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

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 km$^2$ 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, 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 δ$^{34}$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.

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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 (δ$^{34}$S$_{sw}$ and δ$^{18}$O$_{sw}$) and of the related marine precipitated gypsum (δ$^{34}$S$_{gyp}$ and δ$^{18}$O$_{gyp}$) have changed through geological times. Sulfate isotope compositions of δ$^{34}$S = -22‰ and δ$^{18}$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 (Garcia-Vegas 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 (δ$^{34}$S: 22 - 24‰ and δ$^{18}$O: 12 - 15‰). The isotope composition of UG evaporites (MSC
stage 3) in Sicily and Cyprus provide similar isotopic sulfur values (δ^{34}S ~ 23‰) but significant higher values for oxygen isotopic compositions (δ^{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 isotopic 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 carbonatereich 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 selenites (Lugli et al., 2010) surrounded by a terrigenous matrix in the upper part (NE sector, Pollenzo section).

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
Isotopy of MSC evaporites in the Piedmont basin (Italy)

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 δ³⁴S (22.8‰ in Arnulfi, 23.4‰ in Pollenzo) and δ¹⁸O (12.4‰ in Arnulfi, 12.7‰ in Pollenzo) values.

Important differences exist in the average values obtained for the SKB bed in Arnulfi (δ³⁴S: 22.4‰; δ¹⁸O: 12.5‰) with respect to the same bed in Pollenzo (δ³⁴S: 25.1‰; δ¹⁸O: 14.5‰).

Conical structures of non-vertically oriented selenites of the upper part, only present in Pollenzo, show higher average isotopic values (δ³⁴S: 26.0‰; δ¹⁸O: 15.1‰).

δ³⁴S values in the lower part of the Piedmont evaporites (~23‰) are similar to those found in other MSC PLG/RLG deposits. However, δ¹⁸O 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 (δ³⁴S ~ 22‰; δ¹⁸O ~ 12‰). However, moving towards the depocentre, in Pollenzo, the same bed shows different values (δ³⁴S ~ 25‰; δ¹⁸O ~ 14‰), with similar δ¹⁸O, but with higher δ³⁴S values than those reported for other PLG/RLG deposits (δ³⁴S ~ 23‰). Isotopic enrichments, mainly in δ³⁴S, are more pronounced in the conical structures of the upper part, only exposed in Pollenzo, reaching values up to 27‰ for δ³⁴S and up to 16‰ for δ¹⁸O. 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 depo-
center; and (3) enrichments, up to 5‰ in $\delta^{13}S$ 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 hydrogeological 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 $\delta^{34}S$, 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 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, interpreted as growing in a little thick gypsum-saturated layer where vertically oriented selenite crystals 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.

**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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**References**


