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A new model of the petroleum system in the Northern Apennines, Italy

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A B S T R A C T

A geochemical study on fluids from selected spontaneous seepages and drilled wells was carried out together with geologic investigation and deep cross-sections reconstruction to examine the petroleum system in the western Northern Apennines foothills. The hydrocarbons occurring in the Miocene foredeep units that form the reservoirs are commonly interpreted as generated in a source/reservoir system. However, the low Total Organic Carbon, its elevated dilution in the sediment pile and the limited amount of successions that entered in the oil window indicate a low potential for the hydrocarbons generation. The structures deformation in the Northern Apennines foothills is mainly late Miocene to Pliocene in age and involves successions that are progressively younger towards southeast. The earlier structure forms the Salsomaggiore anticline in the western sector. The comparison of the fluids from the wells and the mud volcanoes shows high geochemical and thermal history similarities. Saline waters originate from the connate pore water entrapped in the Miocene reservoir rocks during their deposition. The gaseous hydrocarbons are a mixture of secondary biogenic methane and primary and secondary thermogenic gases. The associated oils show both early and late maturities. These evidences account for different generation and migration steps, depending on burial conditions and deformation time. The various reservoirs appear confined by the thrust detachment at different depths and by the occurrence of reactivated lateral ramps. These results suggest the occurrence of a common source rock deeper than the Tertiary reservoir units, which progressively entered in the oil window. This source rock could have wide lateral extension, at least comparable with the width of the studied area, and represent a prime exploration target to evaluate the undiscovered oil and gas resources.

1. Introduction

In the first half of the XX century the petroleum exploitation in the Northern Apennines foothills and the near Po Plain was focused on the numerous areas of hydrocarbons spontaneous seepages, by means of simple collecting techniques and hand drilled shallow wells. After the 1950 the exploration increased with the discovery of a wide number of hydrocarbon fields that produced mainly biogenic (in the central Po Plain) or thermogenic gases associated with oil and condensates (along the Alps and Apennines mountain fronts buried in the Po Plain). During the past decades some authors investigated the origin of the hydrocarbons in these regions along the Northern Apennines (e.g. Mattavelli et al., 1983a,b; Riva et al., 1986). Their studies recognized that the main hydrocarbon fields host gas and oil generated in the turbiditic sequences of the Miocene "Marnoso Arenacea" Formation, which represents also the main reservoir of the petroleum system, or in the lower-middle Mesozoic successions. Notwithstanding an almost full comprehension of this petroleum province, some questions concerning the hydrocarbons origin and migration are still open. In the Tertiary foredeep the elevated thickness and sedimentation rate (up to 75 cm/10^3 years) are suitable for the good preservation of the organic matter (Borgia et al., 1988a). However, the low Total Organic Carbon ($\sim$0.5%) (Mattavelli et al., 1983b; Capozzi and Picotti, 2010) and the high dilution of organic matter in the siliciclastic sediments point to a low generation potential. Moreover, only the deeper horizons of the Miocene foredeep have reached the oil window temperatures, thus consistently reducing the thickness of sediment successions suitable to generate hydrocarbons. Recent data suggest that in the western Northern Apennines, the source rock responsible for the generation of the hydrocarbons could be located at greater depth, corresponds to older sedimentary successions than the Miocene units and could be of Cretaceous age (Capozzi and Picotti, 2010).

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The hydrocarbon fluid seepages are widespread in this area and are related to the occurrence of petroleum reservoirs. The study of their geological and geochemical characteristics is often carried out during the exploration of oil and gas accumulations at depth (Schumacher and Abrams, 1996; Abrams, 2005).

The spontaneous fluid seepage is a well-known phenomenon occurring mainly in compressive tectonic settings (e.g. Dimitrov, 2002; Morley et al., 2011), even if it is well documented also in other geological settings, such as deep sea fans and subsiding basins with high sedimentation rates (e.g. Aslan et al., 2001; Davies and Stewart, 2005; Calvès et al., 2009).

During the last centuries accurate lists and numerous descriptions of fluid seepages occurring in the Northern Apennines have been compiled (e.g. Spallanzani, 1795; Stoppani, 1871; Scicli, 1972; Ferrari and Vianello, 1985). More recent works focus on their mud volcano nature, pointing to the geological setting (e.g. Martinelli and Rabbi, 1998; Martinelli and Judd, 2004; Bonini, 2007; Capozzi and Picotti, 2002, 2010) and to the geochemistry of the emitted fluids (e.g. Mattavelli et al., 1983a; Capozzi and Picotti, 2002, 2010). In the Northern Apennines the cold seeps are roughly aligned along two bands striking northwestwards, located close to the main water divide and along the foothills (Fig. 1). In this sector of the Northern Apennines the fluids migration is related with the regional tectonic deformations and with the burial, mainly caused by the upper tectonic nappe of the chain (the Ligurian Units).

This study investigates the hydrocarbons and saline waters in the western Northern Apennines foothills through the analysis of selected spontaneous fluid emissions and deep wells. In this work the three mud volcano fields of Nirano, Torre and Rivalta have been studied. The published data of Regnano mud volcanoes were also considered (Capozzi and Picotti, 2002) in order to obtain a continuous fluid characterization along the foothills. A different condition is represented by the Salsomaggiore anticline, where the lower Miocene foredeep reservoir units crop out. This structure is actually exploited by SPA activities, and the presence of numerous wells allowed outlining the end-member of both connate waters and hydrocarbons that presently occur in the Miocene reservoirs.

A geochemical study has been carried out to better define their characteristics, which help to shed light on the possible source rock and the processes responsible for fluids alteration during migration and accumulation.

The information resulting from the fluid geochemistry allow defining some basic constraints for the local subsurface geology and the petroleum system. Our approach represents a first step for a new phase of hydrocarbon exploration in the western Northern Apennine chain; since both the insufficient covering and/or rough data quality of the aged reflection seismic and the occurrence of the thick and highly deformed Ligurian Units prevent the accurate reconstruction of the petroleum system components at depth.

2. Geological setting

The Northern Apennines are a folds and thrusts belt deforming the continental margin of the Adria plate since the Cretaceous. The oceanic accretionary prism formed due to the subduction of the European plate below the Adria plate. From the Middle Eocene,

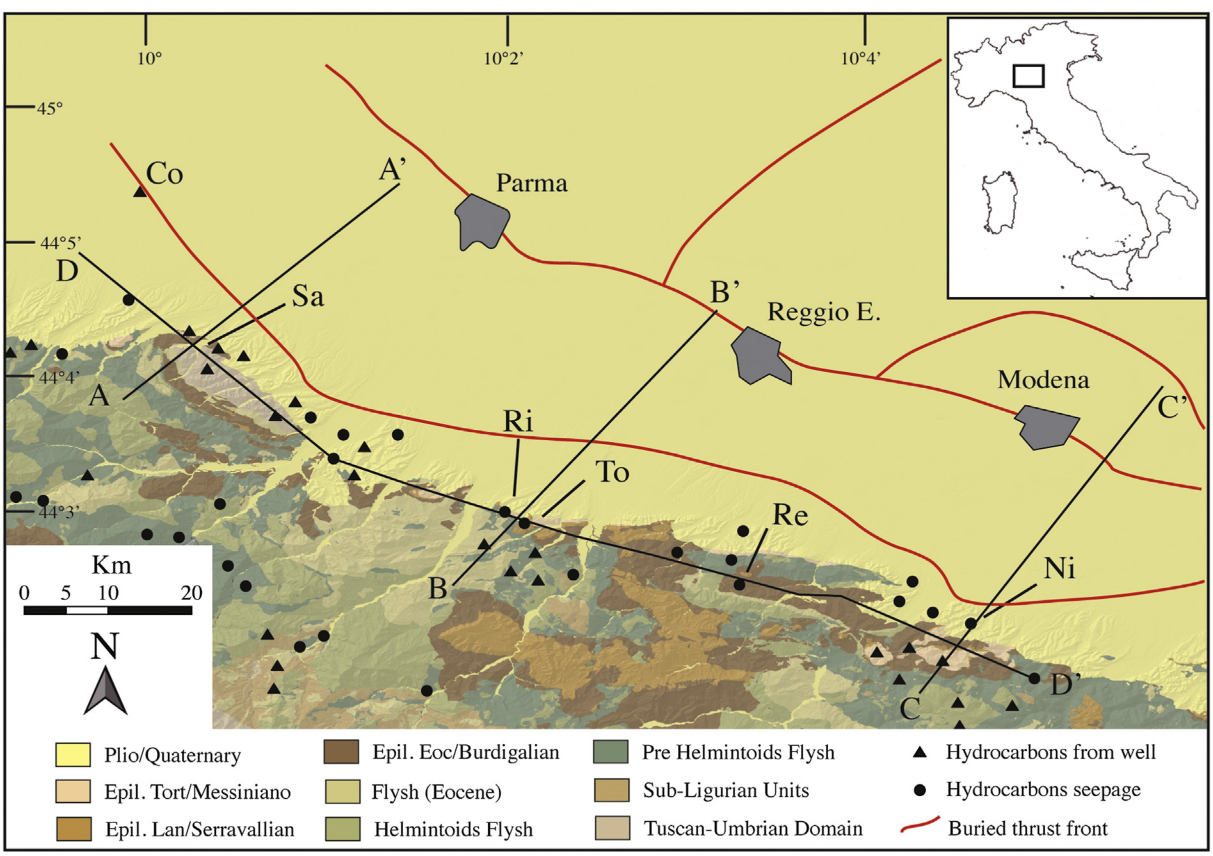

Figure 1. Geological map of the investigated sector of the Northern Apennines and location of the sampled mud volcanoes (Ri: Rivalta; To: Torre; Re: Regnano; Ni: Nirano) and deep wells (Sa: Salsomaggiore). The traces of cross sections of figures 2 and 3 are indicated. The locations of spontaneous fluids seepage and hydrocarbon occurrence in wells are modified from Scicli (1972). Co: Cortemaggiore Field.

Adria became the lower plate and the flip of the subduction allowed a change in the vergence and the consequent encroachment of the accretionary prism against the Adria continental plate. The pre-Middle Eocene evolution, characterized by oceanic tectonic accretion, is responsible for the strong deformation of the oceanic wedge deposits, now forming the Ligurian Units. Following the Middle Eocene flip, the retreating Adria subduction led to the opening of the Ligurian-Provençal and Tyrrhenian back-arc basins (Elter et al., 1975; Malinverno and Ryan, 1986). The Ligurian Units tectonically cover the Adria plate and its foredeep successions (Fig. 1). The deposits of the foredeep have been progressively incorporated into the orogenic belt, forming the structural highs, which currently form the hydrocarbon traps in the subsurface of the Northern Apennines and Po Plain. Furthermore, the Eocene–Pliocene Epiligurian successions were deposited in satellite basins located atop the Ligurian Units, during their emplacement above the deformed foredeep (e.g. Ricci Lucchi, 1986). The main orogenetic phase of the northern sector of the Northern Apennines took place between the Oligocene and early Miocene. Afterwards, the evolution of the chain decelerated, as is highlighted by the decreased advancement rate of the Ligurian nappe on the more recent units (Picotti et al., 2007), until its complete stop after the Messinian. During the Quaternary, the northwestwards reactivation of lateral ramps belonging to the Miocene–Pliocene thrusts caused the modification of reservoirs geometries, thus leading to a new phase of fluid migration and accumulation (Picotti et al., 2007). It is worth to note that the counterclockwise rotation of the belt during its evolution led to the diachronous collision of the orogeny, apparently due to the increasing velocity of the slab retreat towards southeast (Thomson et al., 2010). Consequently, gradually younger structures and sediments are found moving in this direction.

Modern studies have shown that most of the investigated Apennine foothills are affected by recent tectonic activity. The mountain front is correlated with the activity of a deep thrust that deforms the whole belt up to the Holocene continental deposits (Picotti and Pazzaglia, 2008). Extension occurs in shallower portions and it is responsible for the formation of high-angle normal faults (Picotti et al., 2009), which are the main pathways for the upward fluid migration and the formation of mud volcano structures at the surface (Capozzi and Picotti, 2010).

3. Structures and stratigraphy

The stratigraphic architecture and structural setting of the considered Northern Apennines have been reconstructed integrating the study of surface geology with exploration well logs and industrial seismic lines (Fig. 2). To determine the stratigraphy and the structures controlling the fluids generation and migration, we constructed three cross sections along dip of the mountain front (Fig. 3). These have been integrated by a tie section, running NW–SE along strike of the main structural axis, to show the lateral terminations of the thrust sheets and the lateral variation and closure of the stratigraphic units along the Apennine foothills (Fig. 4).

The studied sector is characterized by the wedge-shaped closure of the Ligurian Nappe over the Miocene foredeep successions. This peculiar geometry is likely due to the gravitational reworking (olistostromes) at the tip of the Ligurian nappe. Folds and thrusts in the underlying foredeep succession occurred during and after the tectonic and gravitational emplacement of the Ligurian Nappe (Zattin et al., 2002).

The outward migration of the foredeep depocenters through time and the gradual thinning of its units moving towards the foreland are the consequence of the progressive encroachment of the deformed wedge against the subducting Adria plate.

Figure 3 shows two different thrust sheets, detaching in the pre-Burdigalian succession (section AA') and in the Burdigalian/Langhian units (sections BB' and CC'). The section AA' shows the Salsomaggiore anticline, which started growing in the Langhian and developed during the Serravallian as an intrabasinal structure that folded the Burdigalian–Langhian foredeep succession of turbiditic sandstones and marls. The deformation went on up the Tortonian, bringing about the exposure and erosion of the thrust-top. As a consequence of a renewed subsidence pulse, during the Messinian the thrust-top was covered by an olistostrome detached from the Ligurian nappe that sealed the upper thrust sheet. The Plio-Pleistocene activity of the deeper structure led to the large wavelength folding and erosion, with the passive refolding of the upper thrust sheet and a northwest vergence (section DD', Fig. 4). This deeper thrust sheet, cored in the crystalline basement, propagates up-section to the north (sect. AA', Fig. 3), fading out in the Pleistocene succession.

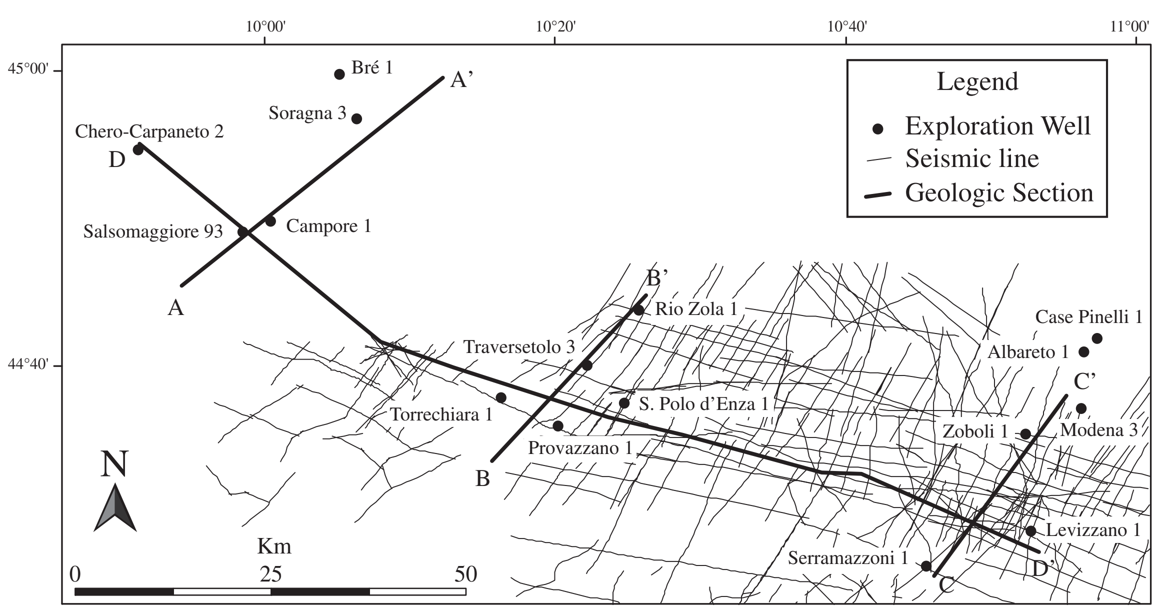

Figure 2. Base map showing the location of public and industrial data used for the cross sections reconstruction. Unrestricted access exploration wells and seismic lines are available at Videpi (2013).

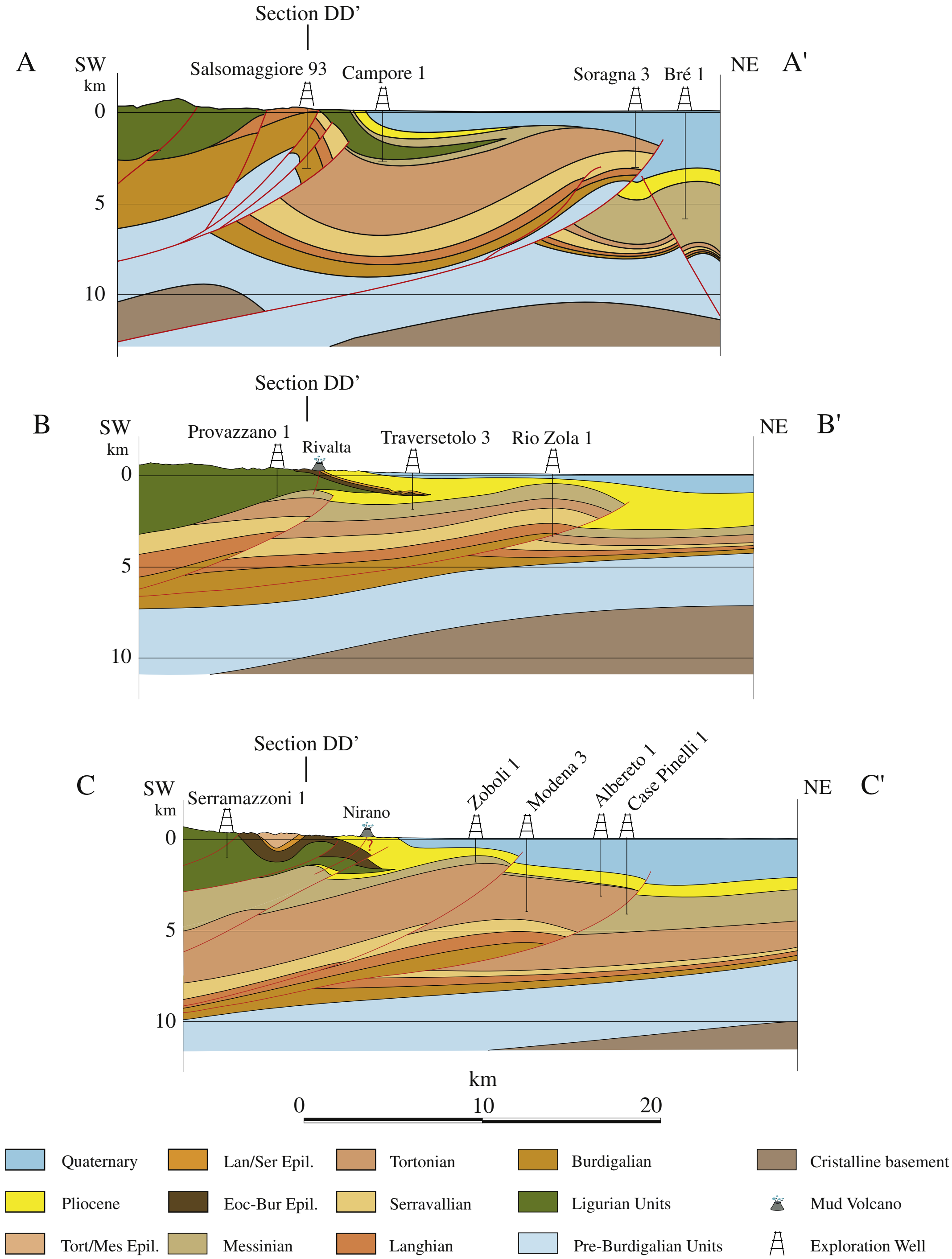

Figure 3. Cross-sections along dip of the Northern Apennines front in the area studied (see Fig. 1 for location). At Salsomaggiore the fluid reservoir outcrops (section AA'), the Ligurian and Epiligurian units seal the reservoirs at Rivalta and Nirano (sections BB' and CC'). The spontaneous emissions are associated with the ramp anticlines along the Northern Apennines foothills. High angle normal faults are the main fluid migration pathways to the surface. The hydrocarbons migrate in the traps up-dip from the deep sediments located in the SW areas. Section AA' is modified after Picotti et al., 2007.

In the section BB' two thrust sheets deform the Burdigalian to Pliocene succession. The internal one shows a thinner Messinian respect to the external structure, which suggests the thrust top growth since then. The external structure grew essentially during the Pliocene and basal Quaternary.

The thrusts occurring in Section CC' show a thick succession of Tortonian, whereas the Messinian succession thins from the internal to the external structures. The progressive thinning atop of the more external structures has been calibrated by the drilled wells and it documents growth during this time interval. The geometry of the Pliocene succession suggests a decrease of the thrust activity, coupled with a minor advancement of the Ligurian nappe (Early Pliocene). A renewed pulse of deformation is documented by the Quaternary dramatic thickness variations.

The section DD' (Fig. 4) evidences the progressive westward thickening of the Burdigalian to Serravallian units, which form

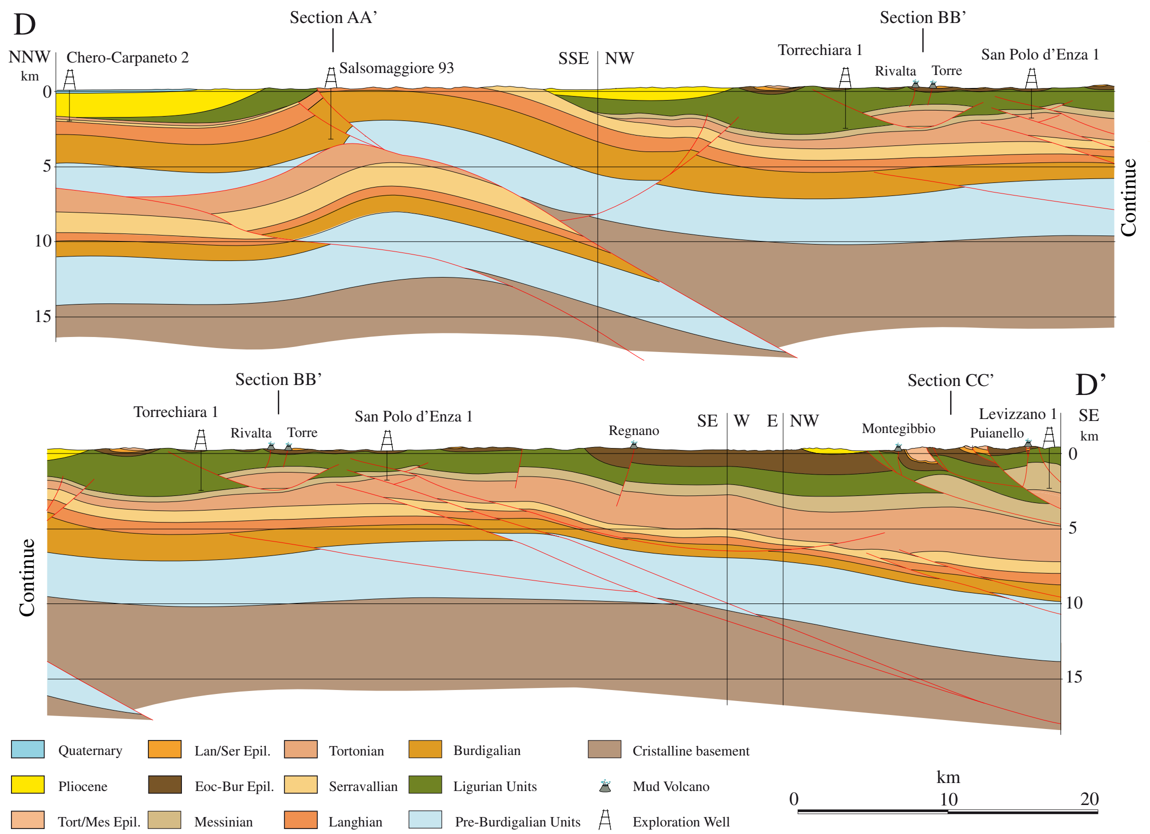

Figure 4. Cross-section along strike of the Northern Apennines front in the area studied (see Fig. 1 for location). Three systems of NW verging thrust modify the geometries of the reservoirs during the Quaternary. It is evident the separation of the different structural traps.

the main foredeep sequences in the Salsomaggiore area. On the other hand, the Tortonian and Messinian units thicken toward the east, where they are involved in the thrusting. The area of Rivalta and Torre is located in an intermediate position, likely representing a transition zone between the Salsomaggiore and Nirano systems.

The progressive younger age of the sediments deformed by the thrust sheets of Figures 3 and 4 moving southeastwards is related to the gradual divergence of the Burdigalian to Pliocene foredeep depocenters respect to the Quaternary mountain front, across which the three sections of Figure 3 are located. For these reasons the mud volcanoes are fed by Miocene foredeep units that are younger toward the southeast.

The mud volcanoes formed in correspondence of high angle normal faults, which are widespread along the Northern Apennines foothills (Picotti et al., 2009) and crosscut the sealing Ligurian and Epiligurian cover down to the Miocene sediments. Figure 4 shows several NW verging lateral ramps, which deformed the previous geometries and are rooted at depth within the crystalline basement. This latter deformation, reworking the Miocene thrust belt, led to a renewed fluid migration actually forming the mud volcanoes.

The external and younger thrust sheets buried under the Po plain (Fig. 3) are not associated with spontaneous emissions, likely due to the absence of recent normal faulting and preserved Upper Neogene sealing units. Wells drilled on these structures often report the occurrence of connate saline water and small amounts of light hydrocarbons. However, the occurrence of exploited hydrocarbon fields in other comparable structures is documented.

4. Mud volcano fields

4.1. Nirano mud volcanoes

The mud volcanoes area named "Salse di Nirano" (Ni in Fig. 1) is about 75,000 m^2 wide and represents one of the largest mud volcano fields occurring in Italy (Fig. 5). The mud volcanoes develop on the bottom of a caldera-like structure, which has a maximum diameter of about 500 m (Fig. 5a). The caldera represents the result of a collapse within the Plio-Pleistocene succession (Capozzi et al., 1994; Martinelli and Rabbi, 1998; Castaldini et al., 2005; Accaino et al., 2007), possibly following different paroxysmal events of fluids and mud emission. Bonini (2008) describes this caldera as the result of the collapse of the top portion of a mud diapir arising to the surface, similarly to what happens in some submarine structures (e.g. Henry et al., 1990). However, no evidence of mud diapirism was previously described in the area.

The flat bottom surface of the caldera contains four clusters of mud cones; the largest of them reaches the height of about 3 m (Fig. 5b, c). The amount of emitted fluids vary significantly from well-developed gryphons, with steep slopes generated by the slow dense mud emission, to mud pools with few suspended sediments and where the emission of saline water and gas is generally more abundant and continuous. The frequent occurrence of Pliocene age mollusc shells (Accaino et al., 2007) and a new biostratigraphic study on nannoplankton assemblages (Negri, 2011, personal communication) are indicative of the prevalent role of Pliocene sediments in the formation of the cones. Moreover, the presence of calcareous nannoplankton of Cretaceous age (>10% of total amount), can stress the occurrence of a minor mud component

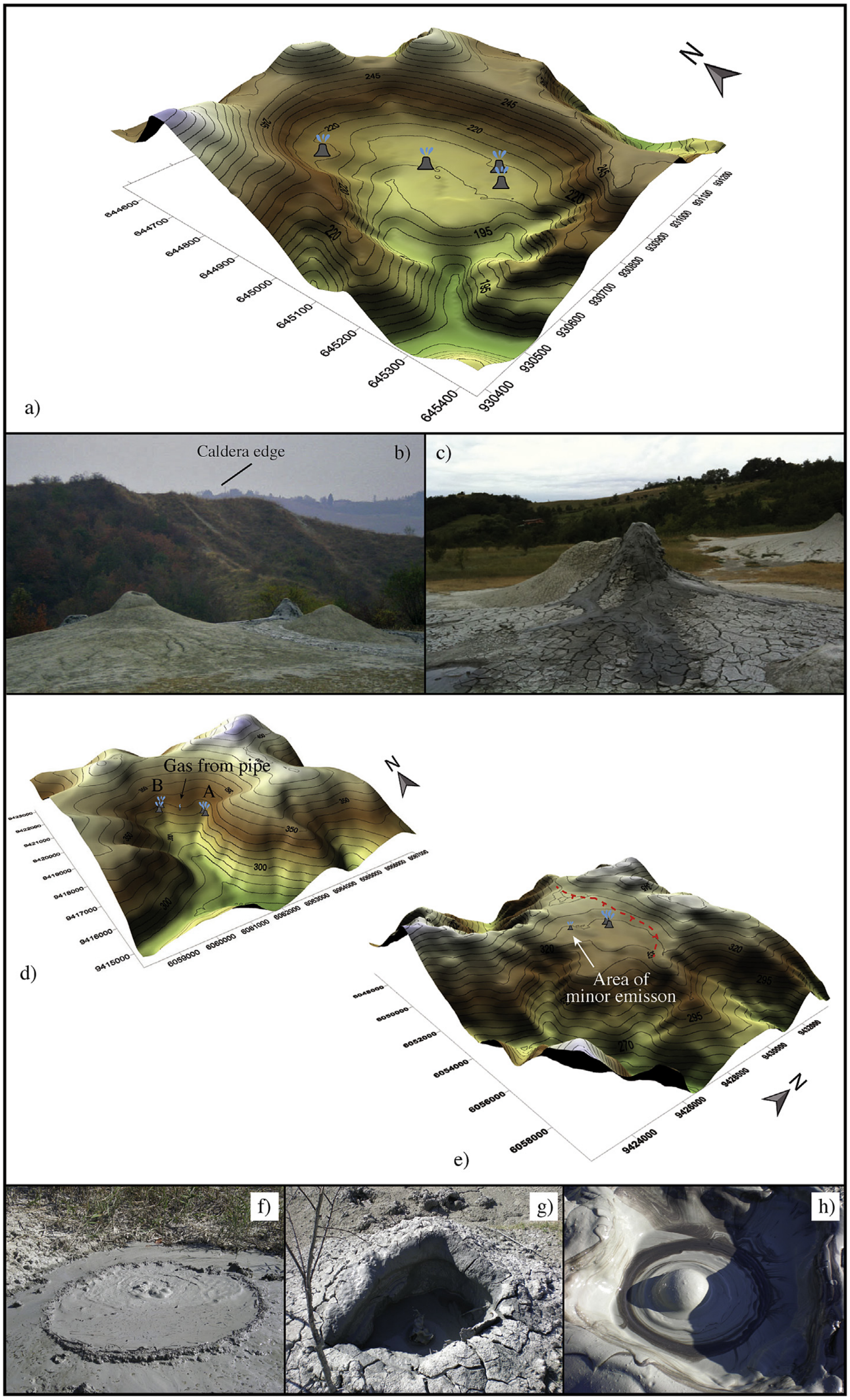

Figure 5. a) The Nirano mud volcano field develops at the bottom of a caldera-like depression likely formed in consequence of the persistent mud emission during time. Four clusters of emission vents, formed by 3–4 m high gryphons, are occurring. b) View of the caldera edge delineating the area interested by mud emission. c) Gryphon where is visible the emission of dense mud, which is responsible for the steep slopes of the cones in the mud volcanoes field. d) View of the Torre mud volcano area. Two clusters of mud cones and pools are located on a steep slope. These latter are separated by a small relief where the constant methane leakage occurs by means of a very shallow dismissed well. e) Rivalta emission area. The mud cones are located in the hanging wall of an inferred normal fault, which is responsible for the fluids migration and seepage to the surface. The emissions of Torre and Rivalta fields include small pools with abundant methane degassing (f) and small cones formed by very dense mud (g). The occurrence of oils and condensates is particularly evident in the Rivalta mud cones (h).

derived from the Ligurian Units, whose occurrence in the subsurface can be observed in the cross section C–C′ of Figure 3.

4.2. Torre and Rivalta mud volcanoes

The mud volcanoes of Torre and Rivalta are located in the Apennine foothills between the Parma and Enza rivers (To and Ri in Fig. 1). The fluid leakage occurs through the Epiligurian Units, in this area consisting of Burdigalian to Serravallian sediments. The calcareous nannoplankton assemblages in the mud emitted by the mud volcanoes of Torre and Rivalta evidenced the occurrence of species belonging mainly to Late Cretaceous, Paleocene to Eocene and Serravallian to Tortonian ages (Negri, 2011, personal communication).

Both sites are smaller than the Salse di Nirano, and gryphons higher than 50 cm are absent. The emission vents at Torre (Fig. 5d) form two main groups (A and B) located on a slope stabilized by crops. The group A is the largest (about 7500 m^2), and shows different morphologies. The principal emissions are constituted by gryphons with a modest water emission and a moderate content of suspended fine material, associated with abundant degassing. Some pools occur, which the largest has a diameter of about 3 m. In the emissions area the first 50 cm of surface sediments are strongly impregnated by fluids, denoting a widespread leakage. The seeping fluids are mainly gas and saline water, with a minor contribution of liquid hydrocarbons. The group B is smaller than group A and includes two major structures and a localized seepage where the emission of gas is associated with small quantities of mud. A gryphon with very dense mud emission constitutes the first structure; while the second is a small pool with an intense degassing (Fig. 5f, g). Smooth layers of mud breccia, including calcarenitic clasts and gastropod shells belonging to the underlying Epiligurian Units, cover the surrounding areas. The group B is separated from group A by a topographic high; at the top of that a leakage occurs through a dismissed very shallow drilled well.

The mud volcanoes of Rivalta develop northwestwards to the site of Torre, in a flat area that interrupts a steep slope (Fig. 5e). This morphology, according with both the geological maps and the field observations, is likely due to the presence of an extensional fault dipping to the south and generated by the downward movement of the hanging-wall. The emissions are mainly localized in correspondence of the fault tip and are constituted by three small gryphons (on average about 20 cm in height). The release of saline water is associated with the emission of liquid hydrocarbons in higher proportions than in the other studied sites and usually with constant gas seepage (Fig. 5h). Less intense fluid leakage interesting a nearby area likely represents the first stage of formation of a new mud volcanoes cluster.

5. Methods

The ions abundances in the saline waters were analysed at the laboratories of the Department of Biological, Geological and Environmental Sciences of the University of Bologna, by means of ion chromatography (IC), inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS). The isotope analysis on waters was performed using a mass spectrometer at the Geosciences and Georesources Institute of CNR (Pisa), which analysed also the gas composition and stable isotopes abundances. The analyses on oil samples and the anaerobic microbiological cultures were performed at the ENI laboratories in San Donato Milanese.

The interpretation of the structures at depth was obtained by integrating the surface geology with logs of exploration wells and public and private seismic lines.

6. Results

6.1. Saline waters

The chemical characteristics of the saline waters seeping in the Northern Apennine foothills provide indications about their origin and the processes occurring during diagenesis and migration.

In this work the comparison between saline waters from the Salsomaggiore drilled wells and those recovered from the mud volcanoes was carried out to obtain a better definition of the oilfield waters occurring in the reservoirs and to unravel some geochemical aspects dealing with the migration trough the sealing units.

The geochemical characteristics of deep saline waters in the Northern Apennine foothills are well known and numerous datasets are available (e.g. Conti et al., 2000; Minissale et al., 2000; Martinelli and Judd, 2004; Capozzi and Picotti, 2010; Boschetti et al., 2011).

During the migration towards the upper layers of the sedimentary column the saline waters often experience changes in their chemical composition. A particular process, which can occur when the water crosses through thick pelitic covers, is defined as reverse osmosis, chemical reverse osmosis, hyperfiltration or membrane filtration (White, 1965; Hanor, 1987). This process is due to the different permeability of the pelitic sediments respect to the various dissolved ions. The buried and compacted clays mechanically delay the passage of ions and large charged molecules. Moreover, the negative charges occurring on the surface of the clay particles slow down the anions movement and, since the aqueous solution tends to maintain the charge equilibrium, the flow of cations is also partially delayed. On the contrary, the small neutral molecules, such as water, are not influenced by this mechanism. In normal conditions the water molecules migrate spontaneously through a membrane from the less saline solution to the more saline, according to the osmosis process. The reverse osmosis takes place when the fluids pressure is sufficient to force their movement in the opposite direction (White, 1965; Kharaka and Berry, 1973; Kharaka and Hanor, 2003). Laboratory experiments (e.g. Kharaka and Berry, 1973; Demir, 1988) and observed trends of the spontaneous potential logs in wells with brine-saturated pelites have proven that these sediments could act as semipermeable membranes (Hanor, 1994). The water that has undergone this process, defined as Membrane Filtered Connate Water, shows content of Total Dissolved Salts (TDS) less than at the origin. To the contrary, the fraction of pore water that remains in the other side of the membrane becomes progressively hypersaline (Membrane Concentrated Connate Water). The process of microfiltration creates a difference in the electric potential between the opposite sides of the membrane, originating a more acid pH in the "concentrated" side and a more basic in the "diluted" one (White, 1965). This sieving effect is not a perfect system within the sedimentary succession, particularly in presence of discontinuous, fractured and/or faulted units.

In the Northern Apennines system, the sedimentary successions potentially responsible for the major filtration are constituted by the Ligurian Units, which also usually represent the seal rocks for the Tertiary foredeep reservoirs.

6.1.1. Salsomaggiore waters

The brines of the Salsomaggiore reservoir have been considered as representative for the formation waters hosted in the Tertiary reservoirs, which are currently feeding the spontaneous seepage systems along the Northern Apennine foothills (Capozzi and Picotti, 2010).

Despite the age range of reservoirs, which extends form Burdigalian through Messinian, the various saline waters can be considered geochemically homogeneous, as evidenced by the comparable waters chemistry of the Burdigalian Salsomaggiore reservoir and the nearby Upper Miocene Cortemaggiore oil and gas field (AGIP, 1959).

The chlorine concentration in Salsomaggiore reaches 76,588 mg/l, evidencing a strong enrichment. In consequence of its conservative behaviour, the variation of Cl is mainly due to diffusion and filtration mechanisms, and not to the thermodynamic equilibrium with one or more mineral phases (Hanor, 1994).

The brines of deep reservoirs frequently show an increase in the concentration of calcium and a decrease of magnesium in the solution, as for Salsomaggiore where the Mg/Ca ratio shows a strong Ca enrichment (Table 1; Fig. 6). The amounts of Ca and Mg in solution are usually controlled by the precipitation and dissolution of mineral phases (Kharaka and Hanor, 2003). The lack of significant carbonate successions in the considered areas indicates that the abundances of these ions have been influenced only by the interactions with the occurring siliciclastic units. Moreover, the processes of precipitation and/or dissolution of carbonate cements are not relevant due to the achieved equilibrium between the carbonate phases in absence of exchanges with the atmospheric CO_2 (see Section 6.2) and the preserved reservoir permeability, which is maintained through the pore saturation by the fluids, in particular methane gas.

With the progressive chloride enrichment during diagenesis, the interactions between the saline water and the solid phases within the Salsomaggiore siliciclastic reservoir can be explained with a ten mineral phases system (Hanor, 1996).

In absence of CO_2 supply, calcite and dolomite are not longer actively involved with the system and the alkalinity does not vary. The quartz is mobilized and the dissolved silica increases slowly because it is rapidly incorporated into other mineral phases (Hanor, 1996). Anorthite partially dissolves leading to an increase in calcium concentration, whereas potassium and sodium do not, because they precipitate as K-feldspar and albite (Hanor, 1996). This mass transfer between mineral phases can locally enhance the reservoir porosity. The magnesium concentration decreases with depth and temperature rising, partly due to its inclusion in the crystal lattice of mica in fine sediments (White, 1965; Kharaka and Hanor, 2003).

In the deep basinal brines the bromine geochemistry is strongly correlated to that of Cl, and the Br/Cl ratio can be useful to trace the main source of this latter (Kharaka and Hanor, 2003). The highly saline Salsomaggiore water shows a Br/Cl ratio equal to the seawater, thus revealing the proportional enrichment of both ions during time. This is typically interpreted deriving from evaporative processes (White, 1965; Hanor, 1994; Birkle et al., 2002; Kharaka and Hanor, 2003). However, the evaporation could not be responsible for the generation of the considered saline waters, as well as the dissolution processes, due to the complete absence of halite in the successions of this Northern Apennines sector.

Therefore, the bromine origin must be ascribed to the diagenetic evolution of the connate waters, more precisely to the water-rock interactions occurring into the reservoirs and during the migration towards the surface.

Moreover, the significantly high bromine content in the Salsomaggiore waters (up to 238 mg/l, Table 1) could be partially related to the alteration of organic compounds during burial and diagenesis (Martin et al., 1993). This latter process is also responsible for the recorded high concentration of iodine (Martin et al., 1993; Kharaka and Hanor, 2003).

The influence of organic compounds in the composition of saline waters is demonstrated also by the content of ammonium ions. The high abundance of NH_4 in Salsomaggiore is ascribed to the

Table 1
Ions concentrations in the analysed saline waters.

		Nirano	Torre	Rivalta	Regnano[a]	Salsomaggiore well 93	Seawater
T	°C	12.8	11.4	9.6	12.2	17.8	
pH		8.3	7.6	7.4	8.2	6.9	
Eh	mV	−219	−207.5	−208.8	−99	−103	
COND	mS/cm	14.5	18.2	18.8	22.0	186	
Na	Solute concentration (mg/l)	4783	4733	5084	6210	41,910	10,770
K		15.7	9.3	16.7	23	381	380
Ca		32	88	143	58	4299	412
Mg		60	95	195	86	1002	1290
HCO_3		1757	1358	1022	2928	122	140
Cl		6635	6082	7686	8875	76,588	19,500
I		bdl	bdl	47	40.5	57.9	0.05
Br		62.90	60.60	57.60	58.8	238	65
NO_3		3.5	7.5	4.0	7.09	bdl	0.23
SO_4		7.2	12.2	17.2	2	114	2649
NH_4		2.16	2.16	1.60	0.80	117	0.07
B		117.8	69.25	53.30	–	73.21	4.6
SiO_2		2.9	8.2	2.3	3.4	10.8	7.0
S_2		0.012	0.035	0.034	2	bdl	0
Li		0.500	0.720	0.850	–	15.11	0.180
Fe		0.076	0.030	0.013	11.53	1.204	0.02
Mn		0.005	0.026	0.020	–	0.559	0.01
Ca/Cl		0.005	0.014	0.019	0.007	0.056	0.021
Mg/Cl		0.009	0.016	0.025	0.010	0.013	0.066
Na/Cl		0.721	0.778	0.661	0.700	0.547	0.552
K/Cl		0.002	0.002	0.002	0.003	0.005	0.019
HCO_3/Cl		0.265	0.223	0.133	0.330	0.002	0.007
SO_4/Cl		0.001	0.002	0.002	0.0002	0.001	0.136
Br/Cl		0.009	0.010	0.007	0.007	0.003	0.003
Mg/Ca		1.905	1.086	1.364	1.486	0.233	3.131
$\delta^{18}O$	‰ V-SMOW	4.62	3.91	4.66	3.05	–	0
δD		−19.5	−10.3	−14.1	−22	–	0

– Not determined; bdl: Below detection level.
[a] From Capozzi and Picotti (2010).

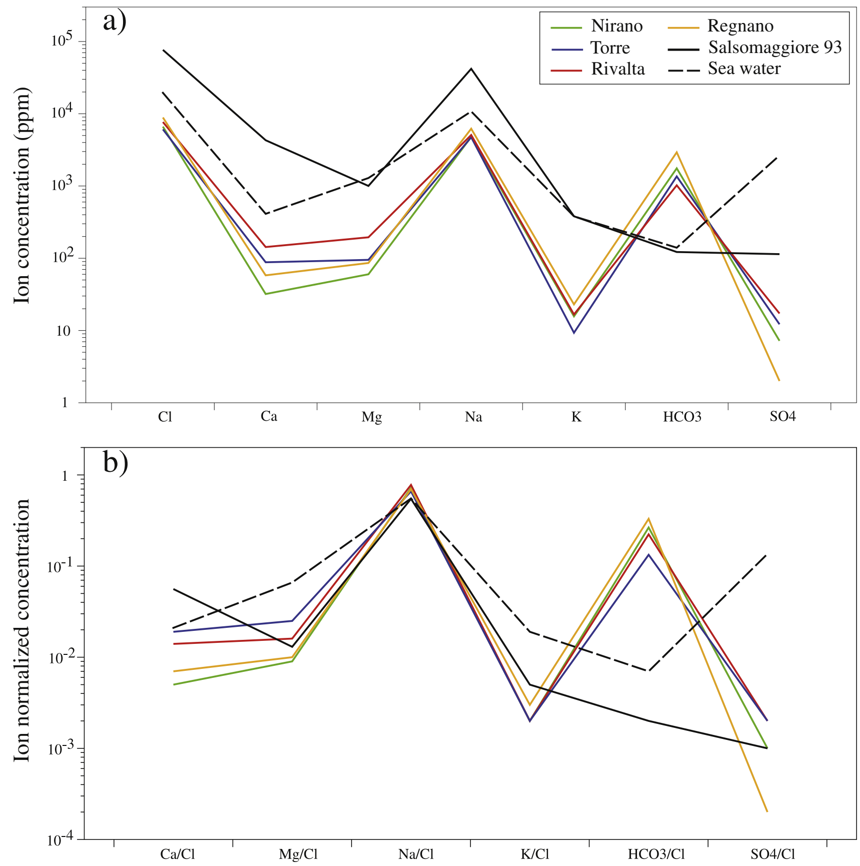

Figure 6. Major ions content in the analysed saline waters: a) measured value; b) concentrations normalized respect to Chlorine. The present day seawater represents the similar pore water during the sediment deposition. The concentration data are represented in logarithmic scale.

hydrocarbons genetic environment, which is rich in NH_3 originated from the anaerobic decay of proteins and that, under the occurring slight acid pH conditions, is progressively transformed into NH_4 (Collins, 1975). These three ions could likely be supplied to the saline water mainly by the liquid hydrocarbons occurring in the system.

6.1.2. Mud volcano waters

The mud volcano waters are derived from the reservoir water that has been modified during the upward migration (Capozzi and Picotti, 2010).

In the mud volcano waters the pH values are slightly alkaline, while the redox potential (Eh) denotes conditions of marked reduction (Table 1). The conductivity indicates that the water is moderately saline, thus being different from Salsomaggiore. These data are consistent with those reported in literature for the Northern Apennines cold seeps (e.g. Minissale et al., 2000; Capozzi and Picotti, 2002, 2010).

The fluids emitted by the investigated mud volcanoes are characterized by lower concentration of the dissolved ions with respect to the modern seawater, as evidenced by the chlorine, which shows concentrations one order of magnitude lower than in seawater (Table 1). They show distinguishing abundances of HCO_3 and SO_4. The high content of HCO_3, combined with the almost complete removal of SO_4 from the solution (Fig. 6), could be derived from the anaerobic sulphate reduction operated by the Sulphate Reducing Bacteria (SRB) found in the mud volcano structures (Heller et al., 2011). The SRB degrade the carbon contained in the hydrocarbons, according with the general reaction (Friedman et al., 1992):

$$SO_4^{2-} + 2H_2O + 2C_{org} \rightarrow H_2S + 2HCO^{3-}$$

The amount of produced H_2S is very low in the solution, since it can precipitate as iron sulphides due to the largely available iron in the siliciclastic sedimentary units.

The deep fluids that are feeding the mud volcanoes do not have CO_2 inputs from the surface, as they are not mixed with meteoric water. Therefore, the concentration of HCO_3 varies in consequence of the described bacterially mediated processes and of the equilibrium reached between the carbonate species during the diagenesis in the reservoir.

Sodium is the most abundant cation in the water of the analysed mud volcanoes. The Na/Cl ratio is greater when compared with the seawater (Table 1) and an influence of both the input from clay minerals and the filtration process can be hypothesized. The waters show a strong enrichment in boron contents, up to 117.8 mg/l in the Nirano mud volcanoes (Table 1). With the increasing of temperature and tectonic stress the B enriches in the fluid phase, since it is released from the sediments during the smectite-illite transformation and the dehydration of clay minerals (You et al., 1993; Kopf and Deyhle, 2002). Therefore, a partial contribution to the water chemistry could be ascribed to this process. Also a partial boron content could derive from the organic matter degradation (Collins, 1975; Kharaka and Hanor, 2003).

A process that favours the removal of the Ca ion from the water (Table 1; Fig. 6) is its reduced mobility through the pelitic membranes as a consequence of both its double positive charge and the large ionic radius (White, 1965), thus being prone to concentrate in the hypersaline residual fraction and to be removed from the uprising fluids.

The amount of bromine in the examined waters is high with respect to the lowering trend identified for the other ions. Although it has not been defined a clear influence of the membrane filtration on the Br abundance (White, 1965), its concentration in the mud volcanoes water seems to point towards a lesser influence of this process on the ion behaviour. The iodine content is also not affected by hyperfiltration, which high amounts are barely slight lower with respect to the Salsomaggiore water. The extremely low content in Torre and Nirano samples (Table 1) is thought to arise from some analytical error, because unpublished data showed values as high as 56 mg/l.

6.2. Saline water stable isotopes

The global scale analysis carried out on the stable isotope composition in sedimentary basin brines showed a progressive increase in $\delta^{18}O$ and δD with time and depth (Clark and Fritz, 1997).

The Salsomaggiore reservoir water shows $\delta^{18}O$ ratios comprised between 9.14‰ and 12.63‰ V-SMOW, while the δD varies between −9.1‰ and −19.7‰ (Capozzi and Picotti, 2010) (Fig. 7).

In the closed water-rock system of the Salsomaggiore reservoir, the original marine pore water was gradually mixed with ^{18}O rich and D poor waters derived by the progressive clay dehydration during the recrystallization of smectite to illite. It is worth to note that the exchange between water and hydrocarbons or H_2S could enrich the δD content at low temperatures (Clark and Fritz, 1997; Horita, 2005).

The mud volcano waters show a minor ^{18}O enrichment and δD comparable with the reservoir waters (Fig. 7). These fall within the range already identified for Northern Apennines cold seepages (e.g. Capozzi and Picotti, 2002).

The stable isotopes abundances in the mud volcano waters can be also ascribed to the processes acting during the fluid migration towards upper sedimentary layers. Some authors recognize the role of the membrane filtration, or in general of the migration process, on the isotopic fractionation (e.g. Clark and Fritz, 1997; Kharaka and Hanor, 2003). Field tests and laboratory experiments show a

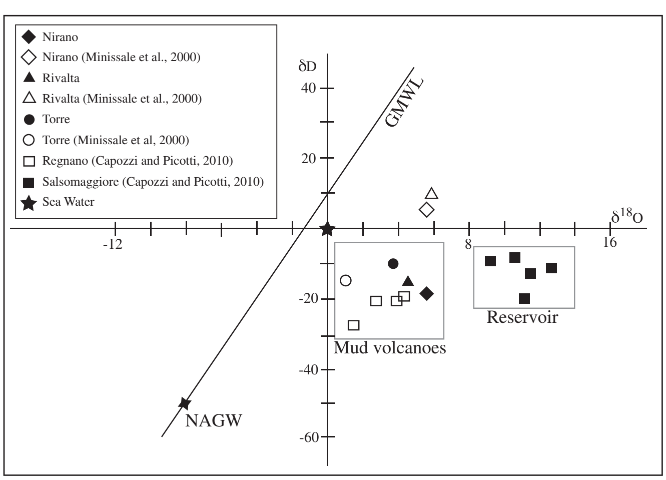

Figure 7. $\delta^{18}O$ vs. δD plot for the considered reservoir and mud volcano saline waters. All the samples are in the field of the formation waters, without mixing with the present day meteoric water. The more negative $\delta^{18}O$ values in the mud volcanoes respect to reservoir water suggest that these were subject to hyperfiltration processes. Otherwise, the δD appears to be not affected by this mechanism. The positive δD in Rivalta and Nirano (from Minissale et al., 2000) are probably due to particular environmental conditions occurring during the sampling. GMWL: Global Meteoric Water Line; NAGW: Northern Apennines Ground Water.

general enrichment in the heavy isotopes, especially ^{18}O, in the "concentrated" waters and the partial removal from those "filtered", if compared (Coplen and Hanshaw, 1973). Therefore, the important decreasing of ^{18}O content in the mud volcano waters respect to the reservoir waters can be ascribed to the filtration mechanism, while the Deuterium does not appear highly influenced by this process.

6.3. Hydrocarbons

The analysis on the hydrocarbons sampled in the Salsomaggiore area and on those emitted by the mud volcanoes allows to reconstruct the thermal history of the gas and oil occurring in the Northern Apennines reservoirs.

In the Salsomaggiore area the hydrocarbons were collected from two deep wells that are actually exploited for gas (Salsomaggiore 93 and Salsominore 16) and from one that is unexploited (Salsomaggiore 7).

Samples of oil and gas were collected in the mud volcanoes during phases of intense seepage, due to the necessity to minimize the alterations caused by the slow rise of the hydrocarbons through the pelitic cover, as well as those related to the prolonged exposure of oils and condensates at the surface condition. Gases were sampled from all the considered structures, while the liquid hydrocarbons were acquired only in the sites of Torre and Rivalta, as Nirano never emitted enough amounts to be analysed.

In this research are considered the gases sampled during two paroxysmal events of Nirano (May 2012) and Regnano (March 1999; Capozzi and Picotti, 2002) mud volcanoes (Nirano Parox and Regnano V9-1 and V9-2 respectively). The importance of these measures lies in the fast and abundant fluid leakage, which could better represent the deep fluids.

6.3.1. Salsomaggiore gas

In the Salsomaggiore area three deep wells has been sampled for gas characterization: Salsomaggiore 7 and 93 and Salsominore 16. Literature data are used for the Salsomaggiore 8 well (Borgia et al., 1988b) and the nearby Cortemaggiore field (Fig. 1) (Mattavelli et al., 1983a; Pieri, 1992).

The gas of the Salsomaggiore reservoir is mainly composed by methane (>93%), with minor amounts of non-hydrocarbon gases (CO_2 <0.52%). The C_{2+} contents vary between 0.63% (Salsominore 16) and 1.92% (Salsomaggiore 7); therefore the calculated gas dryness ($C_1/\sum C_{1-5}$) is up to 0.994.

The stable isotope analysis is a useful tool that allows clarifying some aspects of the thermal and migration history of hydrocarbons. The genetic fractionation acting during the gas generation controls the $\delta^{13}C$ ratios (Prinzhofer and Huc, 1995) and progressively leads to the ^{12}C depletion with the thermal maturation of the source rock (Aali et al., 2006). In Salsomaggiore wells 93 and 7 the carbon isotopic distribution is coherent with the Rayleigh distillation/fractionation model, where $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$ (Table 2; Fig. 8). In Salsomaggiore 7 were also possible to determine the *normal* and *iso-alkanes* C_4 (0.375% and 0.258% respectively) and C_5 (0.396% and 0.008%); they also follow the Rayleigh model (n-C_4: −21.33‰ and n-C_5: −20.65‰ Vienna-Pee Dee Belemnite (VPDB)). Differently, the Salsominore 16 presents ^{13}C enriched ethane, leading to the inversed $\delta^{13}C_2 > \delta^{13}C_3$ due to the occurrence of selective biodegradation, the mixing of different gases or representing the residual fraction of a migrated gas.

The methane $\delta^{13}C$ in the Salsomaggiore gases varies between −42.99‰ and −51.87‰ VPDB (Table 2), which is indicative of thermogenic methane associated with oil (Schoell, 1983).

Figure 8 shows the $\delta^{13}C_n$ vs. $1/n$ diagram for some of the analysed gases. Chung et al. (1988) established that an unaltered isotope curve for thermogenic gases must be nearly linear in this type of diagram and with a progressively gentler slope as maturity increases.

Table 2
Chemical and isotopic composition of the considered gases.

	Type	CH_4%	C_2H_6%	C_3H_8%	$\sum C_{2+}$%	Dryness	CO_2%	$\delta^{13}C_1$ ‰ VPDB	$\delta^{13}C_2$ ‰ VPDB	$\delta^{13}C_3$ ‰ VPDB	$\delta^{13}D$ CH_4 ‰ V-SMOW	$\delta^{13}C$ CO_2 ‰ VPDB
Salsomaggiore 7	Well	96.94	1.392	0.5300	1.920	0.981	–	−51.87	−27.56	−22.32	–	+7.98
Salsomaggiore 8[a]	Well	93.43	2.570	3.0800	5.650	0.943	0.52	−47.40	−23.50	–	–	–
Salsomaggiore 93	Well	96.90	1.220	0.2260	1.450	0.985	0.14	−42.99	−25.70	−25.11	–	−20.91
Salsominore 16	Well	97.44	0.577	0.0523	0.630	0.994	0.33	−44.87	−21.10	−24.60	–	−0.73
Nirano	MV	98.00	0.065	0.0033	0.000	1.000	0.65	−46.87	bdl	bdl	−191.2	+19.90
Nirano Parox	MV	70.10	0.041	0.0031	0.000	1.000	1.70	−48.44	−22.99	−10.82	–	+12.36
Regnano V2[b]	MV	96.70	0.380	0.0100	0.000	1.000	2.83	−44.70	−21.70	−9.57	−149	+20.07
Regnano V9-1[b]	MV	93.68	0.670	–	0.670	0.993	2.32	−46.26	−22.17	bdl	–	+17.36
Regnano V9-2[b]	MV	83.52	0.330	–	0.330	0.996	2.90	−46.21	−22.17	bdl	–	+14.74
Torre	MV	95.30	0.067	bdl	0.000	1.000	3.75	−39.31	bdl	bdl	−169.4	−20.70
Rivalta	MV	89.20	0.033	bdl	0.000	0.995	1.18	−39.60	bdl	bdl	−206.9	+31.31

– Not determined; bdl: below detection level; MV: mud volcano.
[a] From Borgia et al. (1988b).
[b] From Capozzi and Picotti (2002).

The processes acting on Salsomaggiore and mud volcanoes gases alter their carbon isotope ratios and increase the curve offset and slope. The mixing between thermogenic and biogenic methane results in its ^{12}C enrichment, thus shifting the $\delta^{13}C$ towards more negative values respect to the expected trend (Chung et al., 1988; Zou et al., 2007). This process is evident in all the samples of Figure 8.

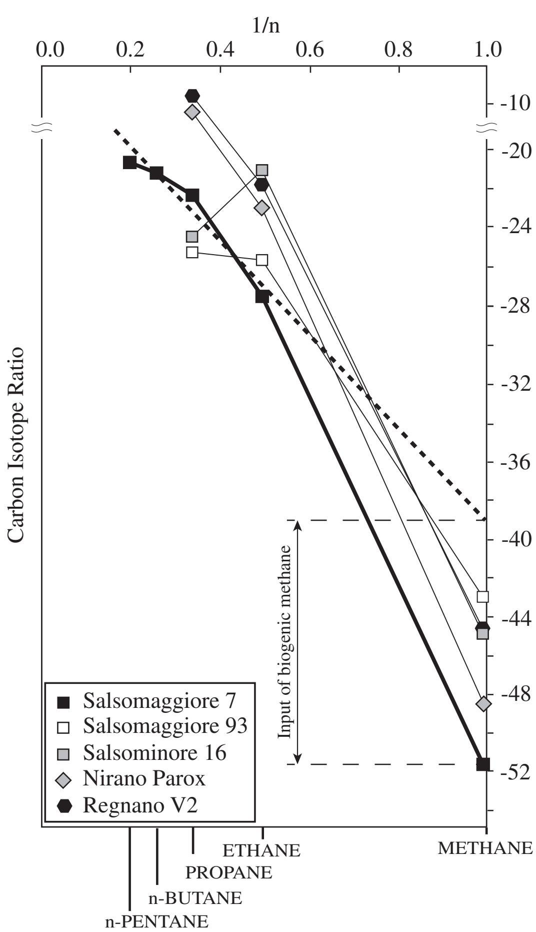

Figure 8. Natural gas plot showing the $\delta^{13}C$ in the C_1–C_5 gas fraction (Chung et al., 1988). The isotopes in C_4 and C_5 were determined only in Salsomaggiore 7 sample. The dashed line represents the tendency for the C_2–C_5 components in Salsomaggiore 7 and depicts the −39.29‰ thermogenic methane end-member. The difference between this latter and the measured methane $\delta^{13}C$ represents the biogenic methane input. Salsominore 16 shows an inversion of C_2 and C_3 $\delta^{13}C$ distribution, likely indicating that this is a residual gas.

However, only the Salsomaggiore 7 is fully analysed due to its complete C_1 to C_5 dataset. Using the approach of Chung et al. (1988) it is possible to obtain both the $\delta^{13}C$ of the thermogenic methane end-member, which for Salsomaggiore 7 is −39.29‰ VPDB, and the fraction of biogenic methane in the mix, which is 41.5% and thus testifies an important contribution from this source. The occurrence of mixing between thermogenic and biogenic methane in the Salsomaggiore and mud volcanoes samples is shown also in Figure 9 and discussed in detail in section 6.3.2.

The progressive thermal evolution of the hydrocarbons leads to the thermogenic gas formation through two different pathways: the primary cracking of kerogen and the secondary cracking of oil. The bulk of primary cracking occurs at temperature up to circa 140 °C, while the onset of secondary cracking starts at temperatures as high as 150°–160 °C (e.g. Aali and Rahmani, 2011).

According to the data illustrated in Prinzhofer and Huc (1995) the C_2/C_3 ratio remains almost constant during the primary cracking and increase only when the cracking of oils takes place. Otherwise, the C_1/C_2 ratio shows an opposite behaviour. Observing Figure 10 we can hypothesize that an undefined amount of the gas in the Salsomaggiore/Cortemaggiore area could be generated by the secondary cracking of oil (see also Section 6.3.3).

Additionally, the *i/n* ratios for C_4 and C_5 are higher in the gases cracked from residual kerogen respect in those generated by the oil cracking (Chang et al., 2011). According with the classification proposed by Chang et al. (2011), the low *i/n* ratios in Salsomaggiore 7 point towards the generation of gas from dispersed liquid hydrocarbons.

However, it is also reasonable the occurrence of primary thermogenic gas generated at lower source rock maturities and, possibly, small amounts derived by the thermal maturation of the low organic matter dispersed in the reservoir sediments.

The difference between $\delta^{13}C_2$ and $\delta^{13}C_3$ is usually negative and tends to zero with increasing maturity in completely closed or open systems (Qilin, 2012 and references therein). Conversely, the positive $\delta^{13}C(C_2–C_3)$ value of the Salsominore 16 sample indicates that the gas is the residual fraction of a gas that leaked through the caprock in earlier periods (Qilin, 2012).

6.3.2. Mud volcanoes gas

The analyses on the gas emitted by the mud volcanoes show prevailing methane (up to 98%), followed by small amounts of CO_2 (<4%) (Table 2). The C_{2+} fraction in the mud volcanoes of Nirano, Torre and Rivalta (respectively 0.065%, 0.067%, 0.033%) is very low and mainly composed by ethane. Literature data show that the C_{2+} concentration at Regnano is one order of magnitude higher during the background emission (0.39% total C_{2+}) (Capozzi and Picotti,

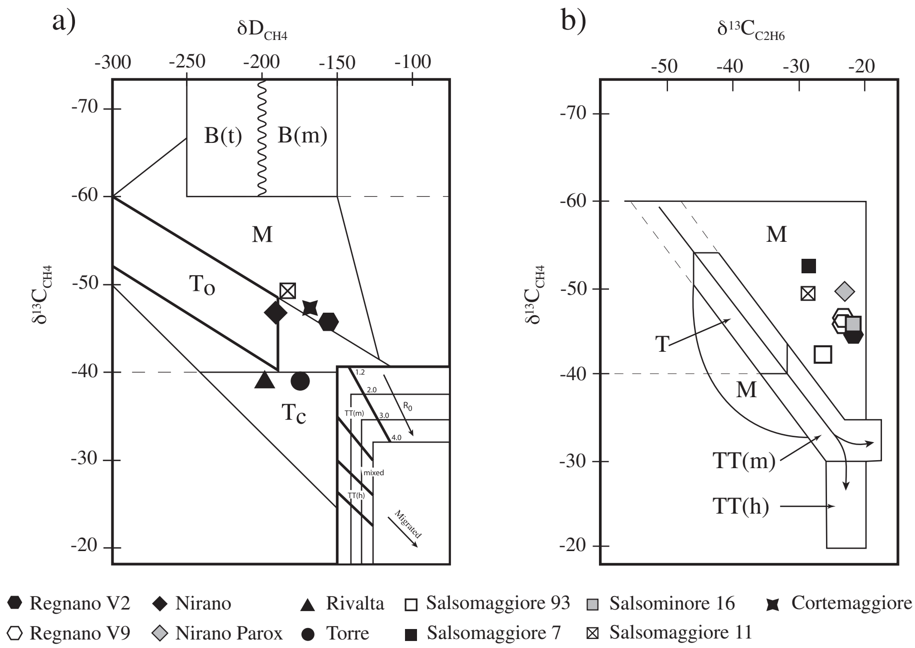

Figure 9. Characterization of the hydrocarbon gases by means of their stable isotopes (Modified from Schoell, 1983). a) The $\delta^{13}C$ and δD in methane indicate that the mud volcanoes gas is thermogenic and associated with condensates. b) The $\delta^{13}C$ in methane vs. ethane shows that all the considered gases are formed by the mixing between biogenic and thermogenic components. The increase in biogenic methane content is responsible for lowering the methane $\delta^{13}C$. Cortemaggiore (Mattavelli et al., 1983a) and Salsomaggiore 11 (Borgia et al., 1988b) data are showed. Gases: B, bacterial methane from marine (m) and terrigenous (t) sources; M, mixing of thermogenic and bacterial gases; T, thermogenic associated with oil (o) and condensates (c); TT, non-associated deep dry gases from humic (h) and marine (m) sources.

2002); Minissale et al. (2000) documented a C_{2+} concentration up to 0.98%.

The gases sampled during the mud volcanoes paroxysmal activity do not show important variations in their composition respect to the background emission, except in Nirano Parox and Regnano V9-2 where was measured a significant lower content of methane (Table 2). Moreover, in Regnano V9-1 the content of C_{2+} fraction is higher than in the other samples. The gas emitted by the mud volcanoes could be differentiated from that contained in the reservoirs due to the lower C_{2+} content, because the mixing with secondary biogenic methane and the influence of the fractionation process linked with the upward migration (Fig. 11).

The mud volcano samples can be subdivided in two groups according with the methane carbon stable isotopes. The mud volcanoes of Torre and Rivalta show circa $\delta^{13}C$ −39‰, while Nirano and Regnano have more ^{13}C-depleted methane (up to −48.44‰). On the base of the methane $\delta^{13}C$ and δD (Fig. 9a) these gases are

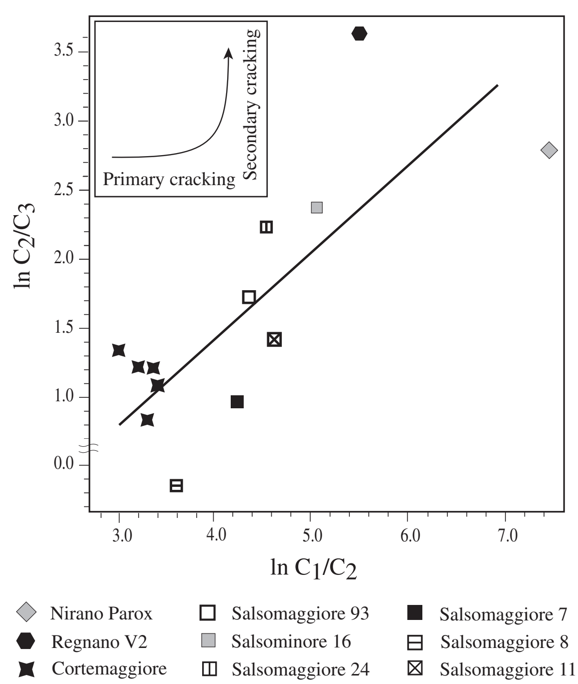

Figure 10. $\ln(C_1/C_2)$ vs. $\ln(C_2/C_3)$ plot, modified from Prinzhofer and Huc (1995). The samples distribution is suggesting the onset of secondary methane generation after the initial phases of oil cracking in the Salsomaggiore and Cortemaggiore gases. Salsomaggiore 8, 11 and 24 (Borgia et al., 1988b) and Cortemaggiore data (Mattavelli et al., 1983a; Pieri, 1992) are showed. Regnano V2 and Nirano Parox samples reflect the alteration due to the migration process.

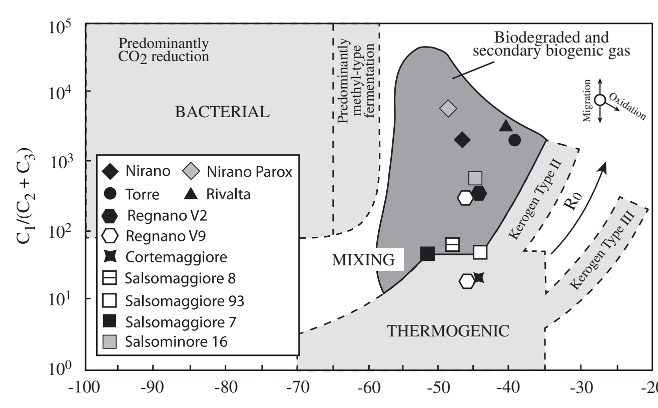

Figure 11. Bernard diagram showing the $\delta^{13}C_1$ vs. $C_1/(C_2 + C_3)$ ratio in gases (after Bernard et al., 1978 and Milkov, 2010). The gas is thermogenic in origin and is subjected to mixing with biodegraded and/or secondary microbial gas. The high $C_1/(C_2 + C_3)$ values, in particular for the mud volcanoes, are also related with the C_{2+} removal due to the migration from the reservoir. Cortemaggiore (Mattavelli et al., 1983a,b) and Salsomaggiore 8 (Borgia et al., 1988b) are shown.

thermogenic in origin (Schoell, 1983). Since the $\delta^{13}C$ of methane could be modified due to the mixing with gases of different origins (Schoell, 1983) and/or to the slow migration through pelitic sediments (Prinzhofer and Huc, 1995; Pinzhofer and Pernaton, 1997; Zou et al., 2007), its correlation with the ethane $\delta^{13}C$ could identify the possible contribution deriving from biogenic gas. According with the diagram in Figure 9b, the samples experienced mixing with gases of microbial origin. Moreover, the mud volcanoes and Salsomaggiore gases are clustered in the same diagram area; thus evidencing their isotopic similarity.

The generation of biogenic methane could be related with the anaerobic biodegradation of oils, which can be associated with secondary methanogenesis within the reservoir or, to a lesser extent, during the slow migration (Etiope et al., 2009; Milkov, 2010). The anaerobic bacterial cultures performed on water samples and the data from Heller et al. (2011) evidenced the occurrence of hydrocarbons degrading bacteria in the analysed mud volcano systems (see Section 7). The evaluation of biogenic methane production is extremely important to highlight the possible changes in the methane $\delta^{13}C$. The secondary methanogenesis follows the CO_2 reduction pathway, which has previously been produced by the anaerobic oxidation of higher hydrocarbons (James and Burns, 1984; Pallasser, 2000). Analyses carried out on numerous mud volcanoes all over the world (Etiope et al., 2009) show that a CO_2 $\delta^{13}C$ enrichment higher than +10‰ is indicative of secondary methanogenesis, even if is not mandatory (Jones et al., 2008). Moreover, according to Jones et al. (2008), the biodegraded oilfields usually contain methane with $\delta^{13}C$ between −45‰ and −55‰; fitting the range of our data. The $\delta^{13}C$ in CO_2 shows a great variability between the considered areas (Table 2 and Fig. 12). The Nirano, Regnano and Rivalta mud volcanoes are markedly enriched in the heavier isotope, confirming the active role of the biodegradation. Torre has distinctly negative CO_2 $\delta^{13}C$, which is a potential indicator for the absence of such a processes. However, the $\delta^{13}C$ ratios in CO_2 are extremely variable in time and in space, even within a single area (Etiope et al., 2009). The occurrence of secondary methanogenesis in Torre mud volcanoes is evidenced by the analyses carried out by Tassi et al. (2012), where $\delta^{13}C$ up to +27.5‰ were recorded. The higher CH_4 $\delta^{13}C$ in Torre and Rivalta respect to the other mud volcanoes suggests that the generation of secondary methane was not relevant during the sampling of these sites. This conclusion is supported by the comparison with the thermogenic methane end member determined for Salsomaggiore 7 ($\delta^{13}C$ −39.29‰). Despite of the lacking of strongly positive CO_2 $\delta^{13}C$ in the Salsomaggiore gas, the occurrence of secondary biogenic methane can be hypothesized.

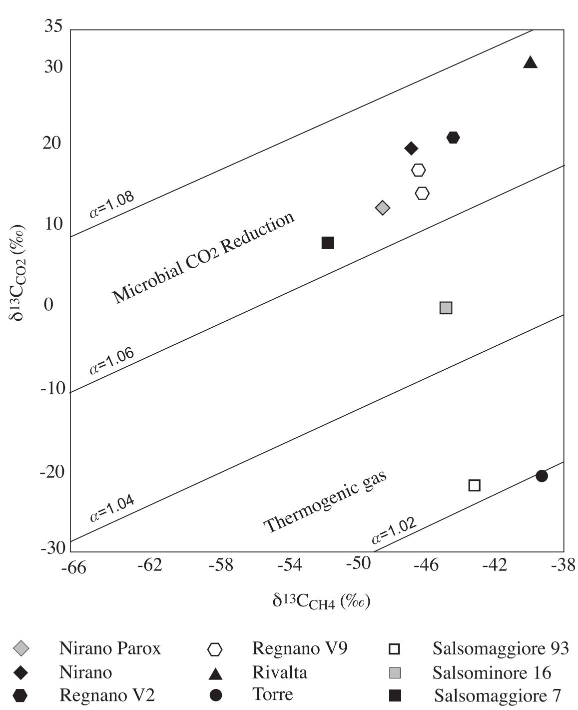

Figure 12. Plot of carbon dioxide $\delta^{13}C$ vs. methane $\delta^{13}C$. Lines and α values represent constant isotope fractionation. All the samples show the contribution of secondary bacterial methane, except Salsominore 16, Salsomaggiore 93 and Torre mud volcano.

6.3.3. *Salsomaggiore oil*

The studied oils comprise three samples from the Salsomaggiore wells 93, 8 and 25. The data on the well 25 oil derived from a previous unpublished work, thus will be presented only the information useful for this work.

The Total Ions Chromatograms (TIC) of Salsomaggiore 93 and Salsomaggiore 8 (Fig. 13a, b) do not show the presence of severe degradation processes acting on the oil, however in Salsomaggiore 25 it was been verified the occurrence of the most common alteration mechanisms, such as biodegradation, water washing and evaporative fractionation, and thus testifying a complex migration history from the source rock to the present reservoir.

According to Roushdy et al. (2010) low Pristane/Phytane values (<1) indicate reducing depositional environments, while values >1 denote the progressive increase of oxygen content, up to ratios ≥3 that represent pure oxidizing conditions. The intermediate Salsomaggiore Pr/Ph ratios are indicative of organic matter deposited in a sub-oxic environment (Fig. 14) (Peters et al., 1999; Obermajer et al., 2010; Aali and Rahmani, 2011). This conclusion is proven also by the Pr/C_{17} and Ph/C_{18} ratios (Fig. 15), which also identify the type of kerogen occurring in the source rock (Peters et al., 1999). The Salsomaggiore oil originated from mixed II/III type kerogen.

The organic matter occurring into the source rock can be further defined by the C_{27}–C_{28}–C_{29} regular sterane distribution (Table 3) (Moldowan et al., 1985; Philip et al., 1991; Tang et al., 2008). The C_{27} and C_{28} steranes derive from marine sources, in particular the first is abundant in phytoplankton and algae (Gagosian et al., 1983; Volkman, 1986), while the latter has been mainly attributed to the diatoms present in coastal environments (Gürgey, 1999). The C_{29} steranes are indicative of higher plants and some primitive algae or cyanobacteria (Volkman, 1986; Peters and Moldowan, 1993; Rieley et al., 1991; Volkman et al., 1999). In the Salsomaggiore samples the subequal steranes abundances are indicating the prevalence of a marine algal flora (Fildani et al., 2005), but with high terrigenous contribution (Table 3, Fig. 16). The Cortemaggiore oil shows similar characteristics, as reported by Riva et al. (1986).

The regular steranes/17α(H)-hopanes ratio is generally high (≥1) in the marine organic matter. Otherwise, low values, as those in the Salsomaggiore oil (Table 2), are more indicative of terrigenous and/or microbially reworked organic matter (Peters and Moldowan, 1993; Chakhmakhchev et al., 1996).

The $\delta^{13}C$ isotopic ratios for Salsomaggiore oil are indicative of prevailing marine organic matter in the source rock (Peters et al., 1999) (Fig. 17), fitting the range for those determined in the nearby Cortemaggiore group oil by Riva et al. (1986). The saturated and aromatic $\delta^{13}C$ show a relative enrichment in ^{13}C, which values could be generally indicative of Paleogene to Miocene source rocks (Peters et al., 1999).

The occurrence of Oleanane in the analysed oil leads to Oleanane Indexes (Oleanane/(C_{30} Hopanes + Oleanane)) higher than 0.20, thus being diagnostic of higher plant input and Tertiary source rocks (Peters and Moldowan, 1993; Peters et al., 1999). Mattavelli and Novelli (1990) reported a similar value in Cortemaggiore oil.

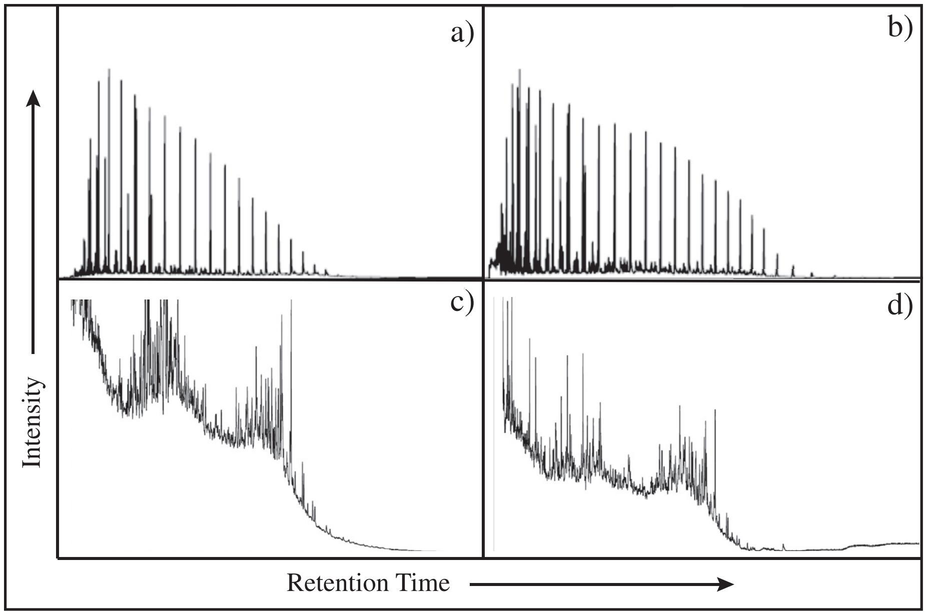

Figure 13. Total Ion Chromatograms of the analysed oils. a) Salsomaggiore well 93; b) Salsomaggiore well 8; c) Torre mud volcano; d) Rivalta mud volcano. The Salsomaggiore oil does not show high levels of degradation. The oil sampled in the mud volcano structures is strongly altered by biodegradation and migration processes.

The Oleanane occurrence, coupled with subequal C_{27-29} distribution can be interpreted as combined terrigenous and marine organic matter contribution. Although the maximum development of Oleanane-bearing angiosperms has occurred during this period, their presence is recorded also during the Late Cretaceous. It is worth to note that the Oleanane could also derive from that occurring in the organic matter dispersed in the reservoir or in the rocks crossed through during the hydrocarbons migration, even if this is an uncommon event because the biomarkers deriving from the source rock are usually dominating (Peters and Moldowan, 1993). The analysed oil shows high amounts of the C_6 to C_{14} fraction (Mosca, 2006, personal communication), which could act as solvent for the Oleanane molecules dispersed in the reservoir sediments. For this reason the input of Oleanane deriving form the reservoir rocks could not be totally excluded.

The low C_{29}Hopane/C_{30} Hopane ratios (Table 3) clearly testify the clayey nature of the source rock (Palacas et al., 1984; Connan et al., 1986) (Fig. 18), as also supported by the high Diasterane ratios (Peters and Moldowan, 1993; Gürgey, 1999). The measured Trisnorneohopane to Trisnorhopane ratios (Ts/Tm) in Salsomaggiore (Table 3) and Cortemaggiore (Riva et al., 1986) are indicative of siliciclastic source rock. The Ts/Tm ratio increases according to the content of shales (Hunt, 1996), due to its sensitivity to the clay-catalysed reactions (Rullkotter et al., 1985). At low maturities (R_0 0.65%), as those occurring in Salsomaggiore (see later discussion), it is affected only by the parent rock typology (van Grass, 1990).

The Odd–Even Preference (OEP; Scalan and Smith, 1970) significantly above or below 1.0 indicates thermally immature organic matter, whereas the value of 1.0 denotes a mature oil and source rock (Peters and Moldowan, 1993; Aali and Rahmani, 2011).

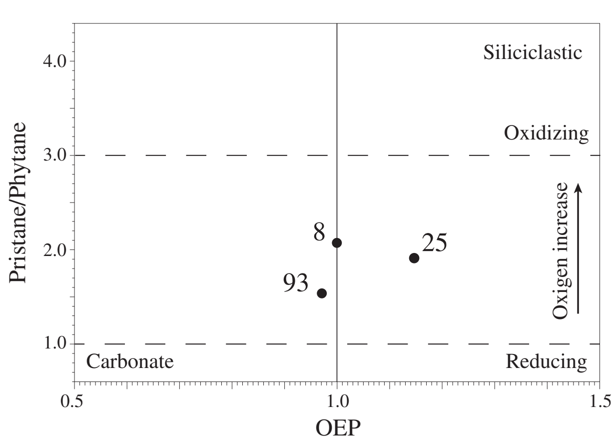

Figure 14. Odd–Even Preference (OEP) vs. Pristane/Phytane ratio in Salsomaggiore oils. The OEP values near 1 suggest thermally mature oils. The measured Pristane/Phytane ratio clearly indicates that the organic matter was deposited in sub-oxic conditions.

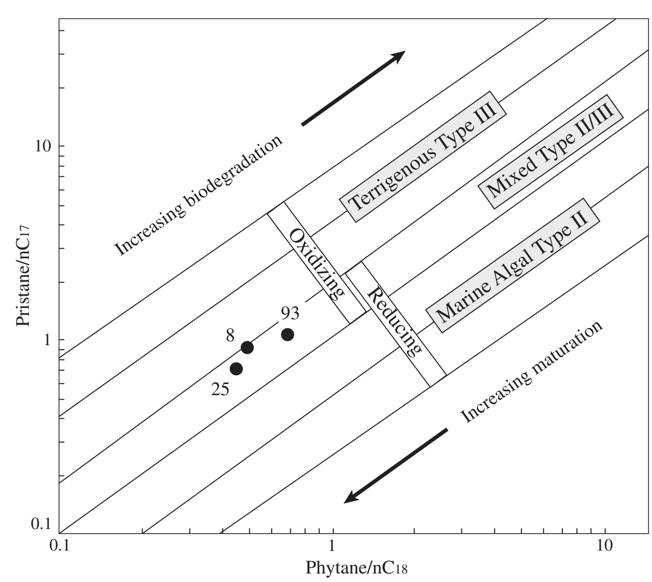

Figure 15. Plot of Ph/nC_{18} vs. Pr/nC_{17} for the Salsomaggiore oils. These latter originated from type II/III mixed kerogen, indicative of the contribution from both marine and terrigenous organic matter, deposited under sub-oxic conditions (Modified from Peters et al., 1999).

Table 3
Geochemistry of the Salsomaggiore oils.

	Salsomaggiore 93	Salsomaggiore 8
OEP	0.98	1.00
PrPh	1.46	1.94
Pr/C_{17}	1.05	0.91
Ph/C_{18}	0.69	0.47
$C_{29}Hop/C_{30}Hop$	0.73	0.72
$C_{29}Ts/C_{30}^*$	3.90	4.03
$C_{30}^*/C_{30}Hop$	0.07	0.06
Diasterane ratio	0.46	0.44
C_{27}/C_{29} sterane	1.50	1.30
C_{28}/C_{29} sterane	1.31	1.42
$\%C_{27}$	40.21	36.02
$\%C_{28}$	35.56	39.13
$\%C_{29}$	24.23	27.85
Steranes/hopanes	0.60	0.47
S/S + R terpane	0.59	0.56
S/S + R sterane	0.33	0.32
$\beta\beta/(\beta\beta + \alpha\alpha)$	0.44	0.45
T/TM	0.50	0.40
MPI	1.05	0.91
TsTm	0.88	0.80
Oleanane index	0.22	0.25
C_{31}/C_{30}	0.30	0.34
Methylhopane	–	2.85
$\delta^{13}C$ SAT	–	−23.52
$\delta^{13}C$ ARO	–	−22.63
$\delta^{13}C$ RES	–	−24.05
$\delta^{13}C$ ASPH	–	−23.56

– Not determined.

The Salsomaggiore oil shows OEP values that suggest thermally mature oils (Table 3, Fig. 14).

The maturity of the oils was estimated by means of the sterane isomerization indexes and the corresponding vitrinite reflectance (% R_0). The conversion of the C_{29} steranes from 20S to 20R leads to an increase in the 20S/(20S + 20R) ratio with the maturity, usually reaching an equilibrium for values of 0.52–0.55 during the main phase of oil generation (0.8/0.9% R_0) (Peters and Moldowan, 1993). In Salsomaggiore 8 and 93 oils the C_{29} isomerization ratios are equal to 0.33 and 0.32 respectively, indicating an early oil generation (circa R_0 0.60%). The C_{29} sterane isomerization in C_{14} and C_{17}

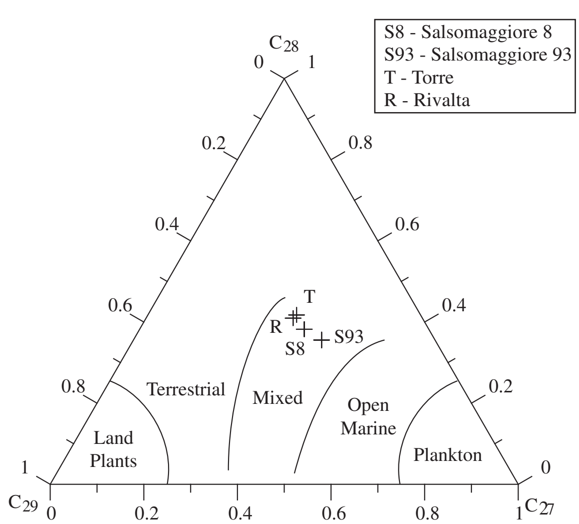

Figure 16. Ternary plot of relative abundances of C_{27-29} regular steranes suggesting that the considered oils are originated mainly from marine algae, but the contribution from terrigenous organic matter should be accounted. The very small differences between the samples indicate the generation from the same source rock. The data reflect the distribution of the Cortemaggiore group oil (Riva et al., 1986) (Modified from Roushdy et al., 2010).

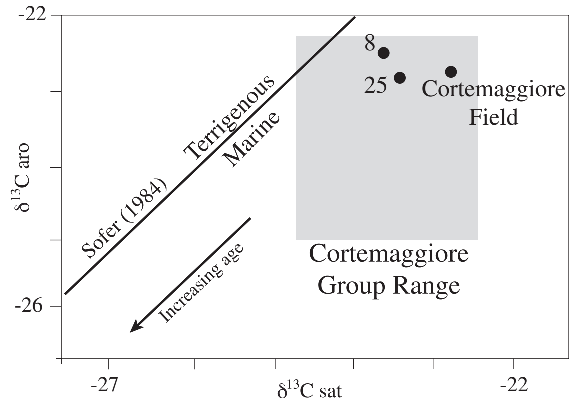

Figure 17. $\delta^{13}C$ in saturates vs. aromatics. Salsomaggiore fall in the range defined for the Cortemaggiore group by Riva et al. (1986). The carbon stable isotopes indicate the Tertiary age of the source rock and a prevailing marine organic matter (Modified from Peters et al., 1999).

positions from the $\alpha\alpha$ to $\beta\beta$ configuration is expressed by the $\beta\beta/(\beta\beta + \alpha\alpha)$ ratio, which reaches a steady state (0.70) around the peak of oil generation (Mackenzie et al., 1980).

However, the Methyl Phenantrene Index (MPI) (Table 3 and Fig. 19) shows higher maturities, up to R_0 1.0–1.1%. Moreover, also the Cortemaggiore oil shows a comparable high maturity (Riva et al., 1986). The use of biomarkers to assess the maturity of highly mature and overmature oils ($R_0 > 1.0\%$) cannot be always applied because they reached the isomerization equilibrium or are thermally degraded (Peters and Moldowan, 1993). Otherwise, the diamondoids hydrocarbons are molecules extremely stable at high temperature and resistant to biodegradation (Wingert, 1992; Jinggui et al., 2000) and therefore can be effective maturity markers for highly mature oils. The Methyl Diamantane Index (40%) and Methyl Adamantane Index (68%), calculated on the oil from the Salsomaggiore 25 well, clearly indicate a thermal maturity equivalent to R_0 1.3% (Chen et al., 1996). The diamondoids hydrocarbon ratios match overmature values, and likely denote an oil where most of the steranes and hopanes were removed or converted into more stable compounds (Chen et al., 1996). Moreover, the corresponding temperature range is suitable for the oil cracking and the gas generation, as hypothesized from the gas analyses (Section 6.3.1). The various maturity levels identified in the Salsomaggiore

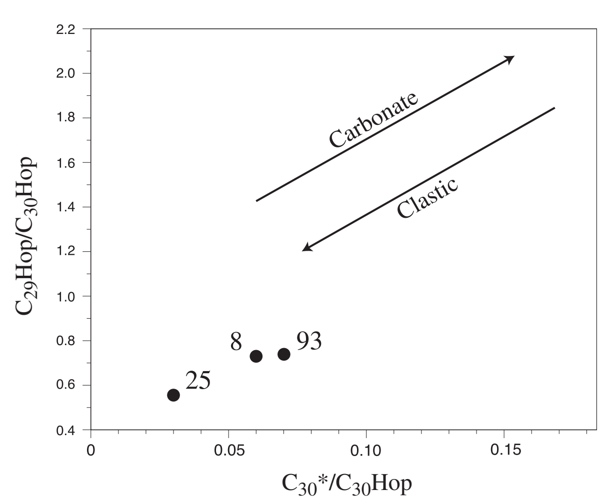

Figure 18. Plot of $C_{30}^*/C_{30}Hop$ vs. $C_{29}Hop/C_{30}Hop$. The low C_{29}/C_{30} Hopanes ratios in the Salsomaggiore oil evidence the clastics nature of the source rock.

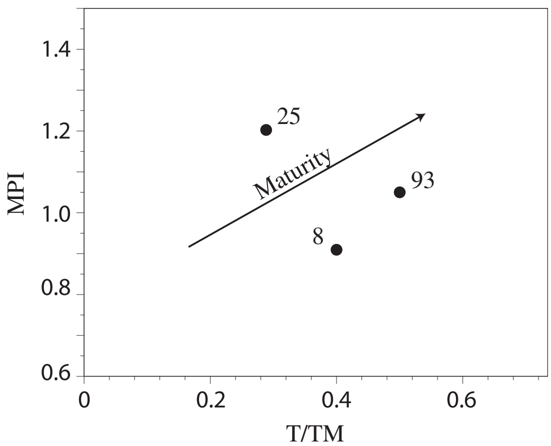

Figure 19. Plot of Methyl Phenantrene Index (MPI) vs. T/TM. The oils from Salsomaggiore show comparable maturities corresponding to the late oil window.

oils are thus indicative of the mixing of highly mature oil with an abundant early generated oil fraction.

6.3.4. Mud volcanoes oil

The mud volcanoes do not have a continuous and abundant emission of liquid hydrocarbons. Therefore, it was been possible to collect oil samples only in the sites of Torre and Rivalta. The information that can be obtained by their analyses is very scarce and potentially inaccurate due to the high degradation.

The TIC of the mud volcanoes oil (Fig. 13c, d) show extremely altered molecular profiles. For this reasons a clear interpretation of their characteristics is difficult.

A strong biodegradation occurs in both sites, corresponding to a PM index of 6/7 (Peters and Moldowan, 1993) determined by the complete removal of *n*-alkanes and steranes. As a result it was possible to define only some of the biomarker commonly used during the oil interpretation. The biodegradation intensity indicates a prolonged bacterial activity in the reservoir (Peters and Moldowan, 1993), thus excluding the alteration of the oils exclusively during the fluid rising along the mud volcanoes conduits.

The Rivalta and Torre oils have higher C_{28} and C_{27} steranes respect to C_{29} steranes (Table 4), indicating a predominant marine organic matter in the source rock (Fig. 16). Similarly to the Salsomaggiore oil, the samples contain the Oleanane molecule. It was detected the occurrence of an unknown sterane “X” (Riva et al., 1986) not present in Salsomaggiore.

The biomarkers analysis revealed a clayey source rock ($Ts/Tm > 0.6$) (Peters and Moldowan, 1993). The sterane C_{29} $20S/(20S + 20R)$ isomerization ratio is 0.51 at Rivalta and 0.66 at Torre. The Rivalta oils have almost reached the equilibrium for the parameter, whereas the value for Torre is much higher. The biodegradation in the mud volcanoes leads to high uncertainties in the parameter interpretation, thus being not reliable in this case (Peters and Moldowan, 1993).

Table 4
Biomarkers in the mud volcano oils.

	Rivalta	Torre
C_{27}%	32.0	32.5
C_{28}%	40.0	40.0
C_{29}%	28.0	27.5
S/S + R sterane	0.51	0.66
T/TM	0.37	0.59
TsTm	0.87	1.05

The only parameter that can be determined and that is stable respect to the biodegradation is T/TM (Monoaromatic steroids aromatization) (Peters and Moldowan, 1993), which increases from 0 to 1 during the thermal maturation. Its values in Rivalta (0.37) and Torre (0.59) are defining early to mature oils, with equivalent R_0 0.62% and 0.72% respectively. The obtained values are comparable with those estimated for the same parameter for the Salsomaggiore oil. Unfortunately, the lacking of a more complete dataset for the mud volcanoes oil do not allows an undoubted interpretation.

7. Discussion and conclusions

The hydrocarbon and mud volcano fields along the western Northern Apennine foothills are always associated with formation saline waters (Capozzi and Picotti, 2010). The geochemistry of these fluids, emitted by spontaneous seepages and exploited from deep wells, allows clarifying some aspect concerning their generation and migration.

The hypersaline water recovered from deep wells in the Salsomaggiore reservoir shows chemical and isotopic characteristics that are consistent with a deep-burial diagenesis, which has driven to the present geochemical equilibrium. This latter is the result of different processes, such as the interaction with the solid phase, the microbial activity related with the hydrocarbon occurrence and the exchanges between water and oil.

Otherwise, the mud volcano waters show a significantly lower salinity due to the filtration mechanism occurring during the migration through the sealing Ligurian Units. The fluids migration from the reservoir up to the surface is in general allowed by the occurrence of normal fault systems, which act as the main migration pathways (Capozzi and Picotti, 2002, 2010).

The analysis of calcareous nannoplankton in the sediments emitted by the mud volcanoes of Torre and Rivalta evidenced the occurrence of assemblages that could be ascribed to Late Cretaceous, Paleocene/Eocene and Serravallian/Tortonian ages. The occurrence of Paleocene/Eocene assemblages is correlated with the “Monte Sporno” flysch, belonging to the Ligurian Units (Zanzucchi, 1980). The stratigraphic and lithological characteristics of this flysch favour the accumulation of fluids in the coarser intervals, as was previously documented by drilled wells (Scicli, 1972). The biostratigraphic analysis that has shown species from Serravallian to Tortonian ages supports the statement that the emitted saline waters are possibly originating in the Tertiary reservoir successions. The nannoplankton assemblage recognized at Nirano evidences that the main source of mud is the Lower Pliocene succession, which also constitutes the outcropping units where the mud volcano structures are developing. Moreover, also in this case the documented species of Cretaceous and Eocene/Oligocene ages testify the contribution of the Ligurian Units as mud source deeper than the Pliocene succession.

The gases in the Salsomaggiore area are a mixture of biogenic and thermogenic methane, associated with small amounts of C_{2+} fraction, condensates and oil (Figs. 8 and 9). The generation of biogenic methane could be ascribed to secondary methanogenesis and to the primary generation from the organic matter dispersed in the shallow reservoirs sediments. The analysis of the C_1–C_3 fraction suggests that the thermogenic component is originated by both the cracking of kerogen and mature oil (Fig. 10) (Prinzhofer and Huc, 1995). The calculated $\delta^{13}C$ of the thermogenic methane end-member in the Salsomaggiore 7 sample (−39.29‰ VPDB) is also indicating its formation at high temperatures.

The mud volcanoes gas is composed almost entirely by methane, with very small amounts of higher hydrocarbons. The documented low volumes of C_{2+} result from the molecular fractionation acting during the migration (Prinzhofer and Huc, 1995;

Deville et al., 2003; Etiope et al., 2009), from partial biodegradation (e.g. Prinzhofer and Huc, 1995; Etiope et al., 2007) and, to a lesser extent, from the mixing with primary biogenic methane.

The overall methane $\delta^{13}C$ in the mud volcanoes shows values comparable with those of Salsomaggiore despite of the higher ^{13}C content in the C_{2+} fraction, particularly in the propane, thus supporting the occurrence of alteration processes. The mixing with biogenic methane is highly plausible as testified by the $\delta^{13}C_1$ vs. $\delta^{13}C_2$, where available (Fig. 9b), and by the carbon isotopes in CO_2, which are indicative of secondary methane generation in most of the sites (Fig. 12). Torre and Rivalta represent exceptions, where the mixing process does not seem to occur during the sampling, as suggested by the higher methane $\delta^{13}C$ and the negative $\delta^{13}CO_2$ at Torre.

The thermogenic methane $\delta^{13}C$ end-members in Salsomaggiore and in the mud volcanoes are equivalent and point towards a common source and generation mechanism. Therefore, Salsomaggiore likely represents the gas contained in the reservoirs along the Northern Apennines foothills, while the mud volcanoes are showing the same gas after the leakage through the sealing units.

It is possible to estimate the depth of gas generation by means the mean thermal gradient in this sector of the Northern Apennines, which is considered about 20°–23 °C per kilometre (Zattin et al., 2002; Pasquale et al., 2008). The 150–160 °C temperature range, which matches the onset of the oil cracking (Waples, 2000), corresponds to the depth of circa 6.5 km (A value of 15 °C was subtracted from the value at depth, because it is considered as the mean open-air temperature).

Further evidences on the thermal and migration histories of the hydrocarbons could be gathered from the analyses of the oils. The Salsomaggiore oil shows almost unaltered molecular profiles, even if previous unpublished results on the Salsomaggiore well 25 have evidenced the occurrence of slight biodegradation, fractionation and water washing. Otherwise, the oils emitted by the mud volcanoes are extremely biodegraded. The biodegradation level implies that the main hydrocarbon reservoirs of the Northern Apennines foothills are located at depth not exceeding 2–3 km, because beyond temperatures of 60–80 °C it would not be suitable the development of the hydrocarbon-degrading bacterial communities (e.g. Pallasser, 2000; Etiope et al., 2009).

In addition to the results presented in Heller et al. (2011, 2012) regarding the Nirano mud volcanoes, we carried out bacterial cultures in anaerobic environment to verify the presence of biodegrading communities in all the investigated mud volcano sites. The results showed the presence of mesophilic bacteria belonging to the groups of APB (Acid Producing Bacteria) and SRB (Sulphate Reducing Bacteria); these latter are responsible for the degradation of oils in reducing conditions. The optimum temperature identified for their growth is 37 °C, thus testifying that all the considered mud volcano emissions are fed by a main reservoir circa 1 km deep. Capozzi and Picotti (2002) reported for the Regnano mud volcano the presence of SRB cells with incubation temperature of both 37 °C and 60 °C. This evidence outlines that more than a single reservoir can occur within an emission system and that different bacteria populations can progressively degrade the oil during its migration towards the surface. The consistency among the biodegrading bacteria characteristics that are presented in this study and those previously documented provides an additional evidence of the strong similarity between the emission systems along the Northern Apennines foothills.

In the Salsomaggiore area the oils analysis evidenced their generation from mixed marine and terrigenous organic matter deposited in sub-oxic conditions. The mean R_0 0.64%, calculated from the sterane isomerization parameters, indicates an early oil generation at temperatures of 95–100 °C and at depth of 3.4–3.7 km. The MPI and the MAI and MDI occurring in the same oil indicate a late generation (R_0 1.0 and 1.3 respectively), corresponding to temperature >150 °C and depth >6.0 km. The contemporaneous presence of markers that indicate both early and late generated oils are indicative of the progressive hydrocarbons thermal evolution, migration, accumulation and mixing during time.

The elevated biodegradation of the oils emitted by the mud volcanoes is sensibly reducing the information that could be obtained from their analyses. However, the few biomarker parameters that can be determined are pointing towards a positive correlation with the oil contained in the Salsomaggiore reservoir. Therefore, they are likely deriving from a common or very similar source rock. The vitrinite reflectance determined for the oils in Torre and Rivalta mud volcanoes is 0.62% and 0.72% respectively, relating to early and mature oil window temperatures and hence corresponding to the same depth as for the early generated fraction of the Salsomaggiore oil.

The information derived from the oil analyses confirmed that the gas has been progressively generated during the whole oil window by primary kerogen and secondary oil cracking processes. Moreover, despite some small compositional differences likely due to different migration histories and the lacking of early oil, the hydrocarbons occurring in the Cortemaggiore field could be related with those present in both the mud volcanoes and the nearby Salsomaggiore field.

According with the commonly accepted theory, in this sector of the Northern Apennines the hydrocarbons should originate directly into the units of the Tertiary "Marnoso-arenacea" Formation (e.g. Riva et al., 1986), which was deposited in the foredeep by turbidity currents during the Miocene. However, according with the results from this work some doubts arise. The NE verging deformation of the Burdigalian–Langhian Salsomaggiore anticline was active since the Langhian through the early Tortonian. During the late Burdigalian–Langhian period a possible deeper source rock reached the temperatures of the early oil window and the sampled early-generated oil could migrate in the forming Salsomaggiore anticline (Fig. 20). This early oil could not migrate in the more external Tortonian–Messinian Cortemaggiore field (Figs. 3 and 4), which is located in the subsurface of the Po Plain and formed later, during

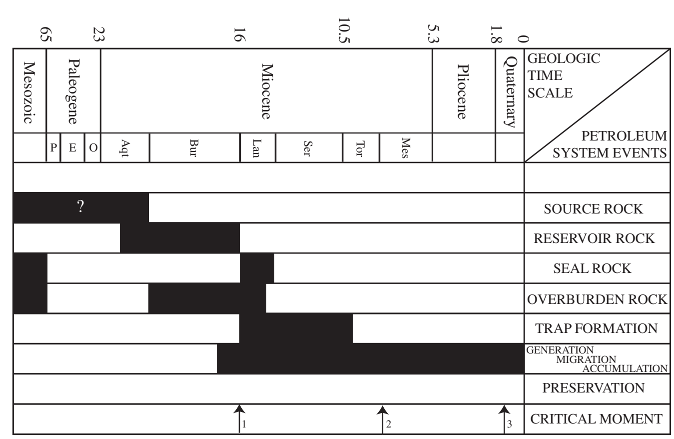

Figure 20. Total Petroleum Chart representing the petroleum system in the Salsomaggiore anticline. In the outcropping thrust top the Langhian units form the seal rocks. The Ligurian units progressively sealed the Miocene reservoir until the Tortonian, since when it was partially eroded. A second phase of advancement of the Ligurian units during the Messinian-early Pliocene period led to the increase of the overburden and the generation of the late mature oil (critical point 2). During the Pleistocene the reactivation of the deformation towards NW led to the present reservoir geometries and to a new phase of hydrocarbon migration (critical point 3).

the Middle-Late Tortonian through the Pliocene. From the Late Tortonian to the Messinian, a new foreland subsiding phase led to the emplacement of the Ligurian Units on top of the Salsomaggiore anticline and, during this time interval, the generation of late mature oil could feed the Salsomaggiore and the deforming Cortemaggiore culmination, likely deriving from an underlying common source rock. In fact, this oil occurs in both Salsomaggiore and Cortemaggiore fields, even if the two structural traps have different age and are not in direct connection due to the Salsomaggiore basal detachment, which is shallower than that of Cortemaggiore (Figs. 3 and 4). The cross-sections A–A′ of Figure 3 shows that only the deeper portion of the Marnoso-arenacea Formation experienced the temperatures suitable to generate the highly mature oil and the secondary thermogenic gas. If the different Members of Marnoso-arenacea Fm. are the source rocks, the Salsomaggiore and Cortemaggiore reservoirs should have different hydrocarbon characteristics, due the expected variations with time in the sandstones/marls ratio, organic matter content and composition, and possibly different thermal maturity. Due to the low Total Organic Carbon content (TOC ~0.5) (Mattavelli et al., 1983b) the volumes of Marnoso-arenacea succession experiencing the temperatures suitable with an overmature hydrocarbon generation should have been larger than those documented. Moreover, the Tortonian to Pliocene structures of the foredeep, reconstructed along strike in section D–D′ (Fig. 4), can suggest possible up-dip carriers as responsible for migration from the eastern part of the studied area and progressively accumulating below all mud volcano sites. It has to be underlined, on the other hand, that the Langhian marls constitute the Marnoso-arenacea interval that is mainly prone to hydrocarbon generation. This unit shows significant changes in thickness and in Salsomaggiore anticline represents the upper horizon that has never been buried.

A more plausible scenario can be depicted if a common source rock, located in the deeper units, fed the Marnoso-arenacea reservoirs. This can account for the accumulation of very similar hydrocarbons in the different reservoir structures. The possible deep source rock is still unknown, but it is mainly siliciclastic and deposited in a disoxic environment. As discussed by Picotti et al. (2007) the source rock could be of Cretaceous age. However, Riva et al. (1986), Mattavelli and Novelli (1990) and Pieri (1992) reported interesting geochemical evidences for the Cortemaggiore oil, where vanadium and nickel contents have been indicated similar to the thermogenic oils generated by Triassic source rock.

The similarity of thermal and evolutive histories of the hydrocarbons occurring in the northern sector of the Northern Apennines, as testified by the comparison of Salsomaggiore with the mud volcano fields, suggests that the source rock could have a wide lateral extension. Therefore, it could be able to generate significant volumes of hydrocarbons that fed reservoirs of different ages, sedimentary successions and deformation, including the structures buried in the portion of the Po Plain close to the foothills. With the progressive increase of the economic return in in-chain hydrocarbon prospectivity, this extended source rock could also represent a high rewarding exploration target.

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