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Sulfate isotope composition of Messinian evaporites in the Piedmont basin (Italy)

Composición isotópica del sulfato de las evaporitas Messinienses de la cuenca del Piamonte (Italia)

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ABSTRACT

The Piedmont basin (NW Italy) records a Messinian Salinity Crisis (MSC) succession including a selenite gypsum deposit assigned to the Primary Lower Gypsum (PLG, MSC stage 1). Strontium isotope ratios are in the range of the PLG deposits of the Mediterranean area. Sulfate isotope compositions of vertically oriented selenite gypsum beds, in the lower part of the succession, are similar to those reported in other PLG deposits. However, flattened branching selenite cones in the upper part show higher isotope compositions, mainly in $\delta^{34}S$ values, suggesting intense BSR conditions, stronger than reported in other PLG deposits. We interpret this chemical shift during deposition of the upper part of the PLG as the result of increased marine restriction assisted by the marginal position of this basin in the Adriatic Gulf during the Apennine and Alpine uplifts.

RESUMEN

La cuenca del Piamonte (NW Italia) contiene una serie Messiniense que incluye una unidad de yeso selenítico atribuida al PLG (MSC estadio 1). La isotopía del estroncio confirma esta asignación. La isotopía del sulfato de los yesos seleníticos de desarrollo vertical de la parte inferior de la serie es comparable a la de otras series PLG del Mediterráneo. Sin embargo, los conos de desarrollo horizontal de la parte superior de la serie muestran composiciones isotópicas mayores, especialmente en $\delta^{34}S$, sugiriendo una intensa actividad bacteriana (BSR) no observada en otros depósitos PLG. Interpretamos esta diferencia como resultado de mayores condiciones de restricción marina de la cuenca del Piamonte debidas a la posición marginal de esta cuenca en el Golfo Adriático durante el levantamiento de los Apeninos y los Alpes.

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Introduction

During the Messinian Salinity Crisis (MSC), the Mediterranean recorded the deposition of a large volume of evaporites (Fig. 1A). Based on seismic reflection profiles, more than 1 million of km^3 of salts have been estimated below the current Mediterranean (Ryan, 1973). MSC evaporites consist mainly of gypsum in circum-Mediterranean basins and include chlorides in the deepest seafloor. The enticing idea of a desiccated Mediterranean transformed in a giant salina suggested by Hsü *et al*. (1973) is today, fifty years after its proposal, under discussion.

Pending on the drilling of the deep Mediterranean, direct observations and studies of the MSC evaporites are limited to gypsum deposits outcropping in western (Spain), central (Italy, Sicily), and eastern (Greece, Cyprus, Turkey) margins of the current Mediterranean. The chrono-stratigraphic framework of the MSC (CIESM, 2008), mainly based on Sicily and extrapolated to the deep Mediterranean areas, propose three evolutionary stages. During MSC stage 1 (5.97-5.60 Ma) selenite gypsum deposits of the Primary Lower Gypsum (PLG) formed in shallow peripheral basins while organic-rich shales and carbonate-rich beds accumulated in deep basinal areas. The acme of the MSC took place in MSC stage 2 (5.60-5.55 Ma), and is characterized by subaerial exposure and erosion of the peripheral basins with the development of the Messinian Erosional Surface (MES). This surface becomes a correlative conformity in the deep basins located at the base of the Resedimented Lower Gypsum (RLG). Halite deposits with K-Mg salts precipitated in the intermediate deep Caltanissetta basin (Sicily) at this time. Upper Gypsum and Lago Mare deposits formed during the MSC stage 3 (5.55-5.33 Ma). The Upper Gypsum, consisting of selenite gypsum beds intercalated within marls, was deposited in Sicily and in the eastern Mediterranean (Cyprus), while evaporite-free clastic sediments deposited in the western basins (Spain). The reestablishment of fully marine conditions at the base of the Zanclean (5.33 Ma) marks the end of the MSC.

The MSC succession of the Piedmont basin was one of the reference sections used for the theory of a catastrophic desiccated Mediterranean (Sturani, 1976). The recent revision of the paleontological data in this basin (Carnevale *et al*., 2019) points to the persistence of marine stenohaline organisms throughout the MSC supporting the 'deep-water deep-basin' model for the Mediterranean.

The isotope compositions of the dissolved sulfate in seawater ($\delta^{34}S_{SW}$ and $\delta^{18}O_{SW}$) and of the related marine precipitated gypsum ($\delta^{34}S_{gyp}$ and $\delta^{18}O_{gyp}$) have changed through geological times. Sulfate isotope compositions of $\delta^{34}S$ ~ 22‰ and $\delta^{18}O$ ~ 12‰ should be expected for late Miocene marine evaporites. However, different but homogeneous sulfate isotope compositions have been reported for MSC evaporites in different western Mediterranean basins (García-Veigas *et al*., 2018). PLG deposits (MSC stage 1) in Betic basins (Spain), and RLG deposits (MSC stage 2) from one section in Sicily provide narrow isotopic ranges ($\delta^{34}S$: 22 - 24‰ and $\delta^{18}O$: 12 - 15‰). The isotope composition of UG evaporites (MSC

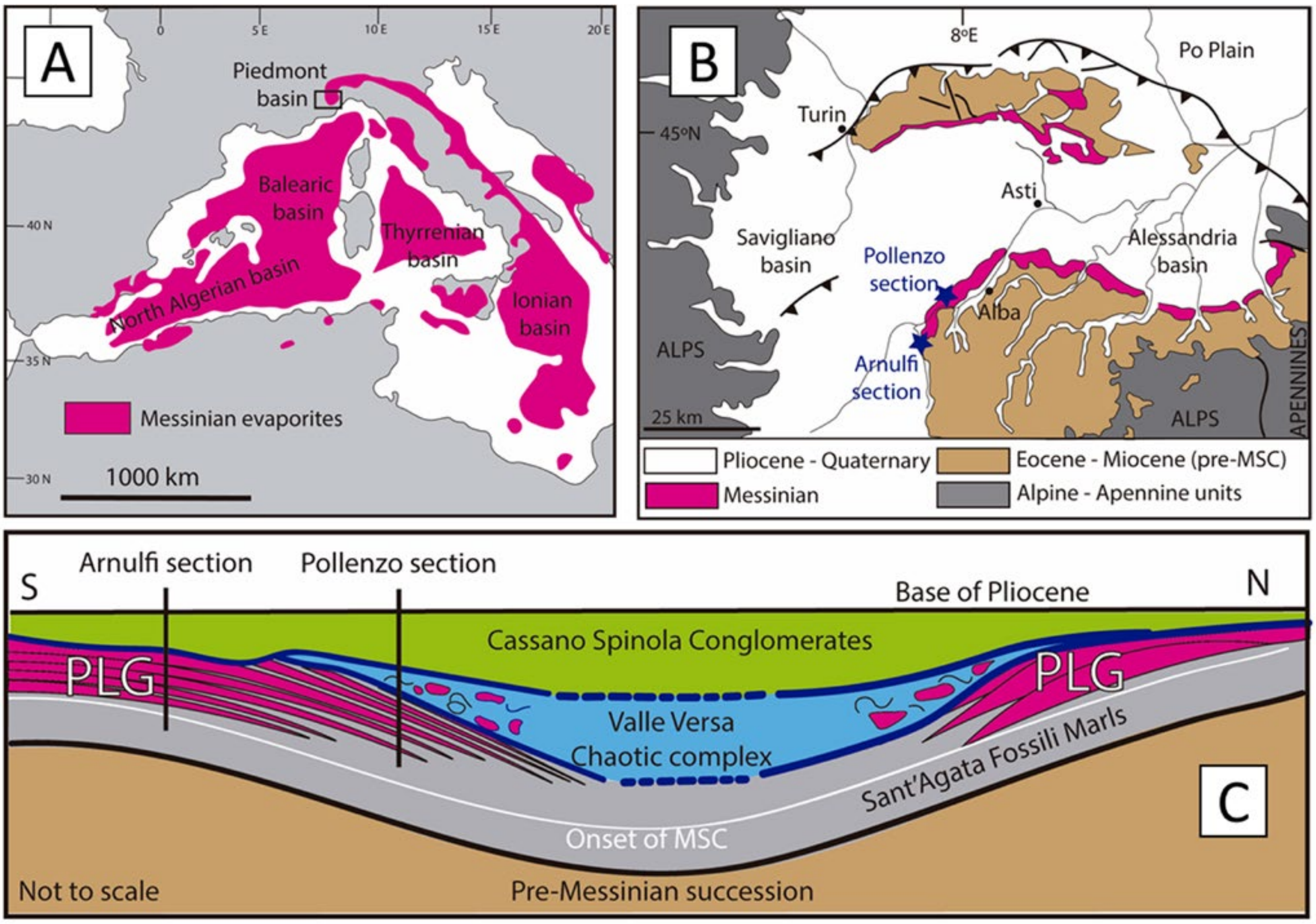

Figure 1. A: Distribution of Messinian evaporites in the Mediterranean. B: Location of studied sections in the Piedmont Basin. C: Schematic cross section of the Messinian deposits in the Piedmont basin. Not to scale. PLG: Primary Lower Gypsum. (After Dela Pierre *et al*. 2011).
Figura 1. A: Situación de las evaporitas del Messiniense en el Mediterráneo. B: Situación de las secciones estudiadas en la cuenca del Piamonte. C: Diagrama idealizado, sin escala, de los depósitos Messinienses en la cuenca del Piamonte. PLG: Yesos Inferiores Primarios. (Modificado de Dela Pierre et al., 2011).

stage 3) in Sicily and Cyprus provide similar isotope sulfur values ($\delta^{34}S \sim 23‰$) but significant higher values for oxygen isotope compositions ($\delta^{18}O$: 17 – 19‰).

A stratified deep-water deep-basin model for the MSC Mediterranean is proposed in García-Veigas *et al*. (2018) based on the homogenous sulfate isotope compositions. The aim of this work is to obtain accurate isotopic profiles of the northernmost MSC succession, in the Piedmont basin, and compare them with those reported for other MSC successions.

The MSC succession in the Piedmont basin.

The Piedmont basin (NW Italy, Fig. 1) is a wedge-top basin located in the inner side of the SW Alpine arc. The basin is filled with upper Eocene – late Miocene sediments. The Messinian succession (Dela Pierre *et al*., 2011; Natalicchio *et al*., 2013) consists, in ascending order, of:

- Sant'Agata Fossili Marls. Outer shelf to slope shale and marl couplets formed under progressively more restricted conditions.
- PLG deposits (MSC stage 1). Selenite gypsum beds intercalated with shales. Towards the basin depocenter, gypsum beds disappear passing into carbonate-rich layers and finally into organic-rich shales and marls.
- Valle Versa Chaotic Complex (MSC stage 2). Chaotic gypsum and carbonate blocks interpreted as RLG deposits.
- Cassano Spinola Conglomerates (MSC stage 3). Fluvio-deltaic and lacustrine conglomerates.

Alba Messinian section

PLG gypsum beds outcrop in the southwestern most part of the basin, close to the town of Alba (Fig. 1B). Gypsum lithofacies change laterally and vertically (Figs. 1C and 2), from bedded and massive beds of vertically oriented selenite crystals, up to 10m thick, in the lower part of the succession (SW sector, Arnulfi section), to discrete beds, up to 2m thick, of flattened conical structures of branching selenites (Lugli *et al*., 2010) surrounded by a terrigenous matrix in the upper part (NE sector, Pollenzo section).

A singular marker bed (SKB, Sturani key-bed) occurs between the lower and upper parts allowing regional correlation (Fig. 2). The SKB consists of flattened conical gypsum structures of branching selenite crystal aggregates growing in a fine-grained laminated gypsum.

Samples for isotope analyses were recovered from the Arnulfi and Pollenzo sections (Fig.2).

Strontium isotope ratios

Seven $^{87}Sr/^{86}Sr$ determinations in gypsum beds (Fig. 2) are close to 0.7089. Such narrow range of values is typical of

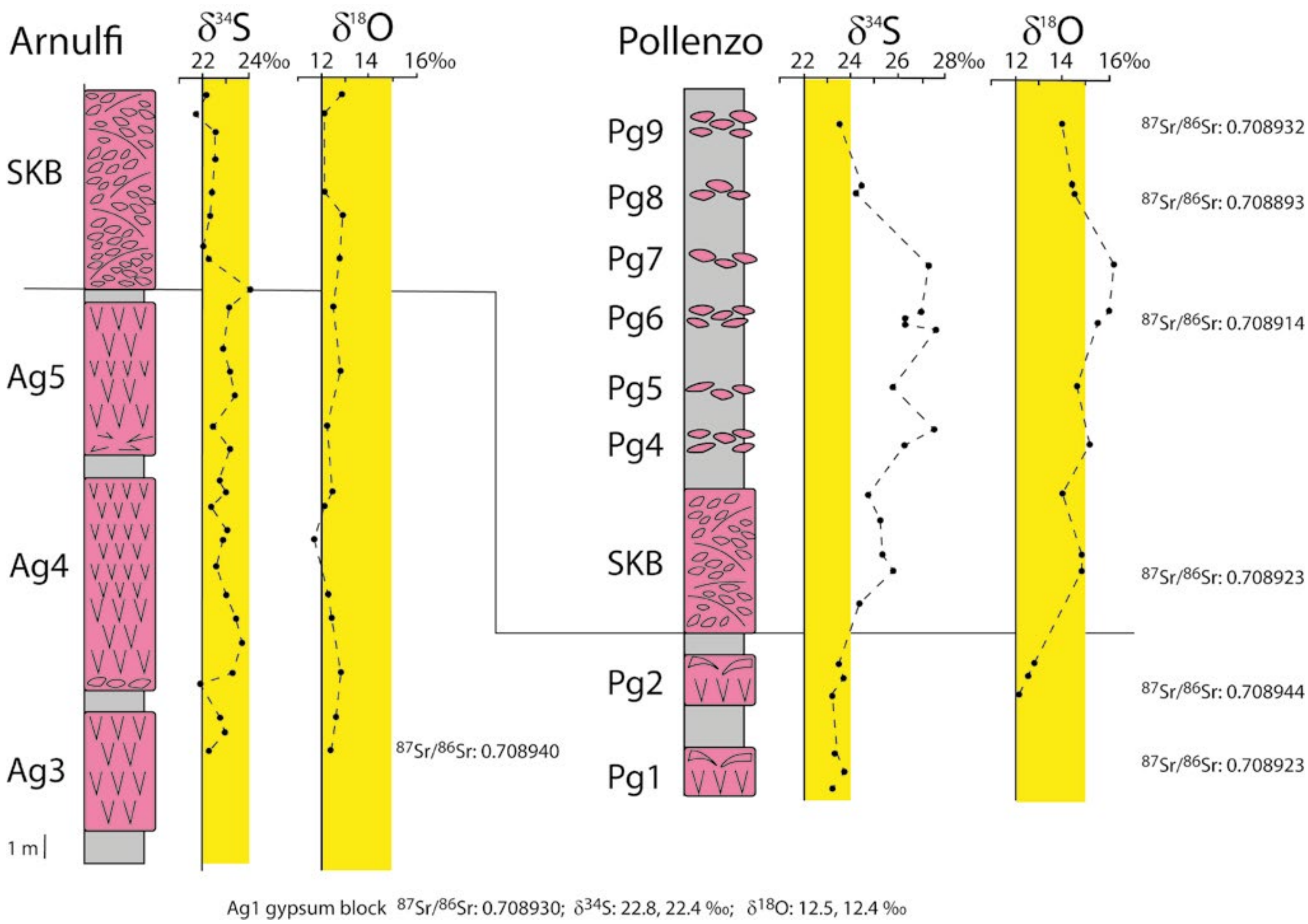

Figure 2. Sulfate isotope profiles ($\delta^{34}S$ and $\delta^{18}O$) and $^{87}Sr/^{86}Sr$ ratios in Messinian gypsum beds of the Arnulfi and Pollenzo sections (Piedmont basin). Data from the Ag1 basal gypsum bed, in the Arnulfi section, correspond to a fallen block. The yellow box indicates the ranges reported for other MSC sections in Western Mediterranean (García-Veigas *et al*., 2018).

Figura 2. Perfiles isotópicos de sulfato ($\delta^{34}S$ and $\delta^{18}O$) y valores de $^{87}Sr/^{86}Sr$ en los yesos Messinienses de las secciones de Arnulfi y Pollenzo (cuenca del Piamonte). Datos de la capa de yeso inferior en la sección de Arnulfi (Ag1) corresponden a un bloque caído. En amarillo: rangos registrados en otras cuencas messinienses del Mediterráneo Occidental (García-Veigas et al., 2018).

the PLG deposits in the Mediterranean area confirming that the studied succession corresponds to the MSC stage 1.

Sulfate isotope compositions

Sulfate isotope composition (Fig. 2) of the beds consisting of vertically oriented selenite crystals in the lower part (4 beds in Arnulfi, 2 beds in Pollenzo) shows a narrow range, with similar average $\delta^{34}S$ (22.8‰ in Arnulfi, 23.4‰ in Pollenzo) and $\delta^{18}O$ (12.4‰ in Arnulfi, 12.7‰ in Pollenzo) values.

Important differences exist in the average values obtained for the SKB bed in Arnulfi ($\delta^{34}S$: 22.4‰; $\delta^{18}O$: 12.5‰) with respect to the same bed in Pollenzo ($\delta^{34}S$: 25.1‰; $\delta^{18}O$: 14.5‰).

Conical structures of non-vertically oriented selenites of the upper part, only present in Pollenzo, show higher average isotopic values ($\delta^{34}S$: 26.0‰; $\delta^{18}O$: 15.1‰).

$\delta^{34}S$ values in the lower part of the Piedmont evaporites (~ 23‰) are similar to those found in other MSC PLG/RLG deposits. However, $\delta^{18}O$ values (~ 12‰) overlap with those expected for late Miocene marine evaporites, being in the lower range reported for other PLG/RLG deposits (12 - 15‰). These data suggest that, vertically oriented selenites of the lower part formed from the 'gypsum saturated layer' affected by bacterial sulfate reduction (BSR) as proposed in other MSC Mediterranean sections (García-Veigas *et al*., 2018).

Sulfate isotopes of the SKB bed in the more marginal Arnulfi section match with 'normal' marine values ($\delta^{34}S$ ~22‰; $\delta^{18}O$ ~12‰). However, moving towards the depocentre, in Pollenzo, the same bed shows different values ($\delta^{34}S$ ~25‰; $\delta^{18}O$ ~14‰), with similar $\delta^{18}O$, but with higher $\delta^{34}S$ values than those reported for other PLG/RLG deposits ($\delta^{34}S$ ~23‰). Isotopic enrichments, mainly in ^{34}S, are more pronounced in the conical structures of the upper part, only exposed in Pollenzo, reaching values up to 27‰ for $\delta^{34}S$ and up to 16‰ for $\delta^{18}O$. Such maximum values are higher than those reported in other PLG/RLG deposits suggesting a significant increase of the BSR rate in the Piedmont basin relative to other contemporaneous Mediterranean gypsum deposits.

The MSC Piedmont basin: a very restricted evaporite basin

Unlike homogeneous isotope signatures in other MSC deposits, the PLG in the Piedmont is characterized by: (1) similar isotopic enrichments in the beds composed of vertically oriented selenite crystals of the lower part of the succession; (2) late Miocene marine values in the SKB in the margins of the basin shifting to higher values towards the depocenter; and (3) enrichments, up to 5‰ in $\delta^{34}S$ and 4‰ in $\delta^{18}O$, relative to expected for marine evaporites, in the upper cycles only developed towards the depocenter of the basin.

The different isotope values of the upper gypsum beds in the Piedmont sections point to specific restriction conditions in the Piedmont basin compared to other contemporaneous MSC basins. Following the 'deep-water stratified model' proposed in García-Veigas *et al*. (2018), the lower gypsum cycles of vertically oriented selenites could have been formed in the intermediate gypsum-saturated layer of the stratified Mediterranean water mass as is interpreted for other PLG deposits.

Most likely, an important hydrological change occurred in the Piedmont basin since deposition of the SKB gypsum bed. The sharp change observed in the gypsum lithofacies of this bed is accompanied by 'normal' oceanic sulfate isotopic values towards the basin margins, whereas strong isotopic enrichments, mainly in ^{34}S, occur towards the depocenter. This change suggests local hydrochemical conditions in the Piedmont basin compared to other contemporaneous Mediterranean basins. Probably, the intermediate gypsum-saturated layer where vertically oriented selenites formed, withdrew towards deeper Mediterranean areas. However, marine inputs of the Mediterranean well-mixed upper layer (García-Veigas *et al*., 2018) must remained feeding the Piedmont basin as indicated by $^{87}Sr/^{86}Sr$ ratios.

Gypsum lithofacies change in the upper beds to small isolated cones of non-vertical oriented branching selenites. Strontium isotopes in these upper beds point to marine connections. However, higher sulfate isotope compositions suggest strong ^{34}S enrichments by BSR processes, much higher than those reported in other PLG/RLG deposits.

We interpret the upper gypsum beds as formed under reducing conditions from anoxic brines particularly developed in the Piedmont basin. Further inwards the Piedmont basin, gypsum disappears passing to marls and carbonates with filamentous fossils formed in anoxic to euxinic conditions (Dela Pierre *et al*., 2014).

Higher terrigenous inputs in the upper cycles point to major hydrologic changes, more humid climate conditions, and a general shallowing trend in the NW termination of the Adriatic Gulf (Dela Pierre *et al*., 2011).

A marked brine stratification occurred in the Piedmont basin during development of the branching selenite cones of the upper cycles. These beds can be interpreted as growing in a little thick gypsum-saturated layer where vertically oriented selenite crystals cannot grow. This particular gypsum-saturated layer was developed between an upper well-oxygenated marine water mass with increasing continental inputs, and a lower anoxic water mass in which strong reducing conditions avoided gypsum precipitation.

The Piedmont basin, during the MSC, is interpreted as having formed in a strongly restricted and stratified basin, located within the northward end of a much larger evaporite basin, restricted and brine-stratified as well: the MSC deep-water deep-basin Mediterranean.

Conclusions

The lower PLG cycles in the Piedmont basin, characterized by beds of vertically oriented selenite crystals, were formed from the same 'intermediate gypsum-saturated layer' developed in the MSC stratified Mediterranean (García-Veigas *et al*. 2018) and can be compared with other PLG sections in the Mediterranean.

Although marine inputs extend through the complete evaporitic succession, the upper PLG beds in the Piedmont basin were formed in strongly reducing conditions developed in this more restricted basin.

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