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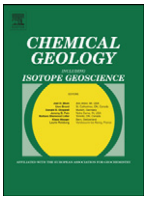

Biomarker and isotope evidence for microbially-mediated carbonate formation from gypsum and petroleum hydrocarbons

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ABSTRACT

Along the western coast of the Gulf of Suez large amounts of evaporitic gypsum of Miocene age have been microbially transformed into carbonates and elemental sulfur in the presence of petroleum. Similar diagenetic transformations have been described from numerous sites worldwide but the role of petroleum, specifically as a carbon source for the sulfate-reducing microbial community, remains elusive. We carried out a geochemical investigation of microbial carbonates from the Gulf of Suez that suggests the presence of a community of sulfate-reducing bacteria thriving on carbon substrates contained in petroleum. Specifically, a set of non-isoprenoidal macrocyclic glycerol diethers (McGDs), that we tentatively ascribe to sulfate-reducing bacteria, have a stable carbon isotope composition close to that of petroleum *n*-alkanes associated with the carbonates. The presence of archaeol that is ^{13}C-enriched relative to bacterial lipids suggests that Archaea are present but either indirectly involved or not involved in the transformation of petroleum-derived carbon. The lipid biomarker pattern we observe is distinct from those observed in settings where sulfate reduction is coupled to the anaerobic oxidation of methane. Our results suggest that petroleum migration has triggered the microbial transformation of gypsum into carbonates in the Gulf of Suez. By extension, the involvement of petroleum in the microbial transformation of gypsum into carbonates in other settings, which was suggested by more indirect, geological and inorganic geochemical evidence, seems very likely.

1. Introduction

Sulfate reduction is one of the most widespread microbial processes in marine sediments (Jørgensen, 1982). In organic matter (OM) rich sediments, it typically involves the reduction of seawater sulfate by microbial communities that use OM or methane as reducing agents (Canfield et al., 1993; Hinrichs and Boetius, 2002). OM and methane-based sulfate reduction have been investigated extensively from the biogeochemical standpoint, with thorough microbiological and organic geochemical characterization of the microbial communities involved (e.g. Kasten and Jørgensen, 2000; Knittel and Boetius, 2009; Teske, 2010 and references therein). The microbial reduction of gypsum, however, has received less attention although gypsum formed in evaporitic environments provides an alternative source of sulfate when it dissolves. In OM or methane-rich environments, gypsum can be reduced by microbes leading to the formation of diagenetic carbonates and elemental sulfur deposits (upon re-oxidation of the H_2S formed by sulfate reduction). Examples of this microbially-driven transformation are the carbonate-sulfur mineralizations of the Zechstein Formation (Upper Permian, Germany) (Peckmann et al., 1999), the Calcare di Base (Upper Miocene, Sicily) (Rouchy, 1981; McKenzie, 1985; Ziegenbalg et al., 2010, 2012) and the diagenetic carbonates of the Lorca Basin (Upper Miocene, Spain) (Rouchy et al., 1998).

In an additional biogeochemical setting, evaporitic gypsum is thought to be reduced by organisms that use petroleum hydrocarbons, rather than recent organic matter or methane, as a source of carbon. This hypothesis is supported by the existence of sulfur-bearing authigenic carbonates in places where petroleum comes in contact with gypsum deposits. Examples of this association are common worldwide, in the cap rock of salt diapirs in the Gulf of Mexico (Feely and Kulp, 1957; Davis and Kirkland, 1970), in the Permian basin in Texas, as well as in the stratabound mineral deposits in the Fergana and Amudaria depression of Central Asia, the Mesopotamian basin in Iraq and the Cis-Carpathian trough in Poland and Russia (Davis and Kirkland, 1970; Barker et al., 1979; Ruckmick et al., 1979).

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Most of the evidence for the microbial nature of the gypsum-carbonate transformation is indirect and comes from i) the ^{13}C-depletion of authigenic carbonates that incorporate dissolved inorganic carbon (DIC) from the microbial oxidation of ^{13}C-depleted organic carbon and, ii) the ^{34}S-depletion of elemental sulfur which originates from the fractionation of sulfur isotopes during microbial sulfate reduction (Pierre and Rouchy, 1988; Aref, 1998; Ziegenbalg et al., 2010).

Recently, the microbial communities that carried out the transformation of gypsum into carbonates and sulfur in the Calcare di Base have been characterized using lipid biomarkers (Ziegenbalg et al., 2012). Biomarkers point to a microbial community very similar to that carrying out the anaerobic oxidation of methane (AOM) coupled to sulfate reduction at recent marine cold seeps (Niemann and Elvert, 2008). In settings where oil is providing the source of carbon, however, the link between reactants (gypsum, oil) and products (carbonates, elemental sulfur) relies solely on the indirect evidence introduced above. Since microorganisms capable of reducing sulfate using non-methane hydrocarbons are known to exist (Widdel and Rabus, 2001; Kniemeyer et al., 2007), we investigated the lipid biomarker content of diagenetic carbonates from the Gulf of Suez (Pierre and Rouchy, 1988; Aref, 1998). These carbonates are formed via reduction of Middle Miocene evaporitic gypsum deposits and often occur in association with petroleum residues. Our main goal was to look for the molecular and the isotopic signatures of the microbial community suspected of mediating this biogeochemical process.

2. Study areas and samples

Diagenetic carbonates were sampled from the Gebel El Zeit and Gemsa areas on the western coast of the Gulf of Suez, Egypt (Fig. 1, Table 1). These areas are well known for the occurrence of diagenetic carbonates and sulfur formed as end products of the microbial reduction of evaporitic gypsum (Pierre and Rouchy, 1988; Wali et al., 1989; Aref, 1998). Outcrops of diagenetic carbonates occur within a sequence of gypsum-anhydrite evaporites of Middle Miocene age that lies unconformably on the Precambrian basement. Authigenic carbonates in the Gebel el Zeit area occur generally as lenticular or irregular stratiform bodies ranging from a few centimeters to a few kilometers in length (Aref, 1998). These stratiform bodies are isolated within the sulfate layers and cannot be correlated with each other. In the Gemsa area the diagenetic carbonates are concentrated in the cap rock of a diapir, where they are associated with native sulfur deposits.

Evidence that gypsum has been diagenetically transformed into carbonates in our study area comes from the petrography and stable isotope geochemistry of diagenetic carbonates and sulfur (Pierre and Rouchy, 1988; Philip et al., 1994; Aref, 1998): 1) the carbonates are generally depleted in ^{13}C relative to seawater DIC implying that they contain inorganic carbon produced during the biodegradation of ^{13}C-poor OM; 2) the elemental sulfur is depleted in ^{34}S relative to seawater indicating that the reduction of sulfate is microbially-mediated; 3) carbonate pseudomorphs after gypsum–carbonate crystals having the crystal habit of the pre-existing gypsum crystals — are abundant; and 4) secondary porosity or brecciation, formed due to the reduction in volume accompanying the mineral transformation, is observed.

Based on the oxygen isotopes of the carbonates, Pierre and Rouchy (1988) showed that the gypsum-carbonate transformation initiated early in a hypersaline solution during the deposition of gypsum and continued as the Miocene evaporites were uplifted and flushed by meteoric waters, inducing contact with petroleum migrating from deeper strata. In fact, both in the Gebel El Zeit and Gemsa areas petroleum seeps often occur in correspondence to the diagenetic carbonate outcrops. The petroleum source rocks in the Gulf of Suez are Upper Cretaceous Shales, lower Miocene marls and upper Miocene intra-gypsiferous diatomites. The Miocene evaporites make up the seal of this petroleum system and cap the reservoir rocks that are Paleozoic, Cretaceous and lower Miocene sandstones, fissured and cavernous limestones of Late Cretaceous, Eocene and Miocene age, and porous basement rocks (Aref, 1998).

The macroscopic appearance of the diagenetic carbonates we sampled (Fig. 2A–D) strongly resembles that of diagenetic carbonates described by Pierre and Rouchy (1988) and Aref (1998) from the same outcrops. Samples EG-06-11 and EG-06-17 are gray to dark gray, hard, porous carbonates with vugs up to about 2 mm in diameter. This porosity is interpreted as the result of the reduction in volume occurring during the transformation of sulfate minerals (gypsum or anhydrite) into carbonates (Aref, 1998). In addition to a strong oil smell, all samples contain light brown to black bitumen stains or oil microseeps that appear when breaking the sample mechanically. Samples EG-06-13, EG-06-14, EG-06-15 and EG-06-16 also contain macroscopic crystals of elemental sulfur, while sample EG-06-21 contains gypsum crystals.

3. Methods

3.1. Carbonate content and mineralogical composition

The carbonate content of diagenetic carbonates was measured twice on 100 mg of powder using a Mélières manocalcimeter (MMC) accounting for the different stoichiometries of calcium carbonate (calcite or aragonite) and dolomite (Baudrand et al., 2012). The bulk mineralogy was determined by X-Ray diffractometry using a Siemens D-500 instrument (Ni filtered Cu Kα radiation) scanning 2°–64° (2θ) at a rate of 0.02° 2θ per second. The MacDiff program by Rainer Petschik (servermac.geologie.unifrankfurt.de/Rainer.html) was used to quantify the relative proportions of calcite and dolomite in carbonate mixtures from X-ray diffractograms using the peak surface method. The relative intensities were corrected using correction factors (I/Icor) from the PDF2 database of International Centre for Diffraction Data. Standard forms used are 05-0586 for calcite and 73-2324 for dolomite. The carbonate content measured by MMC was then used to calculate absolute concentrations of calcite and dolomite in the sample from the relative concentrations obtained by XRD. More details on the carbonate content and X-Ray diffractometry are presented in Baudrand et al. (2012).

3.2. Carbon and oxygen stable isotope compositions

The authigenic carbonates we investigated contain mixtures of calcium carbonate and dolomite, which potentially have distinct diagenetic origins (Pierre and Rouchy, 1988). The carbon and oxygen stable isotope compositions of these different carbonate phases were determined according to the semi-automatic on-line method of Baudrand et al. (2012). Briefly, the stable isotope composition of dolomite is calculated after having measured that of calcite and bulk sample with an auto sampler MultiPrep™ system coupled to a Dual-Inlet GV-Instruments Isoprime™ isotope ratio mass spectrometer (irms). Results are expressed in ‰ relatively to Vienna Pee Dee Belemnite (VPDB) standard. The analytical precision depends on the proportions of calcite and dolomite in the sample (Baudrand et al., 2012).

3.3. Total organic carbon (TOC) and lipid biomarker analysis

The amount of TOC in each carbonate sample was determined by Rock-eval-Pyrolysis (Espitalié et al., 1985–86) using subsamples devoid of hydrocarbon stains. Samples with the highest amount of non-petroleum TOC (selected by visual inspection) were analyzed for their lipid content. The carbon stable isotope composition of TOC ($\delta^{13}C_{TOC}$) was measured on hydrocarbon stained carbonate subsamples following dissolution of the carbonate in 0.1 M HCl at ambient temperature. $\delta^{13}C_{TOC}$ values were obtained using a Eurovector Elemental Analyzer (EuroEA3028-HT) connected to a GV instrument