: Lower or Saline Unit,
 25 Intermediate or Middle Unit, and Upper Miocene Units and the Pliocene Unit. Based on the
 26 study of core from several drillholes, they divided the Lower Unit into a Lower Saline Subunit
 27 that occupies a broad area of the Tajo basin, and the Upper Saline Subunit that contains the
 28 thenardite deposits, which is restricted to the area south of the Tajo River.

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Con formato: Fuente: Sin Negrita

29 During the lower Miocene (23.2-16.2 Ma), the Lower Unit was formed by syntectonic
 30 coarse alluvial detrital deposits located close to the tectonically active margins of the basin,
 31 gradually passing into finer clastic sediments (sandstones and shales) and wide saline lake
 32 systems that occupied the basin centre (Calvo et al., 1996). The saline deposits, a succession
 33 up to 500 m thick, is composed by alternating anhydrite, halite and glauberite beds with some
 34 thin layers of fine interbedded detritic sediments. This unit grades laterally into shale beds
 35 with abundant calcium sulphate nodules (of both gypsum and anhydrite), followed by coarser
 36 siliciclastic deposits that correspond to alluvial fans formed at the foot of the surrounding
 37 mountain ranges. To the south of the Tajo river valley, the upper part of the Lower Unit (Fig.
 38 2A, B) contains a massive deposit of thenardite, 7-12 m thick (Fig. 2B, C) (Ortí et al., 1979). This
 39 thenardite overlies a massive halite and decimetres-thick beds of glauberite. Thus, unlike the
 40 broadly-distributed glauberite, the deposit of thenardite is restricted to a relatively small area
 41 in the central part of the basin (Ordóñez et al., 1991). Above the thenardite layer, there is a
 42 several cm thick-layer of mirabilite, (several cm thick), product of recent hydration of the

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1 thenardite by meteoric water (Ortí et al., 1979). At the top of the Lower Unit there is a 10 to 20
 2 m thick alternation of layers (tens of cm) composed of secondary gypsum, both alabastrine
 3 (Fig.2D) and macro-crystalline (Fig. 2E), interbedded with shales and marls. This unit has been
 4 interpreted as a weathering cover, product of the replacement of glauberite and anhydrite by
 5 gypsum (Ordoñez and García del Cura, 1994). The top of the Lower Unit is established at a
 6 paleokarstic surface (Cañaveras et al., 1996).

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7 Higher up in the sequence, the Miocene Middle Unit is mostly composed of primary
 8 gypsum forming tabular beds up to 1 m thick (Fig. 2F). This unit passes upwards into abundant
 9 carbonate bodies and is characterised by the absence of evaporitic minerals such as halite or
 10 glauberite. During this period there was a significant progradation of siliciclastic sediments that
 11 reached the central part of the basin. Sedimentation during the Miocene Upper Unit was
 12 dominated by carbonates and marls (Calvo et al., 1996).

13 3. Materials and analytical methods

14 3.1. Sampling

15 A total of 30 samples have been collected from different levels of the evaporitic
 16 sequence, both from the ~~underground~~subsurface mine walls and from drilled cores provided
 17 by SAMCA, the company that owns the sodium sulphate deposit. The thenardite samples were
 18 collected from the mine face, while the halite-glauberite samples have been obtained from
 19 exploration drill cores. In order to avoid the alterations produced during drilling (by the
 20 interaction with drilling fluids, the pressure and heat transmitted by the coring bits, etc.) only
 21 the centremost part of the core has been used. Special care has been taken during sample
 22 preparation in order to prevent mineral alteration, avoiding high temperatures (>25 °C) and
 23 exposure to humid conditions.

Con formato: Fuente: Negrita

24 3.2. Optical microscopy and SEM analysis

25 For the petrographic study, rock samples were cut with an oil-refrigerated 1 mm thick
 26 diamond disc saw (Struers Discoplan-TS). A low viscosity oil was used (rhenus GP 5M) for
 27 cutting, grinding and polishing. When cutting samples in the disc-saw, extra rock was included
 28 at the cut (~ 1 mm) and was removed by hand grinding, thus eliminating any possible
 29 alteration of the samples. Grinding to the final thickness has been made using emery papers
 30 with different grit-sizes, impregnated with oil. Unconsolidated samples were previously
 31 indurated with a resin under vacuum (Struers Epofix Resin). The thin sections were glued on
 32 4.8 cm X 2.8 cm glass slides using LOCTITE 358, and cured afterwards under ultraviolet light.

33 Petrographic characterisation was performed using a Zeiss West Germany Optical 316
 34 Microscope (OM) at the Department of Petrology and Geochemistry of Complutense
 35 University of Madrid (UCM). By analysing the doubly polished plates it has been possible to
 36 undertake a petrographic characterization of fluid inclusions, determining the moment of
 37 formation in relation with the crystal growth.

38 Textural characterization of the samples was completed by Scanning Electron
 39 microscopy observations performed using a JEOL 6.400 instrument working at 20 kV 320
 40 Microscopy (SEM), at the CAI Geological Techniques Laboratory (UCM).

1 3.3. X-Ray Diffraction analysis

2 To obtain the whole rock mineralogy by X-ray diffraction, a portion of 20 of the 30
3 samples were ground in an agate mortar at low rotation speed (avoiding high temperatures). A
4 Bruker D8 Advance diffractometer equipped with a Sol-X detector was used. The mineralogical
5 composition of crystalline phases was estimated following Chun's (1975) method and using
6 Bruker software (EVA). The XRD analysis was performed at the Geological Techniques
7 Laboratory (UCM).

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8 3.4. Low Temperature Scanning Electron Microscopy (LTSEM).

9 This technique was used to assess the chemical composition of fluid inclusions and to
10 establish qualitatively and quantitatively the elemental characterization of the host minerals
11 and the fluid inclusions fluids (Ayora et al., 1994). Low Temperature Scanning Electron
12 Microscopy (LTSEM or Cryo-SEM) was performed in 20 fluid inclusions from 11 samples using
13 small pieces of thenardite and halite that were cut, mounted, and mechanically fixed onto a
14 specimen holder at room temperature. The instrument used was a CT 1500 Cryotrans system
15 (Oxford Instruments) mounted on a Zeiss 960 SEM. This study was done at the Spanish
16 Institute of Agricultural Sciences (ICA) of the CSIC.

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17 4.- Results

18 4.1. Mineralogy

19 The lower part of the Lower Unit sequence, below the thenardite deposit (Fig. 3A), is
20 characterised by evaporitic layers composed of a mixture of glauberite (45.8 %) and halite
21 (41.7 %) (Fig. 3B) with a minor content of polyhalite (7.8 %), dolomite (2.1%), and clay minerals
22 (1.8 %) (Table 1). This mineral assemblage is common in evaporitic Neogene continental basins
23 of the Iberian Peninsula such as those of the Zaragoza (Salvany et al., 2007) or the Lerín
24 Gypsum Formations (Salvany and Ortí, 1994), both in the Ebro basin (Spain). The relative
25 proportions of halite and glauberite are variable, with halite ranging between 30 % and 51 %
26 and glauberite between 23 % and 59 %. Glauberite crystals (Fig. 3B), with sizes between 1 mm
27 and 10 cm, occur either forming banded or nodular layers with abundant structures indicating
28 fluid-escape, or as irregular masses or nodules accompanying halite crystals in the halite-rich
29 horizons (Fig. 3B). No stratification or competitive growth typical of primary halite formation is
30 found. Therefore, a secondary origin of these halite crystals can be inferred.

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31 Higher up in the sequence a sharp change of mineralogy takes place passing upward
32 into a fairly pure and thick sodium sulphate body mainly composed of thenardite (96.5 %) with
33 a minor content of glauberite (2.5 %) and anhydrite (1.0 %) (Table 1). Thenardite (Fig. 3C)
34 occurs as cm-sized subeuhedral to anhedral crystals, with sizes from 1 mm to several cm,
35 forming aggregates. Crystal colour is also variable, ranging from blue to clear and transparent.
36 When crystals have a high volume of fluid inclusions, they have a cloudy aspect. Thenardite
37 layers usually present abundant fluid escape structures (Ortí et al., 1979).

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38 4.2. Fluid inclusion analysis

1 Fluid inclusions are abundant within the thenardite and halite crystals, whereas they
 2 are very scarce in the glauberite crystals. Most of them are primary fluid inclusions that were
 3 formed during the growth of the crystals. Therefore, the brine trapped in the primary fluid
 4 inclusions is the same from which these minerals precipitated. In the case of diagenetic
 5 minerals, fluid inclusions show the conditions of recrystallization rather than the conditions of
 6 formation of the precursor mineral (Goldstein and Reynolds, 1994). There appear to be few
 7 primary inclusions in the form of two-phase inclusions (containing gases or solids), most of
 8 them being single-phase aqueous liquid inclusions at room temperature.

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9 In this study only primary fluid inclusions have been analysed, established as primary
 10 by their relationship to the crystals growth zonation (Fig. 3D), mainly because voids that house
 11 these fluid inclusions are crystallographically regular (mimic crystal terminations) (Goldstein
 12 and Reynolds, 1994). Some sparse secondary fluid inclusions have been found aligned with/ or
 13 associated to fractures.

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14 The primary fluid inclusions chemical composition has been analysed by Cryo-SEM.
 15 Fluid aqueous inclusions analysed (15 analyses) in the thenardite crystals (Fig. 3E, F) have
 16 shown that systematically the only elements founds in the brine are Na and S (Fig. 3G). The
 17 composition obtained by analysing the fluid inclusions from the halite crystals (5 analyses) is
 18 Na and Cl with trace contents of Ca (Fig. 3H).

19 5.- Discussion

20 5.1. Dates and climate during the thenardite formation.

21 The formation of the many Cenozoic lacustrine systems in Spain was mainly controlled
 22 by the tectonic activity that affected the Iberian microplate and by changes in the
 23 paleogeography and paleoclimatic conditions of the Western Mediterranean- Eastern Atlantic
 24 zone (De Vicente et al., 1996). The base of the Lower Unit of the Miocene (the Lower Saline
 25 Subunit) of the Tajo basin is at the Oligocene-Miocene boundary (~23 Ma) and ends at top of
 26 the Burdigalian stage (~16 Ma) (Calvo et al., 1993). Paleoclimatic curves have been obtained
 27 through the study of mammal associations (Calvo et al., 1993; Daams and Freudenthal, 1988;
 28 Van der Meulen and Daams, 1992), and show that this period was warm and humid and
 29 became relatively more arid towards its end. Nevertheless, within this unit, the temperature
 30 and humidity curves for North Central Spain (Van der Meulen and Daams, 1992) show the
 31 existence of a stage where both temperature and humidity were reduced. The thenardite of
 32 this study appears within the sequence that corresponds to this time period. Previous authors
 33 (Calvo et al., 1996; Ordóñez et al., 1991) have interpreted the thenardite layer as the result of
 34 thermal evaporative concentration when the lake water volume was reduced, although they
 35 indicated that the environments required to follow this brine concentration path do not fit
 36 with the temperature and humidity curves proposed for that time span in other parts of the
 37 Iberian Peninsula. This difference in environmental conditions has been explained as the
 38 establishment of a microclimate in this area, placed in a "rain shadow" region that resulted
 39 from the uplift of the surrounding mountain belts (Ordóñez et al., 1991) and also the existence
 40 of highly concentrated brines sourced by recycling of older evaporites (Calvo et al., 1996).
 41 Ordoñez and García del Cura (1994) suggested, as one of the options for the formation of the

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1 thenardite deposit, that mirabilite formed within these lakes, could have been transformed
2 into thenardite during early diagenesis.

3 5.2. Cryophilic and Cryogenic salts Evaporative concentration versus frigid precipitation:
4 mineralogical criteria.

5 ~~There are salts that form in arid terrains due to evaporative concentration, but, there~~
6 ~~are other cases where the main precipitation driver is the brine cooling (cryophilic salts~~
7 ~~according to Borchert and Muir (1964)) and freezing (Salts precipitation from a given aqueous~~
8 ~~solution undersaturated with respect to a given mineral, can be achieved in three different~~
9 ~~ways: 1) removal of the solvent (water) at more or less constant temperature by evaporation~~
10 ~~(evaporative concentration); 2) removal of water by freezing, called frigid concentration,~~
11 ~~producing cryogenic salts according to Strakhov (1970);-; 3) change in temperature at constant~~
12 ~~salinity (or total concentration) producing the precipitation of cryophilic salts, according to~~
13 ~~Borchert and Muir (1964)). By the first two mechanisms there is an increase in the~~
14 ~~concentration of all the dissolved species leading to the formation of a brine. The third~~
15 ~~mechanism, related to changes in mineral solubility with temperature, only modifies the~~
16 ~~concentration of the dissolved species that constitute the precipitating mineral. The second~~
17 ~~mechanism (freezing) compulsorily implies the third one (solubility change with T) and~~
18 ~~therefore they should be able to happen together in natural environments.~~

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19 These distinct ~~ways~~ pathways of brine concentration result in two different pathways
20 of salts formation: by evaporation of the solvent (evaporative concentration) or by cooling ~~or~~
21 /freezing (frigid concentration). Nevertheless, the resulting mineralogy is obviously also
22 dependent on the ions content of the mother brine (Eugster and Hardie, 1978; Hardie and
23 Eugster, 1970).

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24 When a brine is concentrated by evaporation, the salt content increases, reaching
25 saturation and precipitating progressively from less soluble to more soluble minerals. If
26 evaporation continues, at the eutonic point all the remaining salts precipitate simultaneously.
27 In natural conditions with natural brines the eutonic point is reached at temperatures above
28 32 °C, with salinities between 35 % and 40 % (Strakhov, 1970).

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29 ~~Freezing~~ The freezing process concentrates the brine in ~~at the same way similar to as by~~
30 ~~evaporation, by removing H₂O from the solution, but in this case~~ in the form by formation of
31 ~~ice, leading to a concentrated residual brine as well as the progressive precipitation of saline~~
32 ~~minerals (Stark et al., 2003). Freezing ends when the eutectic or cryohydric point is reached, at~~
33 ~~the point when all compounds (including H₂O) pass to the solid state (Mullin, 2001). Depending~~
34 ~~on the initial mineralization and composition of the brine, the eutectic point is reached~~
35 ~~between -21 °C and -54 °C (Marion et al., 1999; Strakhov, 1970). The liquid brines, called~~
36 ~~cryobrines, are those that reach the eutectic point at temperature below 0 °C (Möhlmann and~~
37 ~~Thomsen, 2011), and such brines probably exist on Mars as well as in the Earth's polar regions.~~
38 ~~The minerals formed under these conditions are called cryogenic (Babel and Schreiber, 2014;~~
39 ~~Brasier, 2011)(Garrett, 2001).~~

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40 and probably on Mars (Peterson et al., 2007) . The minerals formed under these
41 conditions are called cryogenic (Babel and Schreiber, 2014; Brasier, 2011).

1 Sodium salts precipitate in nature by both mechanisms: 1) concentration of the brine
2 by solar-driven evaporation like in the Quaternary playas of the USA, and 2) by brine cooling/
3 and freezing, like in Kara Bogaz Gol in Turkmenistan, and the Great Plains of Canada (Last,
4 1994; Warren, 2010).

5 The different results obtained from the same brine, by using evaporative or frigid
6 concentration, can be illustrated with the different resultant mineral paragenesis obtained
7 from the sea water (Fig. 4A). Path 1 is the result of evaporative concentration: calcite (CaCO_3) –
8 gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) – halite (NaCl) and finally the bittern salts (K and Mg salts) (Harvie et al.,
9 1980; Ortí, 2010); path 2 is the result of frigid concentration: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) –
10 hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) – sylvite (KCl) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ – $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Dort and Dort, 1970).
11 Recently it has been proposed a new sequence of precipitation for frigid concentration of
12 seawater named the Gitterman pathway (Marion et al., 1999) that consist of mirabilite
13 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) – gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) – hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) – sylvite (KCl) and
14 $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, which also offers a significantly different mineral paragenesis to the one
15 obtained by evaporative concentration from sea water. Nevertheless, the final mineralogy that
16 is found in the geological record depends not only on the primary mineralogy, but on the
17 diagenetic history of the rock (Schreiber and El Tabakh, 2000).

18 *Precipitation of Mirabilite*

19 Attempts to classify evaporitic minerals by their temperature of formation have been
20 carried out by Zheng et al. (2000), with mirabilite being the typical product of cool periods,
21 bloedite for slightly warm phases and primary thenardite indicative of warm phases. If the
22 mean annual air temperature is lower than $-3\text{ }^\circ\text{C}$ it is possible for the newly created mirabilite
23 layers to persist (Wang et al., 2003). With at least 7 months of mean temperatures below $0\text{ }^\circ\text{C}$
24 it is possible to obtain thick mirabilite layers, although they are unstable through the rest of
25 the year and would not persist in time. Therefore, only thick mirabilite beds that have
26 undergone the temperature conditions necessary for the precipitation and preservation of this
27 mineral can be indicators of sustained cool periods (Minghui et al., 2010).

28 The sodium sulphate solubility curve shows a rapid decrease when the temperature
29 drops (Dort and Dort, 1970) resulting in mirabilite crystallization from concentrated brines
30 during cool temperature periods like in glacial periods or during fall and winter at high
31 latitudes. Thick beds of mirabilite are common in modern Canadian playa lakes (Last, 1994,
32 1984). Mirabilite may naturally crystallize even from diluted brines such as seawater if
33 temperature drops severely (GarretGarrett, 2001). This is the case in the McMurdo area,
34 Antarctica, where average air temperatures are about $-20\text{ }^\circ\text{C}$. Mirabilite precipitates at higher
35 temperatures from more concentrated brines (GarretGarrett, 2001). In the Ebeity Lake in
36 Siberia (Russia) mirabilite starts forming at the end of the summer when the brine
37 temperature drops below $19\text{ }^\circ\text{C}$ (Strakhov, 1970). When the environmental temperature of $0\text{ }^\circ\text{C}$
38 is reached, 70 %, of the mirabilite has already precipitated, and almost all the mirabilite has
39 formed when temperature reaches $-15\text{ }^\circ\text{C}$. If the brine continues freezing, hydrohalite
40 precipitates at $-21.8\text{ }^\circ\text{C}$ (Strakhov, 1970). We have recorded mirabilite currently precipitation in
41 Burgos (North Spain) at a height of 820 m a.s.l., under night-time temperatures between $-2\text{ }^\circ\text{C}$

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1 and 0 °C. At this location, mirabilite precipitates in ponds as microterraces (Fig. 4B, C) that
2 form from emergent groundwater that flows through Cenozoic glauberite deposits.

3 *Precipitation of thenardite*

4 From the range of sodium sulphate minerals, thenardite is the most commonly found
5 in ancient deposits (GarretGarrett, 2001). Thenardite can be formed as a primary mineral by
6 direct precipitation from warm brines in shallow lakes (Last, 1994), or as capillary efflorescent
7 crusts in playas with sulphate-rich waters (Jones, 1965). Primary thenardite normally occurs
8 together with many other evaporitic minerals forming salts assemblages (GarretGarrett, 2001),
9 usually as layered evaporite deposits like in Lake Beida, Egypt (Shortland, 2004). According to
10 Lowenstein and Hardie (1985), layered evaporites can accumulate in: (1) ephemeral saline
11 pans, (2) shallow perennial lagoons or lakes, and (3) deep perennial basins. Evaporitic
12 sediments occurring in saline pans consist of centimetre scale crystalline salt levels, alternating
13 with millimetre to centimetre scale detrital siliciclastic-rich muds. Thenardite precipitating in
14 modern saline pans appears associated to halite, gypsum, mirabilite, epsomite and trona
15 (Lowenstein and Hardie, 1985) and there are no thick deposits of pure thenardite described in
16 the literature as being formed as a primary deposit. Lake Beida (Egypt) contains the purest
17 primary thenardite deposit in the world, reaching 60% of thenardite at some locations, with
18 variable contents of halite (up to 60%), sodium carbonate (trona, up to 14%), sodium
19 bicarbonate (nahcolite, up to 16%) and minor amounts of other K, Ca and Mg salts (Nakhla et
20 al., 1985).

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21 Instead, thenardite can be formed by the transformation of other minerals during
22 diagenesis (secondary thenardite), being the most common case the mirabilite dehydration by
23 increasing temperature, evaporation rate, burial, or by interaction with NaCl-concentrated
24 brines (Last, 1994).

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25 *Transformation Mirabilite - Thenardite*

26 Mirabilite is a very reactive mineral due to its low melting point and high solubility
27 (GarretGarrett, 2001). This high reactivity is the main reason of the lack of this mineral in
28 ancient deposits because when the conditions of formation of mirabilite change, it usually
29 dissolves or is transformed into other more stable minerals such as thenardite (GarretGarrett,
30 2001). The mirabilite to thenardite transformation commonly takes place at about 32.4 °C, but
31 in the presence of NaCl this transition occurs at approximately 18 °C and drops down to 16 °C if
32 Mg²⁺ is present (Charykova et al., 1992). The impact of additional ions within the solution in
33 the transition temperatures in the sodium sulphate system is due to the double salt effect
34 (Warren, 2010). The transformation of mirabilite into thenardite may occur soon after
35 deposition (in the early diagenesis) or later, when the change in the conditions makes
36 mirabilite unstable, for example by compaction during burial (GarretGarrett, 2001). An
37 example of an early diagenesis transformation is found in Kuchuk Lake (Russia) where
38 mirabilite precipitates during the cool winters, and, during summers, the level of the lake
39 drops due to evaporation and becomes NaCl saturated producing the transformation into
40 thenardite (Stankevich et al., 1990). Mirabilite can also be transformed into thenardite directly
41 by heating upon burial (Warren, 2010). The water of crystallization of mirabilite, which escapes
42 during the transformation into thenardite, produces fluid escape structures within the

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1 sedimentary sequence. Part of this water also may be trapped as fluid inclusions within the
2 emerging thenardite crystals.

3 *Sedimentology and diagenesis*

4 There are several characteristics that indicate that mirabilite is the precursor
5 mineralogy of the thenardite beds from the lower Miocene deposits of the Tajo basin. Textural
6 features (Ordoñez and García del Cura, 1994; Ortí et al., 1979), mineral assemblage and fluid
7 inclusion chemistry presented in this study suggest this mineral progression. This information,
8 combined with paleontological evidence, is indicative of the existence of cool and arid
9 environmental conditions at the time of formation, and therefore, it can be correlated with a
10 time period having these characteristics.

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11 The thenardite deposit of the Tajo basin commonly occurs as large crystals in thick and
12 fairly pure layers that present fluid escape structures. The thenardite deposit appears as
13 interbedded layers of pure thenardite (cm to m thick) with thin intercalations of black shales
14 (Ortí et al., 1979), similar to the sequence described in Lake Kuchuk in the Volga region of
15 Russia (Stankevich et al., 1990). No textural characteristics such as dissolution (flooding stage),
16 crystal growth (saline lake stage), or syndepositional diagenetic growth features (a desiccation
17 stage) (Lowenstein and Hardie, 1985) have been found in the Tajo basin thenardite deposit,
18 which would indicate a primary thenardite origin within a salt-pan environment. Instead, there
19 appears fluid escape structures that are indicative of the fluids produced during the mirabilite
20 dehydration and transformation to thenardite.

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21 *Fluid inclusions*

22 Primary fluid inclusions within evaporitic minerals contain and preserve samples of the
23 brine where the crystals were growing. In our case, the chemistry of the fluid inclusions is
24 mainly chlorine and sodium within the halite fluid inclusions, and sulphur and sodium within
25 the thenardite ones. This is not surprising because, in aqueous fluid inclusions occurring in very
26 soluble minerals, like the ones under study, the chemistry of the aqueous solution will very
27 rapidly come to equilibrium with the surrounding mineral. Therefore, the fluid inclusion
28 chemistry will contain a relevant amount of the ions forming the hosting minerals. The most
29 common mineral precursor for diagenetic thenardite is the original hydrated sodium sulphate
30 (mirabilite) (Dort and Dort, 1970). Part of the water of crystallization escapes, but another part
31 may be trapped in the fluid inclusions that are formed during the growth process of the
32 resulting thenardite crystals. The chemical composition of such aqueous inclusions should be
33 exclusively water and ions from the hosting mineral (in this case sodium and sulphate).

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34 Previous studies of fluid inclusions in other primary salts of the Cenozoic sequences of
35 the Tajo basin show a broad range of cations defining a mother brine rich in Ca^{2+} , Na^+ , Mg^{2+}
36 and K^+ (Ayllón-Quevedo et al., 2007). The fluid inclusions, within the thenardite crystals,
37 exclusively contain the same ions as the host mineral (sodium and sulphate), highlighting the
38 lack of any trace of K^+ , that would be the last ion to combine in this kind of brines. This is
39 evidence of thenardite being a diagenetic product (secondary mineral) formed after a
40 precursor mineralogy. A similar mechanism could explain the chemistry of the halite fluid
41 inclusions, in this case being produced by the dehydration of hydrohalite, another salt formed

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1 in severe cool environments, although the origin of the halite in the Tajo Basin sequence is still
2 under study.

3 Consequently, based on the textural patterns of the thenardite crystals, the internal
4 arrangements of the sedimentary structures and the ionic content of the fluid inclusions, the
5 thenardite deposits of the Tajo basin are clearly a diagenetic product of a precursor mirabilite,
6 which had to be formed under cool temperature conditions.

7

8 5.3. Cool and arid climate indicator

9 The Lower Unit of the Miocene in the Tajo basin (~23-16 Ma) (Alberdi et al., 1984;
10 Calvo et al., 1993) is subdivided into different stages based on mammal associations (Daams et
11 al., 1997). The time span of the lower Miocene sequence of other Iberian basin (Calatayud-
12 Teruel basin, 200 km to the north-east of the Tajo basin) corresponds to Zone A (~22-18 Ma)
13 (Van der Meulen and Daams, 1992) established on the basis of particular stages of evolution of
14 rodents and other species (Daams et al., 1997). The fauna from the younger part of this unit is
15 characterized by the existence of a particular *Gliridae* (a dormouse) that lived in forest or open
16 forest environments, as well as other rodent taxocenoses, which are dominated by *Eomyids* of
17 the genus *Ligermimys*. Zone A is thought to be humid, although there is a change to drier and
18 relatively cooler conditions towards the top of the zone (~18.4 Ma). At this moment, the
19 number of specimens decreases significantly, and it appears a higher percentage of
20 *Peridyromys murinus* (46%), a specie that shows abundance in higher latitudes because of its
21 greater tolerance to lower temperatures than other species such as *Mycrodyromys* (present at
22 a 3%), a thermophile taxon that disappears during cooling events (Daams et al., 1997). During
23 this same time interval, in other parts of Europe a noticeable increase in mesothermic plants
24 and high-elevation conifers has been documented, interpreted as a result of climate cooling
25 possibly caused by Antarctic glaciations or by uplift of surrounding mountains (Kuhlemann and
26 Kempf, 2002; Utesche et al., 2000), process even favoured by the progressive movement of
27 Eurasia towards northern latitudes as a result of the northward collision of Africa.

28 Among other characteristics, it is of great importance to point out that during the
29 upper part of the lower Miocene there is a marked fauna turnover, with the appearance of
30 new mammals such as *Anchitherium*, the first *Proboscideans*, etc. (Morales and Nieto, 1997).
31 The existence of turnover cycles in rodent faunas from Spain (periods of 2.4 to 2.5 and 1 Ma)
32 appears related to low frequency modulations of Milankovitch-controlled climate oscillation
33 (Van Daam et al., 2006). The Earth's climate and its evolution, studied by the analysis of deep-
34 sea sediment cores, experiences gradual trends of warming and cooling, with cycles showing
35 10^4 to 10^6 years rhythmic or periodic cyclicity are explained as related to variations of orbital
36 parameters such as eccentricity, obliquity and precession that affect the distribution and
37 amount of incident solar energy (Zachos et al., 2001). Obliquity nodes and eccentricity minima
38 are associated with ice sheet expansion in Antarctica that altered precipitation regimes
39 together with cooling and aridity. These climatic changes produce perturbations in terrestrial
40 biota through reduced food availability (Kuhlemann and Kempf, 2002; Utesche et al., 2000;
41 Van Daam et al., 2006).

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1 The Oligocene-Miocene boundary (~23 Ma) corresponds to a brief (~200 ky), but deep,
 2 ~~Anctarctic~~~~Antarctic~~ glacial maximum, referred as Mi-1 (Fig. 5), followed by a series of
 3 intermittent but smaller phases of glaciation (Mi-events) where maximum ice-volume took
 4 places at the scale of over 100 kyr in the East Antarctic continent (Mawbey and Lear, 2013).
 5 The Mi-1 event was accompanied by a series of accelerated rates of turnover and speciation in
 6 certain groups of biota, such as the extinction of Caribbean corals at this boundary. This limit is
 7 accompanied by sharp positive carbon isotopes excursions that suggest perturbations of the
 8 global carbon cycle (Fig. 5). Correlating the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of deep-sea sediment cores
 9 with sea-level calibrations has shown that during the early Miocene the ice volume ranged
 10 between 50% and 125% of the present day (Pekar and DeConto, 1996). Tectonic changes such
 11 as the opening of the Drake Passage may have modify portions of the planets ocean circulation
 12 system, promoting synchronous global cooling trends (Coxall et al., 2005). The cold water from
 13 the southern Atlantic and abyssal Pacific basins (Lear et al., 2004) mixed with a warm deep-
 14 water mass located in the Atlantic and Indian oceans (Billups et al., 2002; Wright and Miller,
 15 1996). Wright and Colling (1995) estimated that during these glacial periods there was a
 16 temperature gradient of up to 6 °C, larger than observed today (~3-4 °C). The influence of this
 17 temperature drop at a global scale could have had some influence in the precipitation of
 18 cryophilic and even cryogenic salts from salts concentrated brines during these particular
 19 moments at the Iberian Peninsula latitudes.

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20 Hence, in the upper part of the sedimentary sequence of the Lower Unit, the presence
 21 of a higher proportion of species with high tolerance to cool climatic conditions, and the
 22 lowering of the individual count and species variety indicate the existence of a climatic change
 23 into a cool and arid period within the Iberian Peninsula (~18.4 Ma). This age appears to
 24 coincide with a global Mi-1ab event (Miller et al., 1991) that represented an interval of ice
 25 expansion, at least in East Antarctica. The global low temperature and arid conditions of the
 26 environment could have been magnified in this area by its continental character and the
 27 regional uplift of the surrounding mountains that left this area at a higher altitude and within a
 28 "rain shadow" region. In addition, recycling of ancient saline formations provide concentrated
 29 brines which promotes the precipitation of mirabilite at even higher temperatures. Higher up
 30 in the sequence, the gypsum deposits were formed by evaporative concentration of the saline
 31 brines as a result of the climate warming indicated the temperature curves that show the
 32 trend towards the Miocene optimum (Zachos et al., 2001).

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33 6.- Conclusions

34 The appearance of thick, pure thenardite beds in the geological record can be used as
 35 a paleoclimate indicator of cool and arid periods. By fieldwork analysis and laboratory
 36 techniques we have described a way to establish the diagenetic character of the thenardite
 37 deposits formed after a mirabilite precursor, a salt that is well known to form under cool and
 38 arid weather conditions. Mirabilite deposits require a sustained period of time to develop,
 39 with a fairly continuous, persistent period of a cool climate because it is normally formed
 40 during a frigid-concentration process. This mechanism of formation has led to the
 41 development of a typical salt paragenesis and its fingerprint is recorded within the
 42 geochemistry of its fluid inclusions.

1 The establishment of the age of this unit, based on mammal assemblages, has
2 permitted us to determine the existence of a relatively cool and dry period from a lacustrine
3 record that correlates with an Antarctic ice expansion “Mi” event (Mi-1ab that took place
4 ~18.4 Ma) determined from marine deposits and established at a global scale by isotope
5 studies. This period represents a moment of the expansion of, at least, the East Antarctic ice
6 sheet. This expansion has been interpreted to be related to changes in the Earth’s orbital
7 parameters such as obliquity and eccentricity that even control the turnover cycles of different
8 biotas, as appears to be the case in the Iberian Peninsula. Therefore, the correlation of
9 terrestrial and marine records contributes to a more precise knowledge of environmental and
10 climatic changes at a global scale.

11 Hence, the lacustrine deposits of the upper part of the Lower Unit of the Tajo Miocene
12 succession do not require a regressive sequence of a lacustrine system due to the reduction of
13 water by desiccation alone (due to intense evaporation). Instead, the mirabilite was formed in
14 a lake with high Na^+ and SO_4^{2-} saturated waters. At a time period where temperature was
15 subject to a significant decrease and aridity became a key factor (~18.4 Ma), the brines were
16 concentrated by cooling-freezing mechanism that led to the formation of thick well-
17 differentiated mirabilite layers, which later were diagenetically transformed to thenardite.

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1 Figure 1. A) Location of the Tajo basin in the center part of the Iberian Peninsula. B)
 2 Simplified geological map of the Tajo Basin and surrounding mountain belts (modified from the
 3 Spanish Geological Map, scale 1:50.000, IGME, 2013). The thenardite deposits appear near the
 4 village of Villarrubia de Santiago. C) General view of the upper part of the Lower Unit and the
 5 base of the Middle Unit of the Miocene sequence of the Tajo basin in Villarrubia de Santiago
 6 area. The thenardite deposit is laterally continuous for 10's of kms, although, due to the high
 7 solubility of the thenardite, it is not easily ~~appreciated~~identified at all locations.

8 Figure 2. A) Stratigraphic section of the upper part of the Lower Unit and the
 9 lowermost part of the Middle Unit of the Miocene in the Tajo basin. B) General view of the
 10 Lower Unit outcropping along the current Tajo river (south bank). C) Outcrop view of the
 11 contact between the upper part of the thenardite body and the overlaying unit with secondary
 12 gypsum. This secondary gypsum appears as two main lithofacies: D) alabastrine gypsum, and
 13 E) macro-crystalline gypsum (the coin for scale has 2.2 cm of diameter). F) Outcrop of the
 14 detritic gypsum beds that compose the lower part of the Middle Unit.

15 Figure 3. A) Thenardite crystal under thin section (crossed nicols) with a splintery
 16 fracture along cleavage planes. B) Photomicrograph of idiomorphic crystals of glauberite (Gl)
 17 cemented by halite (Ha) (crossed nicols). C) SEM image of a thenardite crystal showing
 18 splintery fractures along cleavage planes. D) Photomicrograph of primary fluid inclusions in a
 19 thenardite crystal mimicking the thenardite crystal termination. E) and F) Frozen fluid inclusion
 20 within thenardite crystals studied by Cryo-SEM SEM. G) EDX spectrum of a fluid inclusion in a
 21 thenardite crystal with sodium and sulphate as the only ions present, analysed by Cryo-SEM.
 22 H) Cryo-SEM EDX spectrum of a fluid inclusion in the halite, containing sodium, chlorine and a
 23 low quantities of sulphate and calcium ions.

24 Fig.4. A) Mineral precipitation sequences from sea water depending on the
 25 concentration mechanism. Arrow shows the sense of precipitation. Left scale (logarithmic)
 26 shows the percentage of remaining brine during the concentration process. Evaporative
 27 concentration sequence defined by Orti (2010) and frigid concentration by from Dort and Dort
 28 (1969). B) and C) Mirabilite precipitation in a pond near a Na₂SO₄-rich water spring in Belorado
 29 (Burgos, Spain). Photographs taken early in the morning after three days of continuous cool
 30 temperatures (30/11/2011). General view of the mirabilite pond (B). See coin as scale scale
 31 (diameter 1.8 cm). Detail of the mirabilite crystals (C).

32 Figure 5. Correlation of the Oligocene-Miocene of the global deep-sea carbon and
 33 oxygen isotope curves of Zachos et al., (2001), with the Haq et al., sea level curve (Haq et al.,
 34 1987). The main significant ages of the Miocene oxygen isotope events (Mi-events) are shown
 35 (Miller et al., 1991). The green Mi 1 event corresponds to the Oligocene_ Miocene glaciation
 36 produced during the Olig-Miocene limit. The red line corresponds to the Mi-1ab, time at what
 37 the mirabilite deposits (thenardite precursor) of the Tajo basin were formed. The absolute
 38 ages are relative to the USGS Chronostratigraphic Chart (2013)

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40

1 Table 1.- XRD mineralogical composition of the samples .

| Halite - Glauberite Layer | | | | | | | |
|---------------------------|------------|-------------|-------------|------------|------------|-----------|------------|
| Sample ID | Thenardite | Glauberite | Halite | Polyhalite | Dolomite | Anhydrite | Clay Min. |
| 522116-01 | - | 45.7 | 30.2 | 19.6 | 2.6 | - | 0.0 |
| 522116-02 | - | 23.5 | 51.1 | 12.1 | 5.9 | - | 7.4 |
| 522116-03 | - | 54.9 | 45.1 | 0.0 | 0.0 | - | 0.0 |
| 522116-04 | - | 59.4 | 40.6 | 0.0 | 0.0 | - | 0.0 |
| 522116-10 | - | 51.5 | 47.5 | 0.0 | 0.0 | - | 1.0 |
| Mean | - | 47.0 | 42.9 | 6.3 | 1.7 | - | 1.7 |

| Thenardite Layer | | | | | | | |
|------------------|-------------|------------|--------|------------|----------|------------|-----------|
| Sample ID | Thenardite | Glauberite | Halite | Polyhalite | Dolomite | Anhydrite | Clay Min. |
| 522116-05 | 100.0 | 0.0 | - | - | - | - | - |
| 522116-06 | 91.3 | 5.5 | - | - | - | 3.2 | - |
| 522116-07 | 99.0 | 1.0 | - | - | - | - | - |
| 522116-08 | 95.8 | 3.2 | - | - | - | 1.0 | - |
| 522116-09 | 99.0 | 1.0 | - | - | - | - | - |
| 522116-11 | 95.0 | 3.6 | - | - | - | 1.4 | - |
| 522116-12 | 91.3 | 5.5 | - | - | - | 3.2 | - |
| 522116-13 | 99.5 | 0.5 | - | - | - | - | - |
| 522116-14 | 99.0 | 1.0 | - | - | - | - | - |
| 522116-15 | 94.6 | 3.8 | - | - | - | 1.6 | - |
| 522116-16 | 92.9 | 5.0 | - | - | - | 2.1 | - |
| 522116-17 | 100.0 | - | - | - | - | - | - |
| 522116-18 | 94.5 | 4.4 | - | - | - | 1.1 | - |
| 522116-19 | 98.2 | 1.0 | - | - | - | 0.8 | - |
| 522116-20 | 97.3 | 1.7 | - | - | - | 1 | - |
| Mean | 96.5 | 2.5 | - | - | - | 1.0 | - |

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