

Messinian evaporites in the Polemi Basin (South Cyprus): $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotope geochemistry

Evaporitas Messinienses de la cuenca de Polemi (Sur de Chipre): Geoquímica isotópica $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$ y $\delta^{18}\text{O}$

David Artiaga Torres¹, Javier García Veigas¹, Dioni I. Cendón³ and Luis Gibert Beotas²

¹ CCiTUB Scientific and Technological Centers, Universitat de Barcelona, 08028 Barcelona, Spain

² Departament de Geoquímica, Petrologia i Prospecció Geològica, Universitat de Barcelona, 08028 Barcelona, Spain.

³ ANSTO, Australian Nuclear Science and Technology Organisation, Kirrawee DC, NSW 2232, Australia.

* Corresponding author

ABSTRACT

The Polemi basin (S Cyprus) records a well exposed Messinian Salinity Crisis (MSC) evaporite succession divided into three lithostratigraphic units: Lower Gypsum, Intermediate Gypsum Breccia, and Upper Gypsum. Sulfate isotope compositions of the Lower Gypsum show values in range with MSC Lower Evaporites outcropping in other Mediterranean basins. However, the Intermediate Gypsum and the Upper Gypsum show an enrichment of ~5‰ in $\delta^{18}\text{O}$, with respect to the Lower Gypsum unit, as reported in MSC Upper Evaporites outcropping in Sicily and cored in DSDP-ODP sites. Similarly, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Lower Gypsum unit are also in range with MSC Lower Evaporites, while values in the Intermediate and Upper Gypsum units are coincident with those reported for MSC Upper Evaporites of Sicily and of foredeep sites. These geochemical values question the currently more accepted MSC chronostratigraphic model in which clastic (resedimented) gypsum is assigned as prior to the Upper Evaporites.

Key-words: Messinian Salinity Crisis, Polemi basin, geochemistry, evaporites.

RESUMEN

La cuenca de Polemi (S Chipre) presenta una sucesión evaporítica de la Crisis de Salinidad Messiniense dividida en tres unidades litostratigráficas: Yeso Inferior, Yeso brechificado Intermedio y Yeso Superior. La composición isotópica del sulfato del Yeso Inferior muestra valores en el rango de las Evaporitas Inferiores aflorantes en otras cuencas Mediterráneas. Sin embargo, el Yeso Intermedio y el Yeso Superior muestran un enriquecimiento del ~5‰ en $\delta^{18}\text{O}$, respecto al Yeso Inferior, lo que también ha sido registrado en las Evaporitas Superiores de la MSC solo aflorantes en Sicilia y perforadas en sondeos DSDP-ODP. Las relaciones $^{87}\text{Sr}/^{86}\text{Sr}$ en el Yeso Inferior también están en el rango de las Evaporitas Inferiores, mientras que los valores del Yeso Intermedio y del Yeso Superior son coincidentes con las obtenidas en las MSC Evaporitas Superiores de Sicilia y de sondeos profundos. Estos valores geoquímicos ponen en cuestión el actualmente más aceptado modelo cronoestratigráfico de la MSC en el que depósitos de yeso clástico (resedimentado) son asignados como anteriores a las Evaporitas Superiores.

Palabras clave: Crisis de Salinidad Messiniense, cuenca de Polemi, geoquímica, evaporitas.

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Introduction

The Messinian Salinity Crisis (MSC) across the Mediterranean resulted in the deposition of large volumes of evaporites in marginal shallow basins, as well as in offshore intermediate and deep Mediterranean basins (Hsü *et al.*, 1973; Krijgsman *et al.*, 1999; Manzi *et al.*, 2013).

In the last years, the proliferation of numerical models without strong geological background and arguable seismic profile interpretations, have led to the publication, in high impact research journals, of speculative MSC desiccation and refilling simulations. The appeal of these models is also captured by newspapers and is the object of cultural dissemination exhibitions.

However, the development of an en-

compassing stratigraphic model for the MSC across the Mediterranean has been a challenge for decades. This is due to the difficulty to establish a stratigraphic and genetic model. Additionally, challenging geological correlations between outcropping circum-Mediterranean MSC evaporite successions and limited deep offshore core drillings (DSDP-ODP sites) have hindered the development of a comprehensive stratigraphic model for the MSC.

Messinian evaporites were originally subdivided into a "two-step" informal division (Rouchy and Caruso, 2006 and references therein): Lower Evaporites (including Lower Gypsum and Halite Units) and Upper Evaporites (Upper Gypsum Unit). More recently, a different chrono-stratigraphic division of the MSC proposed a three-stage model (CIESM, 2008; Roveri *et al.*, 2014): The first stage

is characterized by the deposition of in situ primary evaporites (Primary Lower Gypsum – PLG, Roveri *et al.*, 2008). The second stage is represented by thick halite deposits in some marginal basins and by deep-water clastic evaporites derived from the dismantling of Primary Lower Gypsum deposits (Resedimented Lower Gypsum – RLG). During the third stage, similar depositional settings to the PLG resulted in the formation of primary in situ evaporites (Upper Gypsum – UG) (Manzi *et al.*, 2009; Roveri *et al.*, 2014; García-Veigas *et al.*, 2018). Both chrono-stratigraphic frameworks proposed for the MSC are, at their core, mainly comparing MSC evaporite successions in Sicily, with seismic profiles under the floor of the Mediterranean.

The Upper Evaporites – Upper Gypsum only outcrop in Sicily and Cyprus.

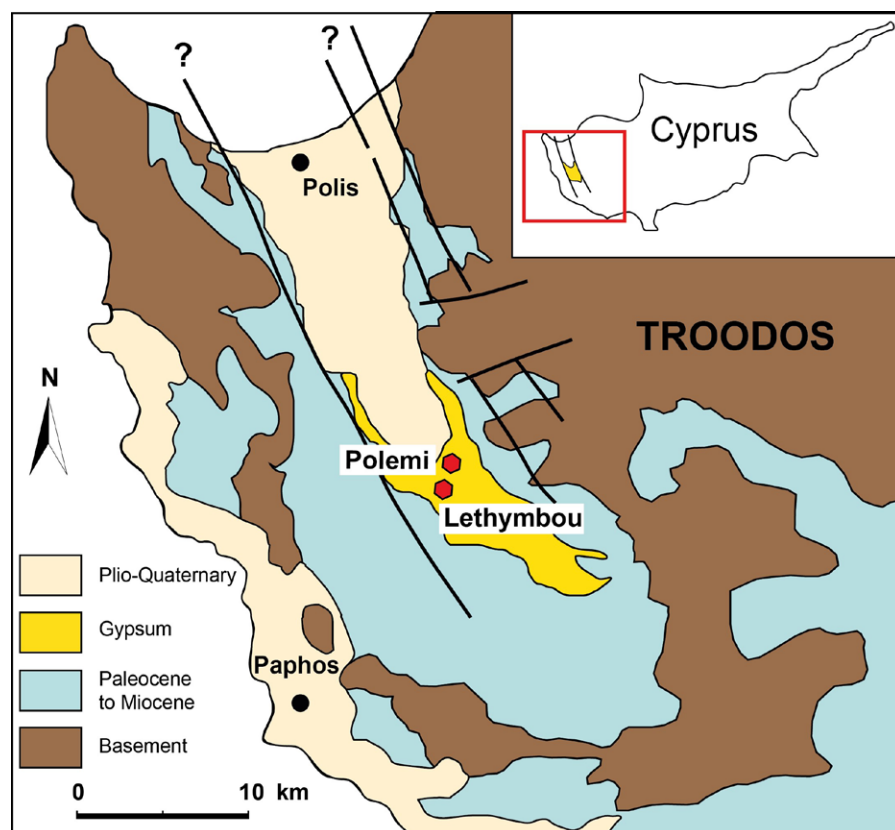


Fig.1.- Simplified geological map of the Polis graben with the location of the studied stratigraphic sections in the Polemi basin (Modified from Robertson *et al.*, 1995). See color figure in the web.

*Fig.1.- Mapa geológico simplificado del graben de Polis con la localización de las secciones estratigráficas estudiadas en la cuenca de Polemi (Modificado de Robertson *et al.*, 1995). Ver figura en color en la web.*

The recent litho- and chemostratigraphic analysis of MSC evaporite successions of Mesoarea basin put into question this assignation in North Cyprus (Artiaga *et al.*, 2021). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of MSC evaporites, from outcropping circum-Mediterranean basins and from DS-DP-ODP sites, show characteristic values of ~ 0.7089 in Lower Evaporites (PLG and RLG) and of ~ 0.7087 in Upper Evaporites (UG) (Müller and Mueller, 1991, García-Veigas *et al.*, 2018).

The isotope compositions of dissolved sulfate in seawater and that of related marine-precipitated gypsum have changed through geological times. Although similar $\delta^{34}\text{S}_{\text{sulfate}}$ values, $\sim 23\text{‰}$, characterize all MSC gypsum deposits, marked differences in $\delta^{18}\text{O}_{\text{sulfate}}$ permit distinguishing between Lower Evaporites (PLG and RLG) units, which show values of $\sim 14\text{‰}$, and Upper Evaporites (UG), with values of $\sim 17\text{--}19\text{‰}$. Both $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}_{\text{sulfate}}\text{--}\delta^{18}\text{O}_{\text{sulfate}}$ are excellent geochemical markers to propose stratigraphic correlations between MSC evaporites (Roveri *et al.*, 2014b) wherein paleontological and magneto-stratigraphic correlations are not available.

Previous work on the MSC succession of the Polemi basin has provided important insights on the MSC evolution, mostly based on stratigraphy, facies analysis (Gass, 1960; Gass and Cockbain, 1962; Robertson *et al.*, 1995) and Sr isotopic data (Manzi *et al.*, 2016). Nonetheless, an accurate chemostratigraphic analysis has not been carried out yet, being necessary for a better understanding of the sedimentation and distribution of MSC evaporites in the easternmost Mediterranean basins.

The aim of this work is to report an accurate chemostratigraphic profile from one of the most continuous Messinian evaporite succession in the eastern Mediterranean and discuss results within the frameworks proposed for western and central Mediterranean MSC deposits.

Messinian evaporites of the Polemi basin

The Polemi basin, located on SW of Cyprus, corresponds to the southern part of the Polis graben (Fig. 1), a fault complex bounded to the north and south by major normal faults (Payne and Robertson,

1995). The basin is filled with early Miocene - Pliocene sediments. The complete MSC evaporite succession of the Polemi basin outcrops between the Lethymbou and Polemi sections and consists of up to 110 meters of gypsum. This can be subdivided into two main gypsum units separated by a chaotic gypsum interval: the Lower Gypsum unit, Intermediate Gypsum Breccia and the Upper Gypsum unit.

The Lower Gypsum, up to 40 meters thick, consists of a gypsum sequence made up of clastic gypsum lithofacies including gypsilitites, gypsarenites and gypsrudites, and finely laminated gypsum (locally named "marmara" type), interbedded with marls and diatomite beds. Scattered selenite clusters of vertically-oriented or non-oriented twinned gypsum crystals (cm-size) are growing within fine-grained laminated gypsum and gypsilitite beds.

The overlying Intermediate Gypsum Breccia, ranging in thickness from 5 to 10 meters, is a chaotic gypsum interval ('Marmara chaotic' of Manzi *et al.*, 2016) made up of brecciated fine-grained laminated gypsum. This gypsum interval is derived from the resedimentation of laminated gypsum lithofacies.

The Upper Gypsum unit, up to 60 meters thick, includes up to six gypsum beds (Rouchy, 1982) interbedded with marls and diatomites. The first two beds are characterized by selenite gypsum lithofacies alternating banded stacked selenite beds with swallowtail selenite facies. The upper beds of this evaporite unit are made up of alternations of finely laminated gypsum, gypsarenites and minor selenite lithofacies. Abundant gastropod and mollusk assemblages are found in the uppermost gypsum bed, similar to those reported from other Mediterranean basins in the latest intergypsum intervals and post-evaporitic deposits (Rouchy *et al.*, 2001; Andreetto *et al.*, 2021).

Samples for isotope analyses were recovered from the Lethymbou and Polemi sections (Rouchy, 1982, Manzi *et al.*, 2016). See in Artiaga *et al.* (2021) for analytical methodology and accuracy.

Sulfate isotope compositions

Isotopic sulfate data of the MSC evaporite succession in the Polemi basin show significant differences between the stratigraphic Lower Gypsum, Intermediate Gypsum Breccia and Upper Gypsum units (Fig. 2).

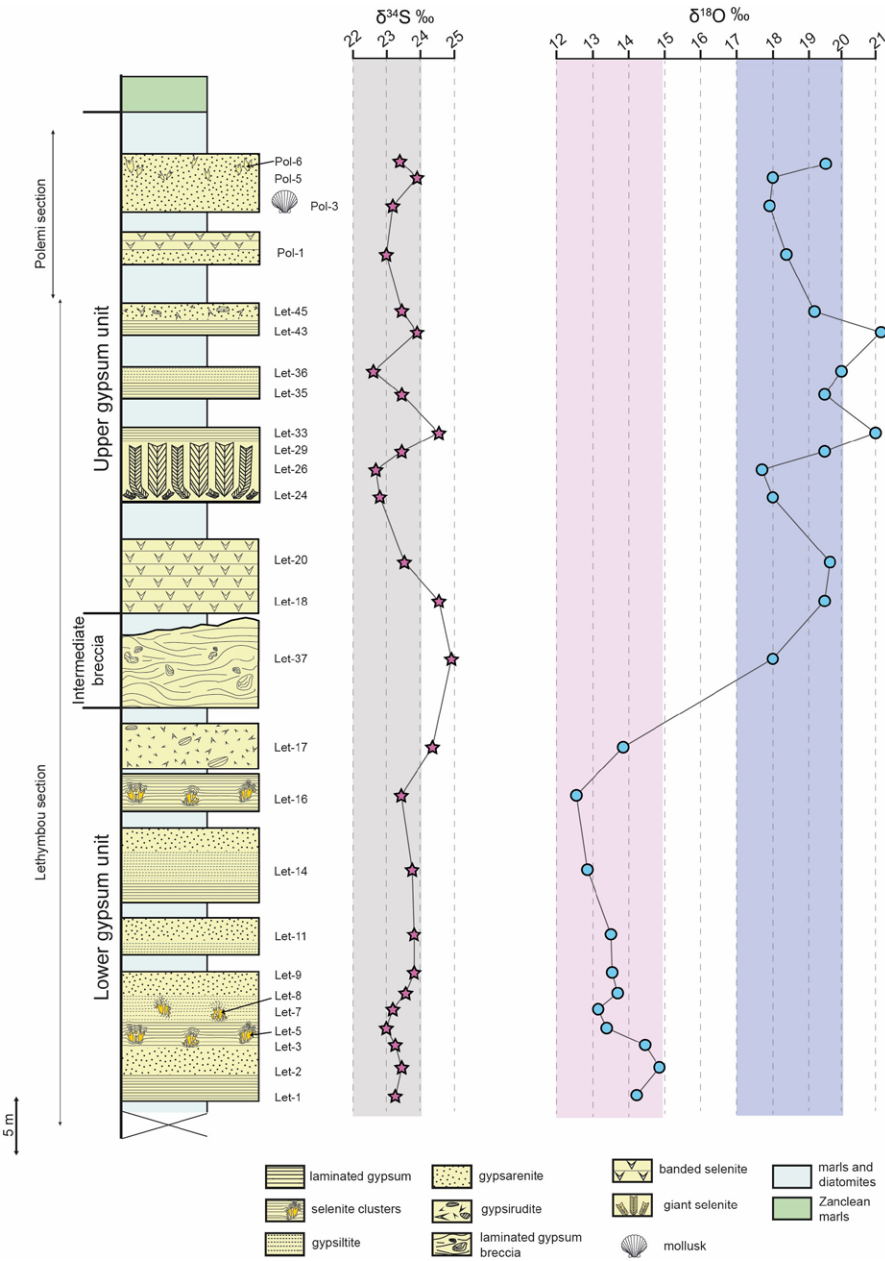


Fig.2.- Sulfate isotope profiles ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) of the Lethymbou and Polemi gypsum sections (Polemi basin). Shaded areas correspond to ranges reported for other MSC gypsum deposits: $\delta^{34}\text{S}$ (grey), Lower Evaporites – PLG and RLG $\delta^{18}\text{O}$ (pink), Upper Evaporites – Ug $\delta^{18}\text{O}$ (blue) (García-Veigas *et al.*, 2018). See color figure in the web.

Fig.2.- Perfiles isotópicos del sulfato ($\delta^{34}\text{S}$ y $\delta^{18}\text{O}$) de las secciones de yeso de Lethymbou y Polemi (cuenca de Polemi). Las áreas sombreadas corresponden a los rangos registrados en otras cuencas messinienses del Mediterráneo: $\delta^{34}\text{S}$ (gris), Evaporitas Inferiores - PLG y RLG $\delta^{18}\text{O}$ (rosa), Evaporitas Superiores - Ug $\delta^{18}\text{O}$ (azul) (García-Veigas *et al.*, 2018). Ver figura en color en la web.

Section	Sample	Lithofacies	$^{87}\text{Sr}/^{86}\text{Sr}$
Lethymbou	Let-3	Gypsarenite	0,708890
Lethymbou	Let-14	Gypsilitite	0,708900
Lethymbou	Let-37	Laminated breccia	0,708796
Lethymbou	Let-18	Banded selenite	0,708790
Lethymbou	Let-45	Gypsirudite	0,708781

Table 1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Polemi basin Messinian evaporites.

Tabla 1. Valores de $^{87}\text{Sr}/^{86}\text{Sr}$ de las evaporitas Messinienses de la cuenca de Polemi.

The Lower Gypsum shows sulfate isotope compositions of $\delta^{34}\text{S}_{\text{sulfate}} \sim 23\text{‰}$ (23.0 – 24.4‰) and of $\delta^{18}\text{O}_{\text{sulfate}} \sim 13\text{‰}$ (12.4 – 14.8‰), similar to those reported for Lower Evaporites (PLG and RLG deposits) (García-Veigas *et al.*, 2018 and references therein).

Isotope compositions in gypsum sulfate change abruptly in the Intermediate Gypsum Breccia. Although $\delta^{34}\text{S}_{\text{sulfate}}$ shows isotopic value (24.9‰), close to isotope compositions of the Lower Gypsum, the corresponding $\delta^{18}\text{O}_{\text{sulfate}}$ (18.1‰) is considerable higher and in range with MSC Upper Evaporites (Pierre, 1982; García-Veigas *et al.*, 2018).

Sulfate isotope compositions of the Upper Gypsum are similar to the Intermediate Gypsum Breccia, showing $\delta^{34}\text{S}_{\text{sulfate}}$ values of $\sim 23\text{‰}$ (22.0 – 24.4‰) and of $\delta^{18}\text{O}_{\text{sulfate}} \sim 19\text{‰}$ (17.7 – 21.3‰). These values match those reported for the MSC Upper Evaporites (Fig. 2).

Strontium isotope ratios

$^{87}\text{Sr}/^{86}\text{Sr}$ values of the Lower Gypsum unit (~ 0.7089) are similar to those reported for MSC Lower Evaporites (Müller and Mueller, 1991). Strontium isotope ratios in the Intermediate Gypsum Breccia and the Upper Gypsum (~ 0.7087) are in range with MSC Upper Evaporites (Table 1).

South Cyprus evaporites within the MSC chrono-stratigraphic framework

Based on the Lago Mare fossil assemblages found in the uppermost gypsum beds and its correlation with similar Lago Mare faunal association described in Site ODP-160-968A (Blanc-Valeron *et al.*, 1998) drilled on the Cyprus lower slope, Orszag-Sperber *et al.* (2009) suggest the assignation of each gypsum unit to the classic MSC stratigraphic division (Lower and Upper Evaporites).

More recently, based on facies association and strontium isotope ratios, Manzi *et al.* (2016) assigned the Lower Gypsum and the Intermediate Gypsum Breccia to the Resedimented Lower Gypsum deposits (MSC Stage 2), while the Upper Gypsum unit was assigned to the Upper Gypsum deposits (MSC Stage 3 in the MSC 'three-stage' model).

The isotopic data presented here point that the Intermediate Gypsum Breccia, assigned by Manzi *et al.* (2016) to the Res-

dimented Lower Gypsum (MSC Stage 2 in the three-stage model), included into the Lower Evaporites in the classical two-stage model, show $\delta^{18}\text{O}_{\text{sulfate}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to those obtained in the Upper Gypsum unit of the Polemi basin and reported in other MSC Upper Evaporites.

Conclusions

The chemostratigraphic analysis of the MSC gypsum succession in the Polemi basin provides new insights for the Mesinian Salinity Crisis in the Eastern Mediterranean. According to sulfate isotope compositions and strontium isotope ratios, the Lower Gypsum unit could be assigned to both the Lower Evaporites in the classical 'two-step' lithostratigraphic division or the PLG-RLG deposits in the three-stage model. However, the Intermediate Gypsum Breccia and the Upper gypsum unit corresponds to the Upper Evaporites – Upper Gypsum (MSC stage 3).

The presence of clastic resedimented gypsum beds assigned to Upper Evaporites – Upper Gypsum (MSC stage 3) deposits points out the significance of local processes in the sedimentation and distribution of MSC evaporites in active tectonic environments and warns against extra-basinal MSC correlations based solely on the distribution of gypsum facies.

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