



Research paper

Anaerobic oxidation of methane in hypersaline Messinian environments revealed by ^{13}C -depleted molecular fossils

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ABSTRACT

The Messinian sequence of evaporitic deposits in Italy includes authigenic carbonates that have been suggested to derive from the microbial degradation of organic compounds, but the biogeochemical mechanisms that led to their formation remained unknown. To unravel these mechanisms, ^{13}C -depleted carbonate rocks including native sulphur-bearing limestone (Calcare Solfifero) from two locations in Sicily and bedded limestone from the northern Apennines have been studied. Their $\delta^{13}\text{C}$ values as low as -49‰ reflect incorporation of carbon derived from the oxidation of methane, which was previously suggested to have been linked to bacterial sulphate reduction. Molecular fossils extracted from the limestones reveal that methane was indeed oxidized in an anaerobic process by archaea and sulphate-reducing bacteria. The observed biomarker patterns resemble those of methane-seep carbonates, which form as a consequence of the anaerobic oxidation of methane (AOM). AOM-specific, ^{13}C -depleted archaeal biomarkers such as PMI ($\delta^{13}\text{C}$: -101 to -75‰) as well as compounds derived from sulphate-reducing bacteria (*iso*- and *anteiso*-fatty acids; $\delta^{13}\text{C}$ as low as -85‰) were identified in the Messinian carbonates. Although the biomarker results clearly point to AOM, the compound inventory also revealed distinct differences to patterns found at marine methane-seeps. For example, *sn3*-hydroxyarchaeol is in some samples the only hydroxyarchaeol present, something usually not found at seeps. Archaeol is less depleted in ^{13}C than PMI at most sites ($\delta^{13}\text{C}$: -55 to -30‰), pointing to the co-occurrence of methanogenic or halophilic archaea with archaea involved in AOM. (1) The presence of calcite pseudomorphs after lenticular gypsum, (2) ^{18}O -enrichment in carbonates, and (3) the biomarkers *O*-phytanyl-*O*-sesterterpanyl glycerolether (extended archaeol), tetrahymanol, and possibly phytanylglycerol monoethers as well as non-isoprenoidal macrocyclic glycerol diethers confirm that carbonate formation took place under evaporitic conditions. AOM has previously been shown to be inhibited in some brine pools on the modern seafloor. Our observations, however, demonstrate that AOM functions in hypersaline environments as well.

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1. Introduction

Sulphur-bearing carbonates with highly negative $\delta^{13}\text{C}$ values were described from several regions worldwide including the Carpathian fore-deep ($\delta^{13}\text{C}$ values as low as -54‰ vs. V-PDB; Böttcher and Parafiniuk, 1998; Gasiewicz, 2000), the Limestone Buttes in Texas (-39‰ ; Kirkland and Evans, 1976), and the 'Calcare Solfifero' in Sicily (-52‰ ; Dessau et al., 1962; Decima et al., 1988; Ziegenbalg et al., 2010). These carbonates were interpreted to result from bacterial reduction of sulphate coupled to oxidation of methane. The rationale of this suggestion is that only the incorporation of carbon derived from the oxidation of methane, which is usually very depleted in ^{13}C , can result in such

negative $\delta^{13}\text{C}_{\text{carbonate}}$ values (see Peckmann and Thiel, 2004 for a review). This interpretation, however, has not been further validated by other analytical approaches.

The Sicilian sulphur-bearing limestones (Calcare Solfifero) are associated with abundant gypsum, which precipitated in the course of one of the greatest evaporitic events in Earth history, the Messinian salinity crisis (Decima and Wezel, 1973). A sea level drop caused by the cut off of the Mediterranean Sea from the Atlantic Ocean resulted in restricted conditions and the deposition of an evaporitic series, including evaporitic carbonate, sulphate, halite, and bittern salts between 5.96 and 5.33 million years ago (e.g., Hsu et al., 1973a,b; Krijgsman et al., 1999; Duggen et al., 2003; Rouchy and Caruso, 2006). A previous study on the petrography and stable isotope composition of the 'Calcare Solfifero' confirmed that sulphur precipitation resulted from bacterial sulphate reduction, as revealed by low sulphur isotope values of native sulphur and highly positive sulphur isotope values of the accompanying sulphate minerals ($\delta^{34}\text{S}$

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values as low as -2% and as high as $+61\%$ vs. V-CDT, respectively; Ziegenbalg et al., 2010). Sulphur-bearing carbonates formed either along a (1) syngenetic pathway or an (2) epigenetic pathway. The late stage, epigenetic carbonates are characterized by negative $\delta^{13}\text{C}$ values (as low as -29%) due to microbial oxidation of organic compounds (e.g., crude oil) by sulphate reduction in the presence of meteoric waters (as indicated by $\delta^{18}\text{O}$ values as low as -4% vs. V-PDB). The syngenetic carbonates are characterized by ^{18}O -enrichment (values as high as $+9\%$), reflecting evaporitic conditions during precipitation. This interpretation is supported by the presence of lenticular gypsum, which grew in the unconsolidated sediment, calcite pseudomorphs after lenticular gypsum, and moulds of halite crystals. The strongly negative $\delta^{13}\text{C}$ values of syngenetic carbonates (as low as -52%) have been interpreted to reflect the oxidation of methane (Decima et al., 1988; Ziegenbalg et al., 2010).

One way to test this hypothesis is the analysis of molecular fossils (i.e., lipid biomarkers). To date, only epigenetic carbonates associated with native sulphur enclosed in Zechstein carbonates of the Harz Mountains, Germany, have been analyzed for their biomarker content. The secondary aragonite ($\delta^{13}\text{C} = -10\%$), which formed in recent times, was found to contain pristine biomarkers of sulphate-reducing bacteria (Peckmann et al., 1999a). Here, we subjected syngenetic carbonates of the 'Calcare Solfifero' from Sicily to a biomarker study in order to investigate the inventory of microorganisms that prevailed in the evaporitic setting. For comparison, a Messinian carbonate layer from below the base of the gypsum in the northern Apennines was analyzed. We also determined compound-specific carbon isotope compositions to identify the dominant carbon sources of the Messinian microbial community.

2. Geological context, rock samples, and methods

Carbonates of the Messinian 'Gessoso solfifera' Formation in Sicily from the localities of Cozzo Disi and Contrada Gaspa as well as of the northern Apennines from the Monticino locality were studied. Petrography as well as stable carbon, oxygen, and sulphur isotope data of carbonates, sulphates, and sulphur from Cozzo Disi and Gaspa was presented by Ziegenbalg et al. (2010). The former sulphur mine of Cozzo Disi is situated southeast of Casteltermini (Table 1). The Cozzo Disi sample studied here comprises sparitic limestone with some accessory sulphate minerals and contains large aggregates of native sulphur (Table 2). The limestone encloses calcite pseudomorphs after lenticular gypsum. The Cozzo Disi carbonate phases exhibit $\delta^{18}\text{O}$ values as high as $+9\%$ (Table 1). The corresponding $\delta^{13}\text{C}$ values range from -49 to -29% (Table 1). The abandoned sulphur mine of Gaspa is situated close to the street S 230 from Enna to Alimena, between Casa Realmesi and Casa Bastione (Table 1). The micritic to sparitic carbonates, sampled from a limestone cliff, contain calcite pseudomorphs after lenticular gypsum (Table 1; 2). They are enriched in ^{18}O and depleted in ^{13}C ($\delta^{18}\text{O} = +3$ to $+8\%$; $\delta^{13}\text{C} = -46$ to -34% ; Table 1). Native sulphur is finely disseminated within the limestone. The Monticino carbonate, sampled from the Monticino Sanctuary near Brisighella (northern Apennines, Italy; Roveri et al.,

Table 1

Coordinates of study sites, stable carbon and oxygen isotopic compositions, as well as petrographic and isotopic indicators for hypersaline conditions.

Location Lat.; Long.	$\delta^{13}\text{C}_{\text{carbonate}}$	$\delta^{18}\text{O}_{\text{carbonate}}$	Salinity indicators
Cozzo Disi 37°30' 51"N; 13°40' 45"E	-49 to -29%	$+4$ to $+9\%$	Calcite pseudomorphs after lenticular gypsum; enrichment in ^{18}O
Gaspa 37°37'00"N; 14°12'26"E	-46 to -34%	$+3$ to $+8\%$	Calcite pseudomorphs after lenticular gypsum; enrichment in ^{18}O
Monticino 44°13' 29"N; 11°45' 50"E	-27 to -23%	$+7\%$	Enrichment in ^{18}O

Table 2

Lithology and mineralogy of studied samples.

Sample	Lithology	Mineralogy
Cozzo Disi	Sparitic limestone, accessory secondary gypsum, native sulphur, and crusts of aragonite (for biomarker extraction the aragonite was avoided)	Calcite, gypsum, native sulphur
Gaspa-1	Limestone consisting of laminated micritic clasts cemented by sparry calcite	Calcite
Gaspa-2	Limestone consisting of micritic to microsparitic calcite with abundant calcite pseudomorphs after lenticular gypsum in sparry calcite matrix	Calcite
Gaspa-3	Limestone consisting of laminated micritic clasts cemented by sparry calcite	Calcite
Monticino	Laminated, finely crystalline dolostone	Dolomite, minor calcite

2006, p. 45 f; Table 1), is laminated and consists of finely crystalline dolomite (Table 2). It is less ^{13}C -depleted than the Sicilian carbonates, but also enriched in ^{18}O ($\delta^{13}\text{C} = -27$ to -23% ; $\delta^{18}\text{O} = +7\%$; unpublished results; Table 1). Because of a non-quantified admixture of minor calcite, oxygen isotope data of dolomite samples were not corrected for their different fractionation compared to calcite during precipitation (McKenzie, 1981) or during analytical procedure (Sharma and Clayton, 1965). No native sulphur was detected in the studied Monticino sample.

Sample preparation, dissolution, extraction, and biomarker analyses were performed according to methods reported by Birgel et al. (2006b). Briefly, limestones were carefully cleaned with acetone and HCl. Afterwards the carbonate was dissolved in HCl. The remaining sediment was saponified and extracted with a microwave extraction system (CEM MARS X) at $80\text{ }^\circ\text{C}$ and 300 W with $\text{CH}_2\text{Cl}_2:\text{MeOH}$ (3:1). The resulting extract was separated into four fractions of increasing polarity by column chromatography (hydrocarbons, ketones and esters, alcohols, fatty acids). In the following we discuss the hydrocarbon, alcohol, and fatty acid fractions. Compounds were examined by coupled gas chromatography–mass spectrometry (GC–MS) with a Thermo Electron Trace GC–MS. Molecules were identified based on retention times and in comparison with published mass spectra. Contents are given in ng/g dry weight of the non-decalcified sample. Compound-specific carbon isotope analysis (irm-GC/MS) was performed with a Thermo Electron GC-combustion-III-interface linked to a Thermo Electron Delta-plus XP mass spectrometer. Carbon isotope values are given in the δ -notation relative to the Vienna-Peedee-Belemnite (V-PDB) standard. Several pulses of CO_2 gas of known isotopic composition at the beginning and the end of the runs were used for calibration. The analytical standard deviation of the compound-specific carbon isotope measurements was $<0.7\%$.

3. Results

3.1. Hydrocarbon fraction

The sample Gaspa-2 shows much higher contents of total hydrocarbons (1046 ng/g ; Table 3) than samples Cozzo Disi, Gaspa-1, and Monticino (260 , 284 and 18 ng/g , respectively). The n -alkanes are the prevalent compound class in the hydrocarbon fraction, ranging from $n\text{-C}_{16}$ to $n\text{-C}_{33}$. They represent more than $50\text{ wt.}\%$ of all hydrocarbons. Short-chain hydrocarbons are predominant in the Cozzo Disi sample, peaking at $n\text{-C}_{20}$, which accounts for 12% of the hydrocarbons. Long-chain hydrocarbons dominate in the Gaspa-2 sample, with $n\text{-C}_{31}$ as predominant compound (13%). Gaspa-1 displays a bimodal pattern, peaking at $n\text{-C}_{20}$ and $n\text{-C}_{31}$ (8 and 9% , respectively). The short-chain alkanes $n\text{-C}_{16}$ to $n\text{-C}_{18}$ as well as the long-chain alkanes $n\text{-C}_{29}$ and $n\text{-C}_{31}$ are the main hydrocarbons in the Monticino sample, representing 7 to 10% of the total hydrocarbons.

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