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Hydrocarbon seepage during the Messinian salinity crisis in the Tertiary Piedmont Basin (NW Italy)

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ABSTRACT

Seep carbonate deposits of Messinian age have been recently found in the Tertiary Piedmont Basin (NW Italy). These carbonates are preserved as blocks within a chaotic unit emplaced during the Messinian salinity crisis (MSC). They show negative $\delta^{13}C$ values (from −27 to −15‰ VPDB) that indicate the involvement of hydrocarbon-rich fluids in their genesis. Three types of carbonates are recognised: (i) vuggy carbonates; (ii) *Lucina* carbonates; and (iii) tubeworm carbonates. Vuggy carbonates are characterised by carbonate pseudomorphs after gypsum and probably formed during the first stage of the MSC. They are the product of a complex diagenesis, influenced by both hypersalinity and seepage of hydrocarbon rich fluids. These rocks lack chemosymbiotic assemblages, reflecting their formation under extreme environmental conditions, inhospitable for most metazoans. In contrast, *Lucina* and tubeworm carbonates are characterised by chemosymbiotic macrofauna, represented respectively by *Lucina* bivalves and putative vestimentiferan tubeworms. The latter have not commonly been documented in ancient seep carbonates and have never been reported from the Messinian sediments of the Piedmont Basin. Both *Lucina* and tubeworm carbonates are interpreted as the product of hydrocarbon seepage during the second MSC stage. These two types of carbonates formed under less severe conditions than the vuggy carbonates, allowing the survival of seep-dwelling metazoans. During the second MSC stage, the seafloor was probably characterised by an irregular topography and a thin bottom layer of dense anoxic brines, produced by the dissolution of gypsum. It is suggested that vestimentiferan worms were able to thrive on morphologic highs with the posterior part of tubes just below the oxic–anoxic interface, but the anterior part projecting into oxic water. The infaunal *Lucina* bivalves were only able to live at seeps with an overlying oxic water column. The studied carbonate deposits show features reflecting the uncommon interaction of hydrocarbon-rich seep fluids and sulphate-enriched waters – the latter resulting from both evaporation and dissolution of gypsum – and allow to reconstruct the evolution of a seepage system during the MSC.

1. Introduction

Cold seeps are sites of localized expulsion of hydrocarbons at the seafloor, predominantly composed of methane or higher hydrocarbons, and containing locally generated hydrogen sulphide. Seep deposits are widely documented in both modern (e.g. Paull et al., 1992; Aloisi et al., 2000; Levin, 2005; Mazzini et al., 2008) and ancient marine depositional settings (e.g. Peckmann et al., 1999; Clari et al., 2004, 2009; Peckmann and Thiel, 2004; Campbell 2006). Marine seeps and their deposits are characterised by several diagnostic features including: (i) authigenic minerals, mainly consisting of carbonates like calcite, aragonite, and dolomite (e.g. Ritger et al., 1987; Paull et al., 1992; Aloisi et al., 2002), (ii) negative $\delta^{13}C$ values (as low as −75‰ VPDB; Campbell, 2006) of early diagenetic authigenic carbonate phases; (iii) chemosymbiotic macro-fauna (dominated by bivalves and vestimentiferan tubeworms), and (iv) a characteristic prokaryotic community represented by methanotrophic archaea, sulphate-reducing bacteria, as well as mat-forming sulphide-oxidising bacteria, and thiotrophic or methanotrophic endosymbionts in chemosymbiotic seep metazoans (e.g., Boetius et al., 2000; Orphan et al., 2002; Duperron et al., 2005). The distribution and the biological activity of the various chemosymbiotic organisms is controlled by parameters such as (i) water depth, (ii) fluid composition, (iii) fluid emission rate, (iv) occurrence of gas hydrates, and (v) sulphide contents (Levin, 2005; Olu-Le Roy et al., 2007; Cordes et al., 2010).

In Cenozoic successions of the Mediterranean, cold seep carbonates are widely distributed and have been described in detail (e.g. Conti and Fontana, 2005; Clari et al., 2009). These carbonates have been reported in strata as old as Eocene (Venturini et al., 1998) in various basin types

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including foredeep, episutural, and foreland basins (e.g. Ricci Lucchi and Vai, 1994). In most cases, such carbonates consist of extensively cemented blocks and lenses, which are mostly hosted in deep-water claystones and siltstones. The largest seep deposits and the highest diversity of chemosymbiotic macrofauna are observed in Upper Serravallian–Tortonian sediments, reflecting intense hydrocarbon seeping at that time (e.g. Taviani, 2001, 2011). Such Miocene carbonates are commonly characterised by chemosymbiotic macrofauna dominated by *Lucina* clams. In contrast, only very few seep carbonates have been reported from the Messinian salinity crisis (MSC) stratigraphic record (e.g. Clari et al., 2004, 2009).

The present paper describes cold seep deposits discovered within the Messinian sediments of the eastern margin of the Tertiary Piedmont Basin (Fig. 1A). This discovery provides the opportunity to trace the evolution of methane seepage into the MSC. The studied deposits contain macro-fossil assemblages and show sedimentological, petrographic, and geochemical features, that reveal an uncommon interaction of hydrocarbon-rich seep fluids and sulphate-enriched waters resulting from both seawater evaporation and dissolution of gypsum deposits.

2. The Messinian salinity crisis

The MSC is a major palaeo-oceanographic event that occurred about 6 Ma ago. In its course the Mediterranean was transformed into one of the largest salt basins in Earth history (e.g. CIESM, 2008). After the discovery of the deep-seated Mediterranean evaporites (Hsü et al., 1973), mostly buried below the abyssal plains of the present day Mediterranean sea, a multitude of studies has been carried out on the Messinian Mediterranean succession, resulting in different and sometimes contrasting interpretations of the MSC (e.g. Rouchy and Caruso, 2006; CIESM, 2008). Recently, a new scenario for the MSC was proposed (CIESM, 2008; Roveri et al., 2008). This scenario envisages that the MSC developed through three main evolutionary stages (Fig. 2). During the first stage (from 5.96 to 5.60 Ma), sulphate evaporites (Primary Lower Gypsum unit, PLG; Roveri et al., 2008) formed in shallow-silled peripheral basins (e.g. Sorbas Basin, parts of the Tertiary Piedmont Basin, Vena del Gesso Basin of Northern Apennines), whereas in deep basinal areas organic-rich shales, interbedded with carbonate-rich layers, were deposited (e.g. parts of the Tertiary Piedmont Basin, Northern Apennine foredeep, Caltanissetta Basin of Sicily; Manzi et al., 2007, 2011; Dela Pierre et al., 2011, 2012). In the second stage (from 5.60 to 5.53 Ma), the PLG unit underwent subaerial exposure and erosion caused by a prominent sea level drop (MSC acme); the products of erosion were transferred downslope and deposited in deep basins by various types of gravity flows. These sediments, referred to as Resedimented Lower Gypsum (RLG unit, Manzi et al., 2005, 2007; Roveri et al., 2008), locally host thick halite bodies (e.g. Caltanisetta Basin). During the third stage (from 5.53 to 5.33 Ma), a cyclic alternation of gypsum and shales with brackish-water fossil assemblages (Upper Evaporites) was deposited in the SE part of the Mediterranean basin (Sicily, Ionian Islands, Crete, Cyprus, and Nile Delta area), whereas shallow to deep water clastic sediments are found in the Apennines and in the Sorbas Basin. In the upper part of these units, fresh and brackish water sediments with Paratethyan fossil assemblages are present, recording the so called Lago-Mare event (e.g. Orszag-Sperber, 2006). The overlying Zanclean (Pliocene) clays

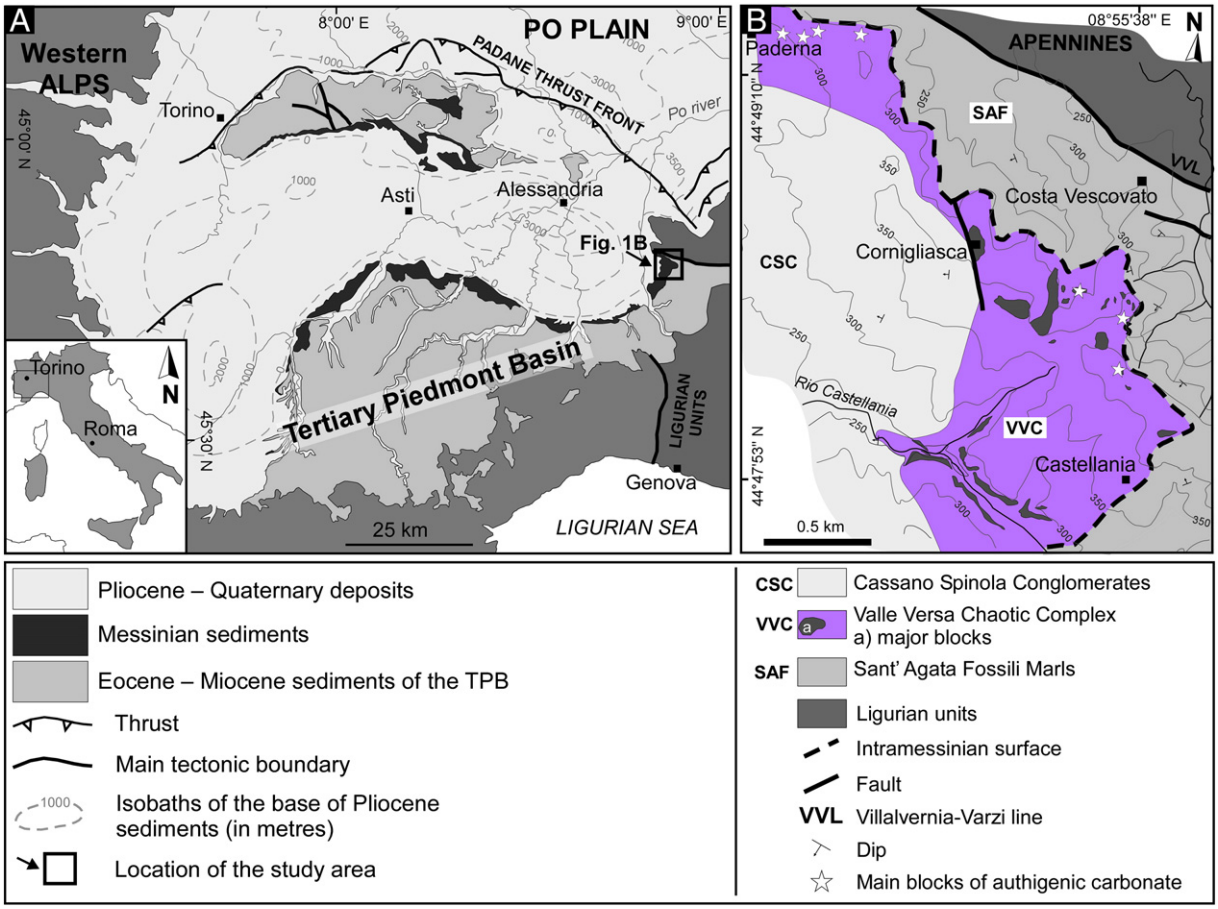

Fig 1. (A) Structural sketch map of northwestern Italy (modified from Bigi et al., 1990). (B) Schematic geological map of the study area showing the distribution of the main blocks of authigenic carbonate within the Valle Versa Chaotic Complex.