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ARTICLE



Geochemistry of fluids discharged from mud volcanoes in SE Caspian Sea (Gorgan Plain, Iran)

Mahin Farhadian Babadi^a, Behzad Mehrabi^a, Franco Tassi^{b,c}, Jacopo Cabassi^{b,c}, Elena Pecchioni^b, Ata Shakeri^a and Orlando Vaselli^{b,c}

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ABSTRACT

A geochemical study was carried out on gas, water and mud samples from four mud volcanoes in Gorgan Plain, SE Caspian Sea (Iran) in order to investigate fluid primary sources and secondary processes controlling fluid chemistry. The chemical composition of light alkanes and the isotopic feature of methane indicated an origin related to a thermogenic source. Gases discharged from Neftlijeh evidenced anaerobic biodegradation processes with addition of secondary microbial methane. Chemical composition of discharged waters revealed two main groups i) brine-type $\text{Na}^+\text{-Cl}^-$ waters from Gharenyaregh and Neftlijeh mud volcanoes, which were marked by relatively high Na^+/Cl^- , B/Cl^- and Li/Cl^- ratios and low $\text{Ca}^{2+}/\text{Cl}^-$, $\text{Mg}^{2+}/\text{Cl}^-$ and K^+/Cl^- ratios, ii) waters from Sofikam and Inche, characterized by relatively low Na^+/Cl^- , B/Cl^- and Li/Cl^- ratios and relatively high $\text{Ca}^{2+}/\text{Cl}^-$, $\text{Mg}^{2+}/\text{Cl}^-$ and K^+/Cl^- ratios. The chemical and isotopic characteristics of the discharged waters suggest that evaporated Caspian seawater trapped in sediments is likely representing a reliable water source. The maximum formation depth at Gharenyaregh and Neftlijeh mud volcanoes were estimated at about 6 km depth whereas the generation depth of the rest was significantly shallower. Thus, the observed compositional differences can be related to the different depths of the fluid source feeding them.

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Mud volcanoes; fluid geochemistry; secondary geochemical processes; Gorgan Plain; Caspian Sea; Iran

Introduction

Mud volcanoes (MVs) are produced by the outflow of mud, water and gas phases, mostly consisting of methane, with significant concentrations of higher hydrocarbons compounds, CO_2 , N_2 and H_2S , released by overpressured organic-rich sediments rapidly buried in sedimentary basins (Dia *et al.* 1999; Milkov 2000; Dimitrov 2002; Etiope *et al.* 2007). Fluids uprising through deep-rooted feeding channels may also be stored in mud chambers located at intermediate-to-shallow depth, giving rise to buried MVs that can be recognized with geophysical surveys (Deville *et al.* 2003; Mazzini *et al.* 2009). MVs occur in many sedimentary basins related to convergent plate margins, accretionary wedges, passive margins within deltaic systems (Kopf *et al.* 2001), and active hydrothermal areas (Etiope *et al.* 2002). They are known to be associated with faults and faulted anticlines in active tectonic settings (Kopf 2002), where the tectonic stress, mainly compressional, acts as the main driving force. MVs are investigated for hydrocarbon exploration, as a possible evidence of subsurface petroleum accumulations (Deville *et al.* 2003;

Milkov 2005; Etiope *et al.* 2009a), and pose environmental concerns, since methane is a potent greenhouse gas (Milkov 2005; Etiope *et al.* 2008).

The origin of methane and light hydrocarbons discharged from MVs is commonly ascribed to (i) thermal degradation of pre-existing organic material (thermogenesis) and/or (ii) microbial activity (Bernard *et al.* 1978; Schoell 1980, 1983; Chung *et al.* 1988; Seewald *et al.* 1998; Whiticar 1999; Seewald 2003; Takai *et al.* 2008), the latter not being necessary related to any potential source rock (Schoell 1983). Gases from these two sources can be distinguished by using the carbon isotopic composition of methane (Milkov and Etiope 2018): $\delta^{13}\text{C}_1$ values lighter than -50‰ vs. V-PDB are typical of microbial activity, i.e. a process proceeding through either fermentation or carbon dioxide reduction, whereas $\delta^{13}\text{C}_1$ values from -15‰ to -75‰ vs. V-PDB are commonly shown by thermogenic methane, i.e. thermal breakdown of pre-existing organic matter, typically associated with relatively high concentrations of heavier hydrocarbons (Whiticar 1994). Carbon and hydrogen isotopes of methane coupled with the relative abundances of light alkanes are used to discriminate

between these two-genetic processes (Bernard *et al.* 1978; Schoell 1980, 1983; Chung *et al.* 1988; Whiticar 1999), since thermogenic gases have relatively high concentrations of ethane, propane, butane and pentane than those recorded in microbial gases (Schoell 1980; Hinrichs *et al.* 2006). However, the original chemical and isotopic composition of deep-originated gas may be affected by post-genetic processes, such as anaerobic biodegradation of petroleum coupled with an addition of secondary microbial methane occurring at relatively shallow depth (Pallasser 2000; Etiope *et al.* 2009b; Milkov 2011, 2018), which may mask the pristine chemical and isotopic features of the primary gases.

Consequently, C₁-C₄ hydrocarbons were widely investigated to reveal the origin of gas discharged from fluid escape in sedimentary structures associated with various geologic settings (e.g. Delisle *et al.* 2002; Deville *et al.* 2003; You *et al.* 2004; Guliyev *et al.* 2004; Etiope *et al.* 2006, 2007; Tassi *et al.* 2012; Prinzhofner and Deville 2013; Ray *et al.* 2013). A data-set including chemical and isotopic signatures of light hydrocarbons discharged from worldwide onshore MVs indicated that they are dominantly related to thermogenic process (Etiope *et al.* 2008, 2009a), suggesting the presence of a potential source rock at catagenetic stage, i.e. occurring at temperatures typically >60°C (Hunt 1984; Milkov 2005). Chemical and isotopic compositions of the water phase discharged from MVs are good tracer to identify type and possible source of fluid. Additionally, useful insights can be obtained on depositional environments (presence of marine or non-marine evaporites), diagenetic processes, such as dissolution and precipitation of minerals, ion exchanges, organic matter degradation and clay mineral dehydration, which can be affected by temperature, depth and mixing processes (Rittenhouse 1967; You *et al.* 1993; Hanor 1994; Worden 1996; Dia *et al.* 1999; Kopf and Deyhle 2002; Kharaka and Hanor 2004; Chung *et al.* 2015).

Solid phases associated with the discharged fluids, called mud breccia, generally consist of clay-rich mud matrix and heterogenic rock fragments extruded from subsurface plumbing systems of MVs (Dimitrov 2002; Kopf and Deyhle 2002). Clay mineral alteration (e.g. illitization of smectite) is commonly assumed to be related to mud volcanism (Kopf and Deyhle 2002; Lavrushin *et al.* 2005). Since MVs mainly consist of smectite-rich mud (Fitts and Brown 1999), boron can be adsorbed by this clay mineral and then released to pore fluids through temperature-driven smectite-illite transformation during burial or tectonic processes (Colten-Bradley 1987; You *et al.* 1996). Consequently, insights into temperatures at depth in the various compressional tectonic settings can be gathered by this element, although

boron can also be enriched by degradation of organic matter in buried sediments (Williams *et al.* 2001; Kharaka and Hanor 2004).

The South Caspian Basin, which includes the Southern Caspian Sea and the coastal zones of Iran, Azerbaijan and Turkmenistan, is one of the oldest gas- and oil-bearing provinces in the world (Smith-Rouch 2006). This basin is well known for a large number of small-to-huge MVs (Figure 1) that occasionally produce impressive eruptions (Planke *et al.* 2003). These structures predominantly release thermogenic gas and are often found in association with petroleum fields (Fowler *et al.* 2000).

This paper reports the chemical and isotopic features of hydrocarbon-rich gases and waters, as well as a qualitative estimation of the mud-forming minerals, emitted from four onshore MVs, namely Sofikam, Inche, Gharenyaregh and Neftlijeh (Omrani and Raghimi 2018) which are located in the Gorgan Plain (SE Caspian Sea, Iran), to provide information about the origin and the main geochemical processes controlling fluid geochemistry.

Geological setting

The South Caspian Basin, one of the deepest sedimentary basins in the world (Devlin *et al.* 1999), is bounded by Caucasus, Talesh, Alborz and Kopeh Dagh mountains. Sediments derived by erosion and dismantling of these mountain belts fill up the subsiding South Caspian Basin and led, in the Pliocene-Quaternary, to the deposition of thickest sedimentary series at a rate of up to 3 km/Ma (Brunet *et al.* 2003). A thick clay-dominated sedimentary cover (up to 25–30 km) and a low geothermal gradient (15–18°C/km) characterize the South Caspian Basin. The high sedimentation rate was likely responsible of under-compacted sedimentary sequences, pore water overpressure, maturation of organic material and formation of structural traps, which are typical of mud volcanism areas (Abrams and Narimanov 1997; Tagiyev *et al.* 1997).

More than 400-active onshore and offshore MVs are present in this region. They are mostly associated with hydrocarbon fields within hydrocarbon-bearing faulted anticlines (Guliyev and Feizullayev 1996; Fowler *et al.* 2000). The geochemistry of fluids discharged from the South Caspian Basin MVs, including those exposed in Cheleken peninsula (western Turkmenistan) and Azerbaijan were extensively studied (Planke *et al.* 2003; Davies and Stewart 2005; Mazzini *et al.* 2009; Oppo *et al.* 2014; Lavrushin *et al.* 2015). The Oligocene-Early Miocene Maykop Formation, including layers of anoxic fine-grained and organic-rich sediments (Abrams and Narimanov 1997; Feyzullayev *et al.* 2001; Hudson *et al.* 2008), is to be regarded as the main fluid source (Figure 2; Inan *et al.* 1997; Fowler *et al.* 2000). However, some clasts found in

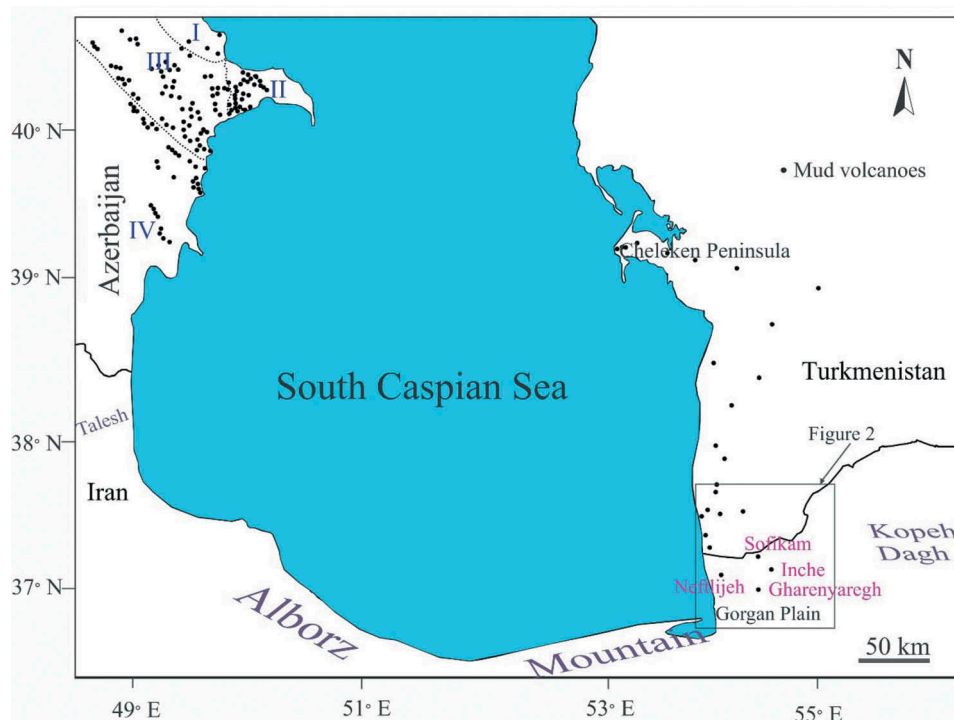


Figure 1. Schematic map showing the location of onshore mud volcanoes in the South Caspian Basin including those of Azerbaijan (mud volcanic regions: (I) Caspian, (II) Absheron, (III) Shemakha–Gobustan and (IV) Kura; Lavrushin *et al.* 2015; Jakubov *et al.* 1971), Turkmenistan (Oppo *et al.* 2014) and Iran.

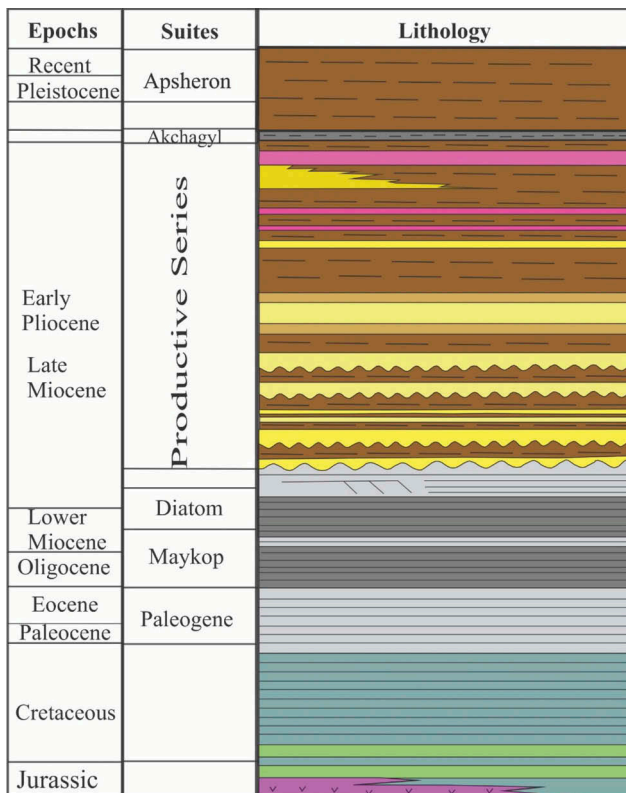


Figure 2. Generalized schematic stratigraphic column of South Caspian Basin (adopted from Green *et al.* 2009).

the mud breccias suggested possible contributions from deeper sedimentary sequences (i.e. Middle-late Miocene Diatom Series and Mesozoic deposits; Guliyev and Feizullayev 1996; Inan *et al.* 1997; Feyzullayev *et al.* 2001).

The Gorgan Plain, where MVs of current work presented, is located at 36° 40' to 37° 30' N and 53° 38' to 55° 38' E (Figure 3) in the Golestan province (NE Iran). The sedimentary successions of this Plain are part of those of the South Caspian and Kopesh Dagh Basins. The Kopesh Dagh Basin, as an elongated E-W trending basin located to the northeast of Iran and east of the South Caspian Basin. The boundary between the thick sedimentary series of South Caspian (Pliocene to Pleistocene) and the faulted and eroded formations of Kopesh Dagh (Jurassic to Eocene) beneath the eastern Gorgan is marked by a major Eocene-Oligocene angular unconformity. Although, above this unconformity, the faulted shale ridge structures on seismic section has been observed which are probably Maykop Formation (Robert *et al.* 2014). Ongoing geochemical investigations on a newly dug petroleum exploration well located near Sofikam MV also revealed the occurrence of a sequence similar to that characterizing the Maykop formation (Dr M. Mosavi Rohbakhsh; personal communication), the latter being possibly the source rock of gas seepages.

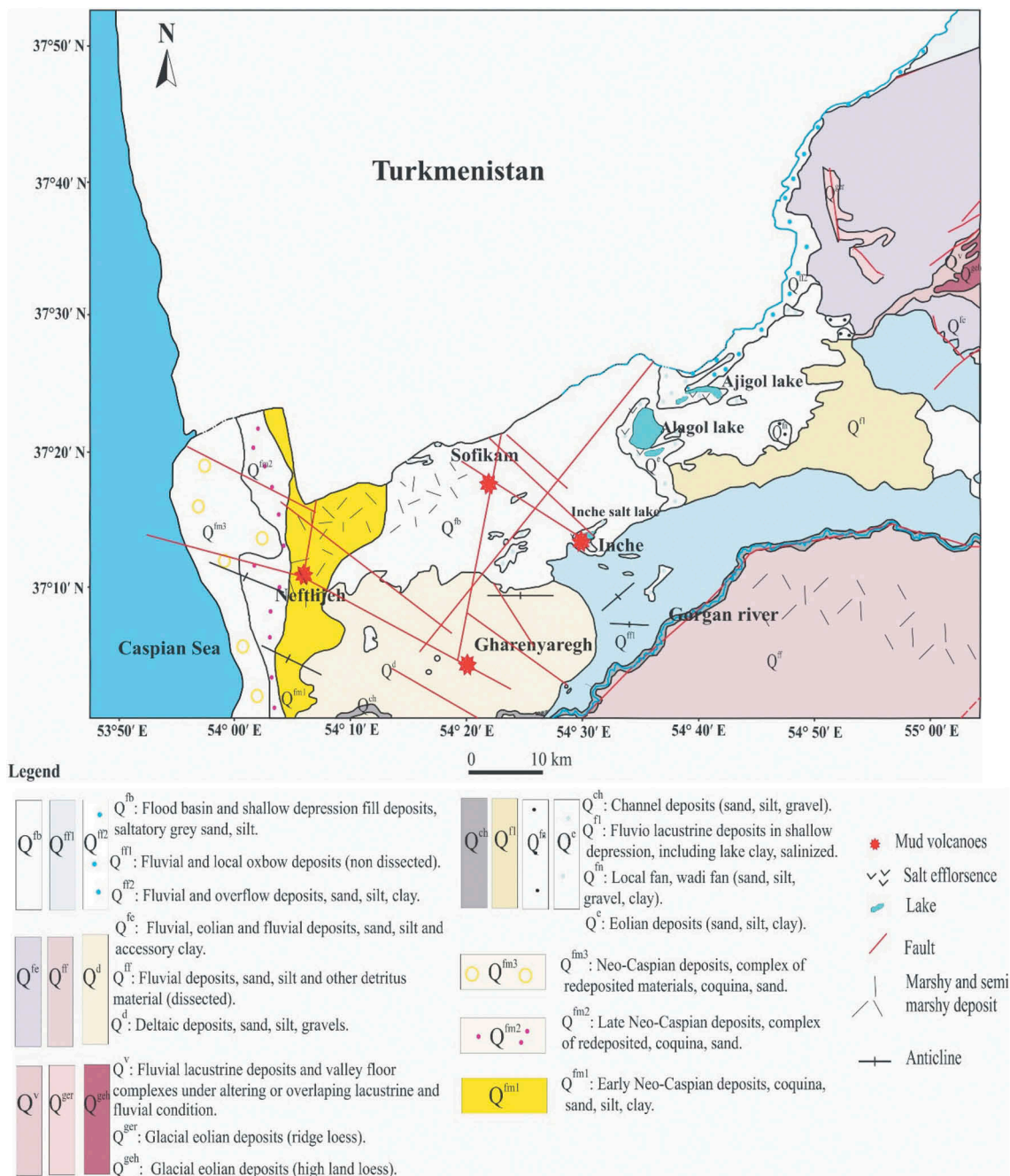


Figure 3. Schematic geological map of southeastern of Caspian Sea, Gorgan Plain, Iran showing the location of investigated MVs (modified after Saeedi and Andalibi 1993) controlled by faults/folds of Kopeh Dagh Basin (adapted from Omrani and Raghimi 2018).

The shale ridge structures are overlain by the Late Miocene yellow horizon and the Pliocene Cheleken formation. In the South Caspian Basin, the main hydrocarbon reservoirs are hosted within the Cheleken formation, which shows an increasing thickness from the Eastern Gorgan Plain towards the Caspian Sea and mainly consists of green or dark red sand-containing marls and thick layers of sandstone and conglomerate deposits (Guliyev and Feizullayev 1996; Abrams and Narimanov 1997; Fowler *et al.* 2000; Planke *et al.* 2003;

Stewart and Davies 2006; Torres 2007). An overpressured gas-dominated layer was found in the Cheleken formation during the drilling of two exploration wells located near Gharenyaregh MV in Gorgan Plain. The Cheleken formation is overlain by Late Pliocene claystone and marls with minor interbedded sandstones (Akchagyl Formation), followed by Pleistocene (Apsheron formation) and late Pleistocene-Holocene strata of the Baku, Khazarian, Khvalynian and Neocaspian stages (Mosavi Rohbakhsh 2001). Thin layers of volcanic ashes were

reported to occur in the Akchagyl and Apsheron formations (Alizadeh *et al.* 2016). In the Gorgan Plain, wells for gas-oil exploration were drilled at shallow-to-intermediate depth (1,000–3,500 m), revealing the occurrence of microbial methane associated with iodine bearing high-salinity waters hosted within the Akchagyl and Apsheron formations (Mosavi Rohbakhsh 2001; Khajeh *et al.* 2007).

The buried Mesozoic Kopeh Dagh formations, which outcrop at the eastern part of Gorgan plain, have up to 10-km thickness (Berberian and King 1981). Upper Cretaceous begin with the glauconite sandstones of Aitamir formation and end with limestones of Kalat (Sharafi *et al.* 2012). Lower Cretaceous begin with the conglomerates and sandstones of the Shurijeh formation and end with the dark-grey shales and siltstones of the Sanganeh (Raisossadat 2004). Jurassic sediments include sandstones and shales of the Kashafrud (Middle Jurassic) are overlain by grey shales and marly limestones of Chaman Bid and the limestone of Mozduran with Upper Jurassic in age. The Kashafrud and Chaman Bid formations are the main source rocks and Tirgan (Lower Cretaceous) and Mozduran formation are the potential and main gas reservoirs in the Kopeh Dagh range, respectively (Robert *et al.* 2014).

MVs of Gorgan

Gharenyaregh, Inche, Sofikam and Neftlijeh MVs (Figure 4(a–f)) formed on the flat Quaternary plain located in the coastal region of South Caspian Sea (Figure 3). In addition, nearly 20 extinct MVs controlled mostly by fault/fold structures have been reported (Omrani and Raghimi 2018). There are also buried MVs identified during seismic surveys in this area (Rezvandehy *et al.* 2011).

The morphology of the four MVs was already described by Omrani and Raghimi (2018). All MVs are as caldera-like depressions with limestone blocks within mud island of Gharenyaregh (Figure 4(c)) and concentric ring collapse structures on the outskirts of Neftlijeh (Figure 4(e)) which can be ascribed to intense and persistent mud fluid emissions during the past. Water pools of Gharenyaregh were characterized by dark oily iridescences, whilst bubbling gases released strong smell of rotten eggs (Figure 4(b)). The rock fragments originating from glauconitic sandstones of the Aitamir Formation (Upper Cretaceous) belonging to underlying Kopeh Dagh units were only found around Gharenyaregh indicating a deep source (Omrani and Raghimi 2018).

The location of MVs coincide with subsurface anticlines and NW-SE and NE-SW trending faults of the western Kopeh Dagh fold-thrust belt (Figure 3). The five pools of

the Sofikam define an alignment with northeast direction (N60°), which is coincident with the fold axes and main faults of Kopeh Dagh (Omrani and Raghimi 2018). Several small seeps, approximately 0.5 m in diameter, occur in the collapsed sectors from the outer flanks of Gharenyaregh along NW-trending faults (Figure 4(a,b)), likely related to the tectonic stress that caused the formation of this MV (Rezvandehy *et al.* 2011).

Materials and method

Bubbling gases of the Sofikam, Neftlijeh, Inche and Gharenyaregh MVs were collected in 2017. The first three MVs were sampled using a plastic funnel up-side-down positioned above the bubbling sites and connected through a silicon tube to a pre-evacuated glass bottle equipped with a thorion valve (Vaselli *et al.* 2006). Gas sampling from three pools at Gharenyaregh was carried out using 40-mL gas vials equipped with a rubber septum instead of the glass bottle.

The chemical and isotopic ($\delta^{13}\text{C}_1$ and $\delta^{13}\text{C-CO}_2$) composition of gas was carried out at the Laboratory of Fluid Geochemistry of the Department of Earth Sciences (University of Florence, Italy). The inorganic gas fraction (CO_2 , N_2 , $\text{Ar}+\text{O}_2$ and H_2) was analysed by gas chromatography (GC) using a Shimadzu 15A instrument equipped with a Thermal Conductivity Detector (TCD). Argon and O_2 were separately analysed using a Thermo Focus gas chromatograph equipped with a 30 m long capillary molecular sieve column and a TCD. Methane and $\text{C}_2\text{-C}_4$ hydrocarbons were determined by using a Shimadzu 14A gas chromatograph equipped with a Flame Ionization Detector (FID) and a 10 m long stainless-steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700 (Vaselli *et al.* 2006). The analytical error for the GC analysis was $\leq 10\%$. The carbon isotopes in CO_2 (expressed as $\delta^{13}\text{C-CO}_2$ ‰ vs. V-PDB) were determined by using a Finnigan Delta Plus mass spectrometer (MS), after extracting and purifying CO_2 by using liquid N_2 and N_2 -trichloroethylene cryogenic traps (Evans *et al.* 1998; Vaselli *et al.* 2006). Internal (Carrara and S. Vincenzo marbles) and international (NB18 and NBS19) standards were used for estimating the external precision. Analytical uncertainty and reproducibility were $\pm 0.05\%$ and $\pm 0.1\%$, respectively. The carbon isotopes in CH_4 (expressed as $\delta^{13}\text{C}_1$ ‰ vs. V-PDB) were measured by Cavity Ring-Down Spectroscopy (CRDS) using a Picarro G2201-i Analyser. The errors of the CRDS analysis was $< 1\%$. In order to avoid interferences, the instrument inlet line was equipped with (i) a Drierite trap and (ii) a copper trap for the removal of water vapour and H_2S , respectively. According to the operative ranges of the Picarro G2201-i



Figure 4. (a) Lateral view of Gharenyaregh MV with a mud island inside, surrounded by a collapsed area filled with saline water and the location of pools (black arrows) probably controlled by a fault, (b) a small seepage (Pool No. 4) within the collapsed area of Gharenyaregh, which is set along other seeps, (c) sedimentary rock fragments within a dried gryphon on island of Gharenyaregh, (d) Sofikam MV showing five pools characterized by permanent fluid emissions define an alignment with northeast direction (N60°), which is coincident with the fold axes and main faults of Kopeh Dagh (Omrani and Raghimi 2018), (e) Neftlije MV where concentric collapse structures are visible in the left-hand side inner flank, and (f) lateral view of Inche MV.

instrument (up to 500 ppm), gas samples were diluted using a N₂-O₂-Ar gas mixture.

Water samples were collected from both pools and crater lakes during two campaigns in 2016 and 2017. They were stored in 50-mL polyethylene bottles after filtering at 0.45 μm in field for chemical and isotopic analysis. One water sample was taken directly from a well (1,000–1,200-m depth) drilled for iodine extraction from brines near Inche in 2017. At each site, temperature and pH were measured in the field using an EXTECH® (ExStik® EC500) portable multi-parametric instrument and one filtered and two filtered and acidified (with

Suprapure HCl and HNO₃, respectively) samples were collected.

Analysis on the major components and trace elements of the water were carried out at the Department of Earth Sciences (University of Florence, Italy). Main cations (Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺) and anions (Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻, Br⁻ and F⁻) were analysed using ion chromatography (Metrohm 861 and 761, respectively). Boron was analysed using the Azomethine-H (AH) method (Bencini 1985) by molecular spectroscopy (MSC) using a Philips UNICAM analyser. The analytical errors for IC and MSC were ≤5%. Li concentrations were

determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using an Optima 8000 Perkin Elmer spectrometer. The analytical error for ICP-OES was $\leq 10\%$. Oxygen (expressed as $\delta^{18}\text{O-H}_2\text{O}$ ‰ vs. V-SMOW) and hydrogen (expressed as $\delta\text{D-H}_2\text{O}$ vs. V-SMOW) analysis were carried out using Finnigan MAT Delta plus XP + Gasbench at G.G Hatch Stable Isotope Laboratory, Faculty of Science, Ottawa University (Canada). The precision (2 sigma) of the analysis was $\pm 0.15\%$ and $\pm 2.0\%$ for $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$, respectively.

Mineralogical analyses of the powdered mud samples from all four MVs under consideration were carried out at the Department of Earth Sciences (University of Florence) by XRD using a Philips PW 1050/37. In order to separate the $<4\ \mu\text{m}$ clay-sized fraction, few grams (2 g) of powdered samples were placed in about 50 mL of MilliQ water, then dispersed by ultrasonic probe and washed and centrifuged at least four times. The wet sediments were transferred to sedimentation cylinders at which 100 mL MilliQ water was added and allowed it to be settled for 1 h (Stocks' law). Once the $<4\ \mu\text{m}$ clay suspension was recovered and dried, few millilitre of water was added and agitated with a glass rod. About 3–5 mL of the water-sediment suspension was placed on glass slides and left to be dried at room temperature. The clay minerals were recognized on the dry sample i) without any further treatment; ii) after spraying ethylene glycol; iii) after heating in a ventilated stove at 450°C for 1.5 h and iv) after heating in a ventilated stove at 650°C for 1.5 h.

Results

The chemical (in % by vol.) and isotopic gas composition are reported in Supp. Table 1. Methane was the dominant alkane in the bubbling vents at Inche (4 samples: from 80.5% to 93.2%), Gharenyaregh (3 samples: from 43.3% to 80.3%), Sofikam (4 samples: from 50.3% to 84.7%), and in the Neftlijeh crater lake (1 sample: 90.7%). Light alkanes (ethane, propane, i-butane and n-butane) had concentrations up to 5.79%, 0.89%, 0.35% and 0.22%, respectively (Supp. Table 1). Concentrations of N_2 ranged from 1.5% to 50.0%, whereas those of O_2 were $<3.31\%$.

The $\delta^{13}\text{C}_1$ values were in a relatively narrow range: from -45.6% to -55.1% vs. V-PDB. The $\delta^{13}\text{C-CO}_2$ values at Sofikam, Gharenyaregh and Inche MVs were from -17.4% to -26.4% vs. V-PDB, whereas that at Neftlijeh was 3.1% vs. V-PDB.

The chemical and isotopic composition of the waters discharged by Gorgan MVs is listed in Supp. Table 2. The pH values of the Sofikam, Inche, Gharenyaregh and

Neftlijeh pools and Gharenyaregh lake were up to 7.2, 6.8, 7.7, 8.9 and 7.8, respectively. Considering that the measured temperatures ranged from 24.0°C to 30.3°C (Supp. Table 2) and that the ambient temperature was from 25°C to 31°C , these emergences cannot be considered as thermal waters. Waters were characterized by a Na-Cl composition, with Na^+ and Cl^- concentrations ranging from 12 to 43.7 g/L and from 34.5 to 102 g/L, respectively. Relatively high concentrations of NH_4^+ (19 to 310 mg/L) were measured. Waters from Gharenyaregh and Neftlijeh showed HCO_3^- (622 to 2,280 mg/L), Li (16.3 to 25.5 mg/L) and B (97 to 1084 mg/L) concentrations significantly higher than those recorded at Sofikam and Inche. The former had relatively low concentration of Ca^{2+} (197 to 855 mg/L) and Mg^{2+} (320 to 914 mg/L). Concentrations of SO_4^{2-} in the Gharenyaregh waters (up to 11,240 mg/L) were one order of magnitude higher than those measured in the other sites.

The water sample from the iodine production well was Na-Cl type and was characterized by relatively high concentration of Ca^{2+} (4,900 mg/L), Mg^{2+} (4,650 mg/L), Li (60.3 mg/L), NH_4^+ (423 mg/L) and SO_4^{2-} (8,620 mg/L).

The $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values of the Sofikam waters ranged from -1.78% to 1.04% and from -30.1% to -17.3% vs. V-SMOW, respectively. Heavier $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values were measured in the lakes from Inche (0.88% to 1.11% and -16.7% to -15.9% vs. V-SMOW, respectively), Neftlijeh (3.17% to 4.10% and -8.9% to -10.0% vs. V-SMOW, respectively) and the Gharenyaregh water pool (1.10% to 1.39% and -20.0% to -18.2% vs. V-SMOW, respectively).

Quartz, calcite, halite, muscovite, illite, albite, clinocllore and microcline were found in the mud samples for all the studied MVs. Gypsum was only found in mud samples from Sofikam and Inche MVs, whereas dolomite and traces of marcasite were recognized in the mud samples from Gharenyaregh and Neftlijeh. Clay minerals in the $<4\ \mu\text{m}$ fraction were consisting of illite, chlorite and kaolinite with low contents of smectite, with no significant differences among the studied mud samples.

Discussion

Processes controlling the chemistry of gases

Gas chemistry from the Gorgan MVs can be related to a mixing process between an N_2 -rich (air-like) and a CH_4 -rich component. The N_2/Ar ratios range from 51.6 to 79.4 (Supp. Table 1), i.e. between those of air (83.6) and air-saturated water (ASW: 38.3), indicating that both N_2 and Ar have a meteoric origin. Considering that deep-originated

gases feeding MVs are O₂-depleted, the occurrence of O₂ (<3%) suggests some air contamination at shallow depth and/or during the gas sampling. A significant contribution of mantle He is to be ruled out due to the low R_c/R_a values ranging between 0.08 and 0.12 (Mehrabi *et al.* 2017).

The CH₄-rich component is typical of gases related to mud volcanism occurring in sedimentary basins (e.g. Dia *et al.* 1999; Dimitrov 2002; Mazzini *et al.* 2009; Tassi *et al.* 2012; Bonini *et al.* 2013). As shown in the $\delta^{13}\text{C}_1$ vs. C₁/(C₂₊) binary diagram (Figure 5; Milkov and Etiope 2018), gases from the Gorgan MVs fall in the field of thermogenic gas. It is worth noting that gases from Azerbaijan and Turkmenistan MVs (Etiope *et al.* 2009a), which are related to a geodynamic setting similar to that of the study area, showed similar $\delta^{13}\text{C}_1$ values, whereas their C₁/(C₂₊) ratios were significantly higher than those of the Gorgan Plain gases. Such geochemical features were interpreted as related to secondary processes acting during the uprising of thermogenic gases: (i) molecular fractionation due to the gas transfer from reservoir to surface; (ii) secondary anaerobic biodegradation (Pallasser 2000; Katz *et al.* 2002; Deville *et al.* 2003; Etiope *et al.* 2007, 2009a, 2009b). Secondary anaerobic biodegradation processes were reported to extensively affect also gases from hydrocarbon fields and MVs located in the western sector of South Caspian Sea (Figure 6), showing isotopically heavy CO₂

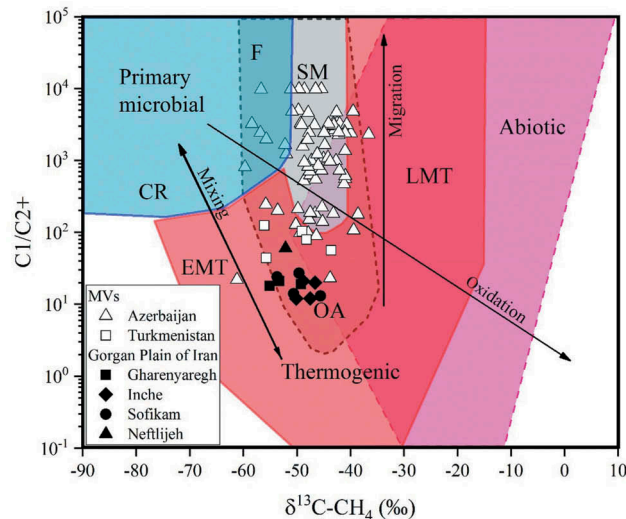


Figure 5. Plot of C₁/C₂₊ ratios vs. $\delta^{13}\text{C}_1$ values for the gases emitted from Sofikam, Gharenyaregh, Inche and Neftlijeh MVs. Typical fields for microbial, thermogenic and abiogenic gases (CR – CO₂ reduction, F – methyl-type fermentation, SM – secondary microbial, EMT – early mature thermogenic gas, OA – oil-associated thermogenic gas and LMT – late mature thermogenic gas; Milkov and Etiope 2018) are outlined. The gas data from MVs of Azerbaijan and Turkmenistan (Etiope *et al.* 2009a, 2009b) are also reported for comparison.

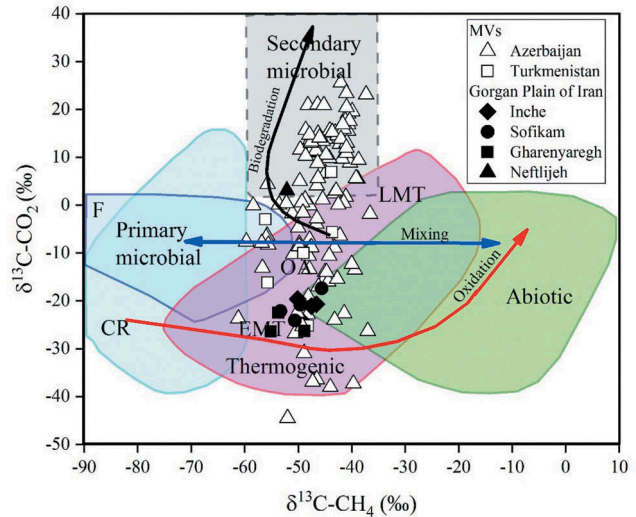


Figure 6. Plot of $\delta^{13}\text{C}_{\text{CH}_4}$ vs. $\delta^{13}\text{C}_{\text{CO}_2}$ values (CR – CO₂ reduction, F – methyl-type fermentation, EMT – early mature thermogenic gas, OA – oil-associated thermogenic gas and LMT – late mature thermogenic gas; Milkov and Etiope 2018) for gases from Gorgan MVs and those from Azerbaijan and Turkmenistan MVs (Etiope *et al.* 2009b) for comparison.

(Feyzullayev and Movsumova 2001). This feature is typical of gases from petroleum reservoirs located at shallow depths (<2000 m) and relatively low temperatures (<75°C), where water temperature and availability of oxyanions (NO₃⁻, SO₄²⁻ and HCO₃⁻) can play a key role in the gas evolution (Pallasser 2000). CO₂ generated by anaerobic oxidation of petroleum or heavy hydrocarbons is consumed by methanotrophs (Pallasser 2000; Head *et al.* 2003; Jones *et al.* 2008; Milkov 2011, 2018). The residual ¹²C-depleted CO₂ is highly indicative of secondary microbial methane formed during petroleum biodegradation (Milkov 2011, 2018). Among the South Caspian gases, secondary anaerobic biodegradation and the occurrence of secondary microbial methane is only documented by the composition of Neftlijeh gas sample, which was characterized by a positive $\delta^{13}\text{C}-\text{CO}_2$ value (Figure 6). Contrarily to the Azerbaijan gases, those from Gorgan Plain seem to be poorly affected by molecular fractionation. This occurs in the presence of high gas fluxes or when the distance from the reservoir to the surface is rather short. In both cases, gas-water-mud interactions leading to loss of C₂₊ compounds are kinetically disadvantaged and thus, they do not affect the ascending gas (Etiope *et al.* 2007, 2009b).

There are two geological evidences suggesting that thermogenic source play a key role in the formation of the Gorgan Plain gases: (i) the gas layers recognized by geophysical investigations in the Cheleken formation around the Gharenyaregh MV (Rezvandehy *et al.* 2011),

and (ii) the potential source rock formations recently identified in wells drilled and on seismic sections in the study area, which are similar to the Maykop formation and Middle Miocene-Late Miocene deposits and probably buried Mesozoic sediments of Kopeh Dagh Basin. Sedimentary basins and MVs from the South Caspian Basin include four potential fluid source rocks; i) Palaeogene–Lower Miocene marine mudstones, comprising organic-rich fine-grained, clay-dominated layers with fine to very fine sandstone strata and dolomite-rich beds, ii) Middle-Late Miocene shales and marls interbedded with sandstones and siltstones with diatom suite, iii) Lower Cretaceous greyish-green claystone, yellowish-red sandstones and subordinate conglomerates and iv) Middle Jurassic sedimentary sequences consisting of clay-rich facies interbedded with fine grained sandstones and siltstones (Inan *et al.* 1997; Feyzullayev *et al.* 2001; Guliyev *et al.* 2004; Hudson *et al.* 2008; Bonini *et al.* 2013).

Water geochemistry and mud mineralogy

The waters collected from the Gorgan Plain MVs have a relatively high TDS values (44–127 g/L), higher than those of water emergencies located in adjacent areas, e.g. Turkmenistan, where the TDS values were from 23 to 50.7 g/L (Oppo *et al.* 2014), and a Na^+ – Cl^- composition (Supp. Table 2), typical of a brine (Hem 1970).

The occurrence of brines in sedimentary basins is commonly attributed to halite dissolution (Dresel and Rose 2010; Pinti *et al.* 2011) or seawater trapped in geological formations (Birkle *et al.* 2009; Lüders *et al.* 2010). Seawater evaporation trend (SET) has extensively been applied to determine the origin of salinity in sedimentary basins (Bottomley *et al.* 1999; Kharaka and Hanor 2004). Gorgan waters follow SET (Figure 7), although variations in the Cl^-/Br^- ratios were likely caused by the concomitant evaporation and halite dissolution (Knauth 1988).

Brine chemistry from oilfields is controlled by a variety of physical processes such as mixing between deep and shallow waters and chemical reactions such as mineral dehydration, adsorption and desorption on clay minerals, precipitation and dissolution of carbonate minerals and degradation of organic material leading to increasing alkalinity, NH_4^+ , B and Br^- and decreasing concentration of oxidized species such as SO_4^{2-} (Kharaka and Smalley 1976; Lagunova 1976; You *et al.* 1993; Kopf and Deyhle 2002).

Chloride shows a conservative chemical behaviour in pore waters and its distribution in fluids from MVs can provide useful insights into the water sources. The TDS

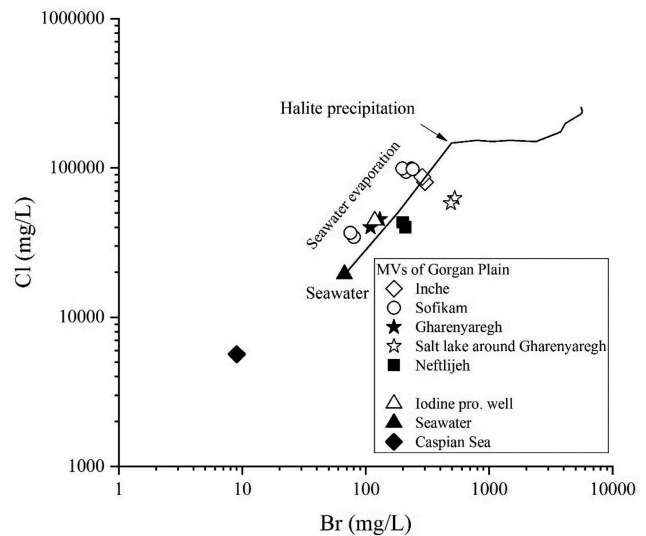


Figure 7. Cl vs. Br (in mg/L) in water from the Gorgan MVs and the iodine production well. The evaporation trend for seawater and water composition of the Caspian Sea are from Carpenter (1978) and Planke *et al.* (2003).

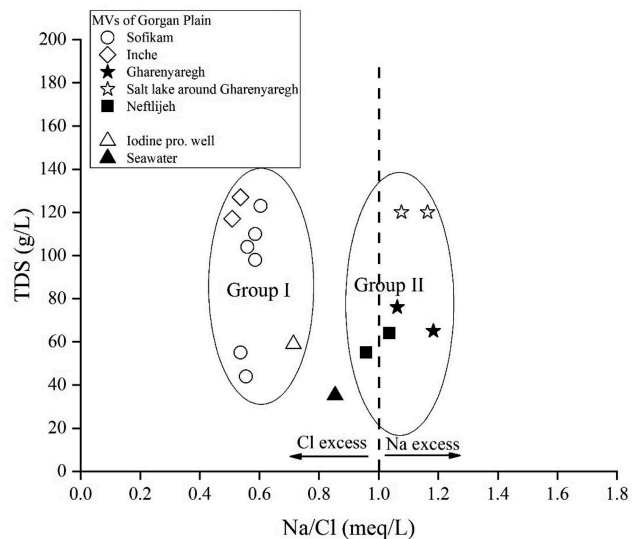


Figure 8. TDS (in g/L) vs. Na/Cl (in meq/L) plot for waters from the Gorgan MVs, the iodine production well and seawater (Fontes and Matray 1993). Gorgan waters are divided to two groups I (Inche and Sofikam MVs) and II (Gharenyaregh and Neftlijeh MVs) according to Cl and Na excess.

versus Na^+/Cl^- plot (Figure 8), as well as the ratios between Cl^- and the main cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and Li^+) and B (Figure 9 and Supp. Table 2), allow to distinguish two groups: i) waters from Gharenyaregh and Neftlijeh MVs, which are characterized by Na^+/Cl^- , B/Cl^- and Li/Cl^- ratios similar or higher than those of seawater, and relatively low $\text{Ca}^{2+}/\text{Cl}^-$, $\text{Mg}^{2+}/\text{Cl}^-$ and K^+/Cl^- ratios; ii) waters from

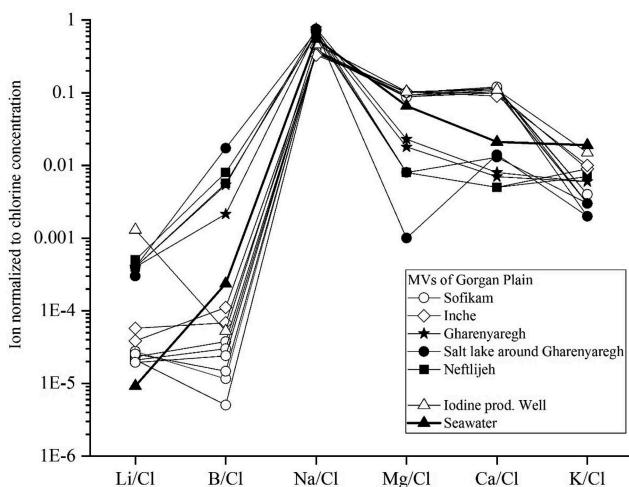


Figure 9. Elemental concentration normalized to chlorine. The concentrations are in logarithmic scale. **Seawater is shown.**

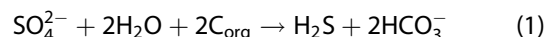
Sofikam and Inche MVs and the iodine production well, which show significantly lower Na^+/Cl^- , B/Cl^- and Li/Cl^- and higher $\text{Ca}^{2+}/\text{Cl}^-$, $\text{Mg}^{2+}/\text{Cl}^-$ and K^+/Cl^- ratios.

Lithium, Na and B, which tend to be enriched in low-temperature clay minerals (Schwarcz *et al.* 1969; Spivack *et al.* 1987; Chan *et al.* 2002) can enter the aqueous media through (i) hydrothermal alteration at moderate temperatures (around 50°C) (You *et al.* 1996; James *et al.* 2003), (ii) desorption and mineral dehydration reactions and (iii) decomposition of organic compounds during burial in response to increasing temperatures (James and Palmer 2000; Williams *et al.* 2001; Kopf and Deyhle 2002; Kharaka and Hanor 2004; Teichert *et al.* 2005). An enrichment in these elements, as shown by the Gharenyaregh and Neftlije waters, is thus to be considered a common feature for oilfield brines (Bottomley *et al.* 1999; Chan *et al.* 2002), suggesting long fluid circulation to reach great depths. Specifically, the high B/Cl^- ratios of these waters (Supp. Table 2) were possibly caused by the release of B due to smectite illitization, a typical process occurring during sediment diagenesis, in analogy to what reported for other MVs worldwide (You *et al.* 1996, 2004; Williams *et al.* 2001; Kopf and Deyhle 2002; Aloisi *et al.* 2004; Hensen *et al.* 2004; Lavrushin *et al.* 2005; Teichert *et al.* 2005; Mazzini *et al.* 2009; Chao *et al.* 2011). This process is also supported by the qualitatively-estimated scarce content of smectite with respect to that of illite in the muds. The relatively high Ca^{2+} concentrations and Na^+ and K^+ depletion characterizing the second group of waters is typically produced by fluid interaction with igneous rocks due to volcanic ash alteration (Gieskes *et al.* 1989; You *et al.* 2004), as also supported by experimental investigations

carried out at relatively low (70°C) temperature (Henderson 1982). Sofikam and Inche fluids likely interacted with the volcanogenic products occurring within the shallow formations of Akchagyl and Apsheron (Alizadeh *et al.* 2016). However, this process causes a decrease in $\text{Mg}^{2+}/\text{Cl}^-$ ratio, in contrast with the relatively high $\text{Mg}^{2+}/\text{Cl}^-$ measured in these waters. The opposite trend identified in waters emitted by these MVs is apparently pointing to another process able to control the Mg content in these waters. The presence of minerals belonging to the chlorite-group (clinocllore), mica and carbonate minerals recognized by XRD in the muds, can likely be representing a potential source of Mg^{2+} , able to explain the high content of Mg recorded in these waters (White 1965).

The relatively high concentrations of NH_4^+ shown by all the Gorgan Plain waters (19 to 310 mg/L; Supp. Table 2) were likely caused by degradation of organic N-bearing compounds or ion exchange processes with the associated hydrocarbons, as also documented in many waters associated with oilfields (Collins 1975), as well as those discharged from Turkmenistan MVs (Oppo *et al.* 2014).

Although no H_2S measurements were carried out in the present study, the occurrence of this compound in the Gharenyaregh and Neftlije MVs was suggested by the strong smell of rotten eggs detected during the geochemical survey. This implies that SO_4^{2-} in the MV waters may be reduced to H_2S by microbial activity, as follows (Friedman *et al.* 1992):



This process is also supported by the presence of marcasite revealed by X-ray analysis. Nevertheless, secondary SO_4^{2-} could be produced through H_2S oxidation at relatively shallow depth.

In the $\delta\text{D}-\text{H}_2\text{O}$ vs. $\delta^{18}\text{O}-\text{H}_2\text{O}$ diagram (Figure 10), where the local-meteoric water line (LMWL; Shamsi and Kazemi 2014) was reported, the Gorgan Plain waters were compared to those from Azerbaijan (Lavrushin *et al.* 2015) and Turkmenistan MVs (Lavrushin *et al.* 2005). The Gorgan Plain waters show significant enrichments in $\delta^{18}\text{O}$ and δD values with respect to LMWL and seem to be aligned along an evaporation trending line. Furthermore, the $\delta^{18}\text{O}$ values are slightly more negative with respect to those of Azerbaijan and Turkmenistan. The isotopic trend depicted by the Gorgan Plain waters is thus possibly related to an evaporation process of seawater diluted by a relatively negative meteoric water (with $\delta^{18}\text{O}$ and δD values of ~ -12 and -80% , respectively). However, isotopic exchange with the mud-

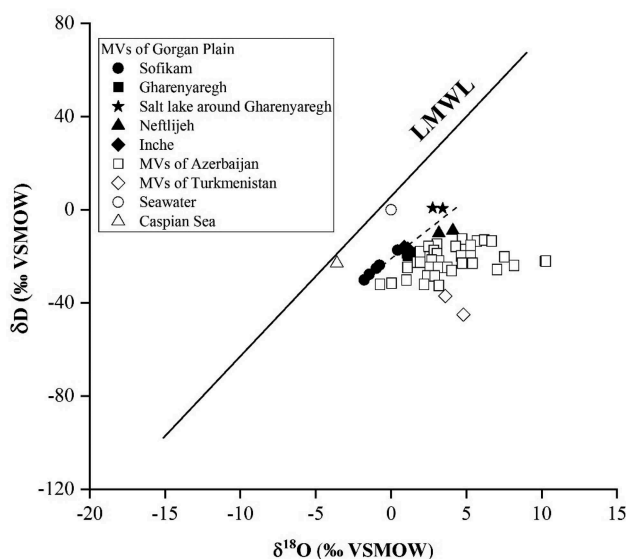


Figure 10. δD vs. $\delta^{18}O$ values of MV waters from Gorgan Plain, Azerbaijan, Turkmenistan, Caspian Sea and Seawater (Lavrushin *et al.* 2005, 2015) compared with the Local Meteoric Water Line (LMWL) (Shamsi and Kazemi 2014). The dashed line refers to the isotopic variation trend of the Gorgan Plain MVs.

hosting clay minerals (e.g. kaolinite and illite), resulting in an ^{18}O -shift, cannot be excluded (e.g. James and Baker 1976; Horbe 2011; Skelton *et al.* 2019).

Temperature-dependent specific cation pairs in solution can usefully be applied to estimate the temperature of subsurface waters (e.g. Giggenbach 1997; Haese *et al.* 2006). However, the typical approach proposed by Giggenbach (1992), based on the combined Na/K and K/Mg geothermometer, cannot be applied due to the contribution of Na and Cl from halite and/or seawater. The Mg-Li geothermometer is considered to be able to provide reliable temperature estimations for brines from MVs (Lavrushin *et al.* 2015, Kharaka and Mariner 1989) as follows:

$$T^{\circ}C = 2200 / \log \left(\log \left(\left(\sqrt{Mg} \right) / Li + 5.47 \right) \right) - 273.15 \quad (2)$$

The Mg-Li calculated temperatures range from 33°C to 40, 44°C to 53, 110°C to 117 and 129°C to 134 for Sofikam, Inche, Gharenyaregh and Neftlijeh MVs, respectively. Considering an average geothermal gradient of 15–18°C/1000 m (Tagiyev *et al.* 1997) and an average-ground temperature of 16.4°C (Kordjazi *et al.* 2014), these equilibrium temperatures can be attained from 1 km for Sofikam and Inche to 6-km depth for Gharenyaregh and Neftlijeh. Owing to Mg in the Sofikam and Inche waters may originate from multiple sources as well as a mixture source for waters, hence, theoretical temperatures for these two MVs calculated using the Mg/Li geothermometer is doubtful and

should be considered with caution. Notwithstanding the uncertainty of obtained temperature estimations, the geochemical features of the Sofikam and Inche are similar to those shown by brines recognized in the Akchagyl and Apsheron formations during drilling for iodine extraction at 1-km depth (Khajeh *et al.* 2007) and a deep source for Gharenyaregh (Omran and Raghimi 2018) are in agreement with the results of the Mg-Li geothermometer.

Model and concluding remarks

Gases, waters and muds emitted from four MVs located in the Gorgan Plain, SE Caspian Sea (Iran) were collected for chemical and isotopic analysis to investigate their origin and the processes controlling their chemistry. Conceptual models summarizing the main findings gathered from fluid geochemistry of MVs in the Gorgan Plain are reported in Figure 11(a,b). Sofikam, Gharenyaregh, Inche and Neftlijeh MVs have caldera-like features and the chemical composition of light alkanes and the isotopic values of methane indicate thermogenic origin for the discharged gases. The Maykop, Upper-Middle Miocene and Mesozoic deposits may be regarded as the probable source rocks for thermogenic gases, although the source rock/s producing thermogenic gas is still questionable due to the complexities and ambiguities in identifying the geological sequences beneath the Gorgan Plain.

The Na–Cl waters can be divided into two main groups: Type 1 waters from Gharenyaregh and Neftlijeh MVs showing relatively high Na^{+}/Cl^{-} , B/Cl^{-} and Li/Cl^{-} ratios and low Ca^{2+}/Cl^{-} , Mg^{2+}/Cl^{-} and K^{+}/Cl^{-} ratios, typically discharged by MVs due to interaction with marine sediments: These waters likely originate from the deep subsurface formations of Gorgan Plain (Mesozoic formation?). Type 2 waters from Sofikam and Inche MVs are characterized by lower Na^{+}/Cl^{-} , B/Cl^{-} and Li/Cl^{-} ratios and higher Ca^{2+}/Cl^{-} , Mg^{2+}/Cl^{-} and K^{+}/Cl^{-} ratios, possibly due to interaction with volcanic rocks and siliciclastic sediments in relatively shallow formations. The relatively high-estimated temperatures for waters from Gharenyaregh and Neftlijeh MVs suggest that they are fed by deep reservoirs (~6 km).

The positive $\delta^{18}O$ - and δD -shifts measured in all the Gorgan waters are likely caused by (i) evaporation processes affecting seawater diluted by a meteoric component and/or (ii) isotope exchange with the mud-hosting clay minerals.

Integration of the information gathered from the geochemical data of the present study with a comprehensive geological, geostructural and geophysical investigation is

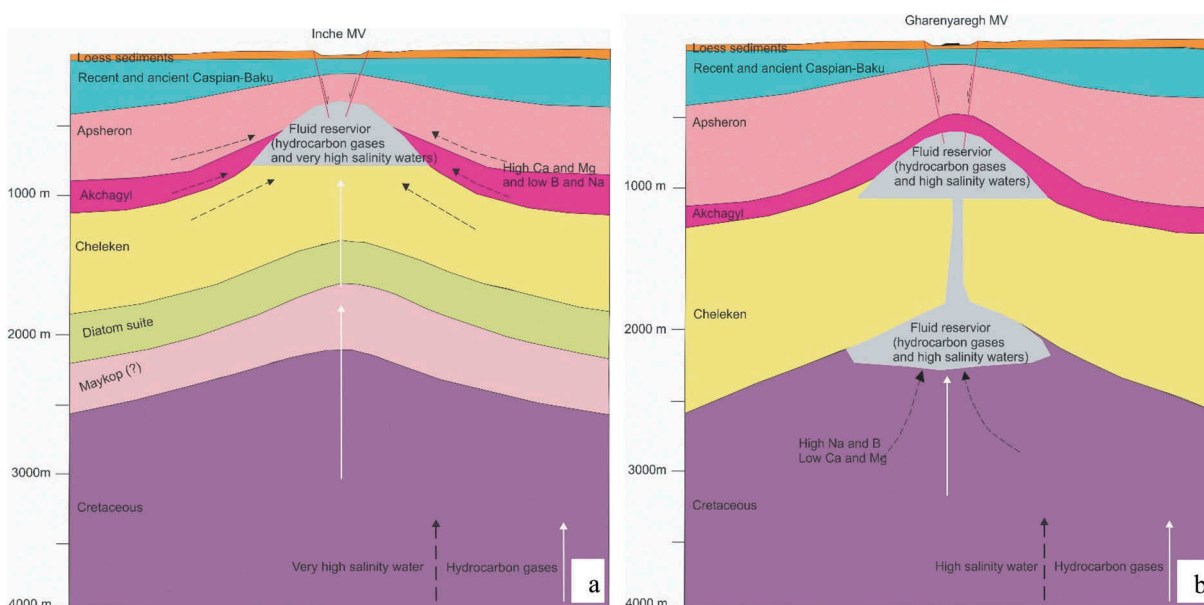


Figure 11. Schematic diagrams show main elements of (a) Inche and (b) Gharenyaregh MVs. The type 1 waters discharging by Gharenyaregh and Neftlijeh MVs may have derived from deep mud-rich layers where acquired the high B concentration from clay minerals transformation. The occurrence of a reservoir at deep layers is also testified by the presence of rock fragments belong to Cretaceous deposits in mud breccia (Omrani and Raghimi 2018). In contrast, the type 2 waters expelling by Incheh and Sofikam MVs may have originated from the relatively shallow reservoirs. In addition to Mesozoic deposits can be regarded as source rocks likely generating the thermogenic gases in Gharenyaregh and Neftlijeh MVs, as they have been observed through the seismic profiles around Gharenyaregh MV (Rezvandehy *et al.* 2011), the Maykop and Middle-Late Miocene sequences reported in the drilled wells around Incheh and Sofikam MVs (adapted from logs of the drilled wells for hydrocarbon exploration and Robert *et al.* 2014), can be considered as another probable source rocks.

invoked to constrain the potential hydrocarbon resource of the study areas.

Highlights

- Mud volcanoes of Northern Iran release thermogenic gases with no secondary isotope fractionation.
- Waters were distinguished in two groups based on the estimated depth of the fluid sources.
- Discharged waters originated from seawater affected by evaporation and dilution processes.

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