Applied Geochemistry 100 (2019) 1–7

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Shallow submarine seep of abiotic methane from serpentinized peridotite off the Island of Elba, Italy

Alessandra Sciarra[a,b,c,*], Anna Saroni[b], Giuseppe Etiope[d,e], Massimo Coltorti[b], Francesco Mazzarini[f], Christian Lott[g,h], Fausto Grassa[i], Francesco Italiano[i]

[a] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 1, via di Vigna Murata 605, 00143, Rome, Italy*
[b] *Department of Physics and Earth Sciences University of Ferrara, Via Saragat 1, 44122, Ferrara, Italy*
[c] *Consiglio Nazionale delle Ricerche, Istituto di Geologia Ambientale e Geoingegneria, Rome, Italy*
[d] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, via di Vigna Murata 605, 00143, Rome, Italy*
[e] *Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania*
[f] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Pisa, Via Uguccione della Faggiola 32, 56126, Pisa, Italy*
[g] *HYDRA Marine Sciences GmbH, Burgweg 4, 76547, Sinzheim, Germany*
[h] *HYDRA Field Station, Loc. Fetovaia, 57034, Campo nell'Elba, Italy*
[i] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, via Ugo La Malfa 153, 90146, Palermo, Italy*

ARTICLE INFO

Editorial handling by Prof. M. Kersten

Keywords:
Abiotic methane
Ophiolite
Serpentinization
Submarine seeps
Elba

ABSTRACT

Abiotic methane (CH_4) is today widely reported in gas seeps and hyperalkaline springs in ophiolites and peridotite massifs characterized by low temperature continental serpentinization. Origin and distribution of this gas have far reaching implications in microbiology, astrobiology and carbon cycle. We report an in-depth study of a recently described abiotic CH_4 seep occurring in shallow seafloor along the western coast of Elba Island, Tyrrhenian Sea (Italy). The gas is characterized by stable C and H isotopic compositions of CH_4 ($\delta^{13}C \sim -18‰$; $\delta^{2}H \sim -141‰$) and a very low CO_2 content that are typical of abiotic gas in continental ultramafic rock systems. Based on local geothermal gradients, the temperature of methane production is estimated to be below 100 °C. The isotope signature of methane is similar to that occurring in the Liguria region, about 200 km north of Elba Island, where the same ophiolite unit exposed. A mantle CO_2 component, suggested by relatively high $^3He/^4He$ ratios, has likely acted as CH_4 precursor. The reconstruction of the geological-structural setting of Elba ophiolite sequence highlighted that the seep occurs in correspondence with a faulted reverse limb of the antiform of the ophiolite unit. The gas bearing fault forms a contact between mafic and ultramafic serpentinized rocks, as typically observed in other continental seeps and springs related to ophiolites. Magmatic intrusions in the island may have contributed to the C feedstock of methane.

1. Introduction

Abiotic gas linked to serpentinized ultramafic rock systems on continents has been detected in many countries, from North America, Europe, Asia to Oceania (e.g., Abrajano et al., 1990; Sano et al., 1993; Boschetti et al., 2013; Boulart et al., 2013; D'Alessandro et al., 2018; Etiope, 2017; Etiope and Schoell, 2014; Etiope et al., 2017; Vacquand et al., 2018). The gas is typically characterized by high concentrations of methane (CH_4, often > 80 vol%), variable amounts of hydrogen (H_2) and C_{2+} alkanes (ethane, propane, butane) and a typical combination of stable C and H isotope composition of CH_4, which only partially overlaps biotic (thermogenic) gas (Etiope et al., 2017; Etiope and Sherwood Lollar, 2013). This type of methane has a key importance in microbiological and astrobiological studies, as it may be an energy source (electron donor), together with H_2, for prebiotic chemistry and origin of life related to serpentinization, on Earth and other planets, (Russell et al., 2010; Oehler and Etiope, 2017). Peridotite gas seeps are a source of methane for the atmosphere, not yet accounted for in global estimates of geological gas emissions (Etiope et al., 2011, 2017).

A wide literature is available on the origin and molecular-isotopic composition of this gas (e.g., Abrajano et al., 1990; Sano et al., 1993; Etiope et al., 2011; D'Alessandro et al., 2018; Boulart et al., 2013; Deville and Prinzhofer, 2016). A major feature that is common in all these studies concerns the apparent low temperature of the geological system where methane was produced, i.e. within the ophiolite nappe or peridotite massif. Clumped-isotope and geological data suggest that this

---

[*] Corresponding author. Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 1, via di Vigna Murata 605, 00143, Rome, Italy.
E-mail address: alessandra.sciarra@ingv.it (A. Sciarra).

https://doi.org/10.1016/j.apgeochem.2018.10.025
Received 4 October 2018; Received in revised form 30 October 2018; Accepted 31 October 2018

methane is typically produced at temperatures below 150 °C (Young et al., 2016; Etiope et al., 2017). These seeps, in fact, are not related to volcanic or geothermal systems. The gas production temperatures are also lower than analogue serpentinization-related seeps documented in mid-ocean ridges (Wang et al., 2018). Furthermore, the seeps occur along faults at the boundary of the ultramafic units, often in contact with sedimentary and C-bearing rocks (e.g., limestones), and in proximity of chromitite and rocks containing Platinum Group Element (PGE), which may be a source of metal catalysts necessary for the abiotic CH_4 synthesis (i.e. catalyzed Fischer-Tropsch Type reactions or CO_2 hydrogenation; $4H_2 + CO_2 = CH_4 + 2H_2O$; Etiope and Sherwood Lollar, 2013; McCollom, 2013; Etiope et al., 2017). A recent study indicated that the abiotic gas is likely produced within PGE-bearing chromitites of the ultramafic sequence (Etiope et al., 2018). The associated serpentinization, from which H_2 can originate, is typically continental, driven by meteoric water (e.g., Bruni et al., 2002; Boulart et al., 2013; Chavagnac et al., 2013).

Here, we report a further study on recently described (Meister et al., 2018) abiotic methane seeps from an ophiolite located on the shallow seafloor along the western coast of Elba Island (Tuscan Archipelago, Tyrrhenian Sea, Italy). Free gas, not associated with water springs, is emitted in a series of bubble plumes from seabed about 12 m deep. These seeps were preliminary documented by Ruff et al. (2016), who described the methane-rich character of the gas and the microbial consortia responsible for anaerobic oxidation of methane (AOM). The objective of this work is to better define the origin of the gas, its relationship with regional heat flow, and to assess relationships between the seepage, petrology and geological-structural setting of the area. Accordingly, we performed (a) geochemical analyses of the gas, including molecular composition, and CH_4 and He isotopic ratios in six seepage points; (b) petrographic analysis of the rock hosting the seep and (c) a detailed geological-structural analysis of the seepage zone. We also compared the geochemical and geological data of the Elba seeps with those of the nearest abiotic gas seepage site, located in the Liguria region (Bruni et al., 2002; Cipolli et al., 2004; Boschetti et al., 2013; Boulart et al., 2013).

2. Geological setting

2.1. General geological, structural and petrographic features

The Island of Elba, located in the westernmost portion of the northern Cenozoic Apennine belt (Fig. 1), is formed by metamorphic and non-metamorphic units derived from oceanic (i.e. Ligurian Domain) and continental (i.e. the Tuscan Domain) domains stacked toward NE during the Miocene (Massa et al., 2017 and references therein). The nappe stacking was followed by the emplacement of Late Miocene magmatic bodies, the Central Elba Sill Complex and the Monte Capanne pluton in western Elba (8–7 Ma; Dini et al., 2002; Barboni and Schoene, 2014; Barboni et al., 2015) and the Porto Azzurro pluton (5.9–6.7 Ma; Musumeci et al., 2015) in eastern Elba.

Offshore, west of the Island of Elba, magnetic and gravimetric data suggest the occurrence of N-S trending ridges that, for the very high magnetic susceptibility, have been interpreted as serpentinites, associated with other ophiolitic rocks (Eriksson and Savelli, 1989; Cassano et al., 2001; Caratori Tontini et al., 2004).

The ophiolite sequences in western Elba are classically interpreted as a well-exposed ocean-floor section emplaced during the Apennine's orogeny at the top of the tectonic nappe stack. Stratigraphic, petrological and geochemical features indicate that these ophiolite sequences are remnants of a slow-ultraslow spreading oceanic lithosphere analogous to the present-day Mid-Atlantic Ridge (particularly to its northern section, Gakkel ridge, Dick et al., 2003; Boschi et al., 2006; Snow and Edmond, 2007; Ildefonse et al., 2007; Piccardo, 2008; Miranda and Dilek, 2010; Silantyev et al., 2011); and Southwest Indian Ridge (Saccani and Principi, 2016; Frassi et al., 2017).

The western area of the island, in proximity of the seepage area, is characterized by a monzogranite intrusive body, the Monte Capanne pluton, emplaced into the upper thrust complexes (Musumeci et al., 2015). The host rocks consist of a metamorphic aureole developed at the expense of the ophiolite. The ophiolite consists of mafic (gabbro, basalt) and ultramafic (peridotites, serpentinite) rocks alternating with shales, marls and limestones, from the Jurassic to the Paleogene (Bortolotti et al., 2001). Principi et al. (2004) noted a remarkable similarity between the Elba ophiolite and the ophiolite of Bracco in the Liguria region, suggesting that they belong to the same tectonic Vara group.

The ultramafic units of Elba (peridotites and serpentinites) are generally markedly fractured and weathered, and experienced contact metamorphism in response to the emplacement of the Monte Capanne pluton. The metamorphism resulted in a local development of olivine, talc, amphibole (actinolite and anthophyllite) and chlorite (Barnes et al., 2006). In this case, olivine recrystallized from serpentine in clear, well-shaped and iso-oriented neoblastic grains, often containing euhedral inclusions of magnetite. Otherwise, olivine is present as a relic, showing strong fracturing and with a high content of forsteritic components. Anthophyllite is only found in strongly thermometamorphosed rocks. Here, mm-sized anthophyllite crystals have statically grown on the original serpentine mesh structure and large fanned bunches trap prograde olivine and the strongly zoned spinel (Frassi et al., 2017). Talc appears in aggregates or in veins of minute iso-oriented scales and chlorites, showing a fibrous appearance, and is frequently found around corroded spinel grains or across fractures. Spinel grains have different sizes, but they not exceed a few millimetres, and show an irregular and slightly lobate shape. They appear fractured, crossed by veins of magnetite, serpentine and/or chlorite and frequently with a magnetitic rim.

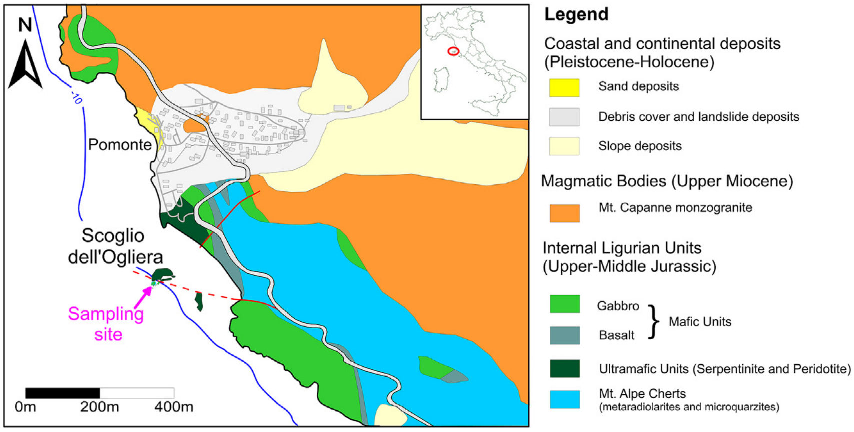

Fig. 1. Location and simplified geological map of Pomonte-Ogliera area (western part of Elba Island) with special attention to the Internal Ligurian Units that host mafic and ultramafic rocks. Modified from Principi et al. (2015). Red line indicates fault lineaments and the inferred fault (dashed red line). Blue line indicates bathymetric level of the seafloor, and magenta arrow the location of sampling site at 12 m asl. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

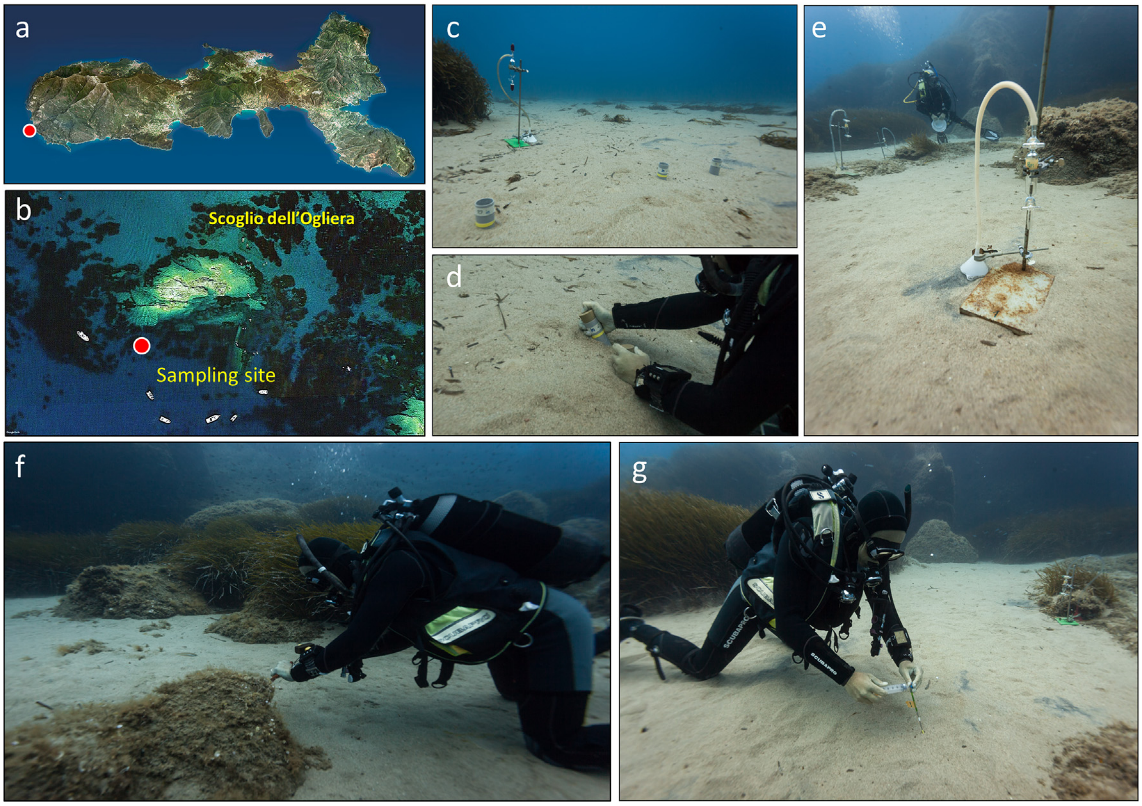

Fig. 2. Pictures of the sampling sites. (a) Elba Island image (Google Earth) with the location of the study area (red dot), Lat N 42°51′12,50"; Long E 10°25′6,48"; (b) Scoglio dell'Ogliera detail with the location of the sampling site (red dot); (c, d) detail of bubbling and sediment sampling; (e, f, g) details of bubbling gas, rock and pore-water sampling by SCUBA diving. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Apart from strongly recrystallized rocks, serpentine is often the main component and it is mostly present in the lizardite variety accompanied by chrysotile in veins. Orthopyroxene is not often present and serpentinization has almost obliterated the original optic characteristics (e.g., bastite). The observable ones are attributed to enstatitic composition. It is found as a thick prismatic structure in which there are evident traces of cleavage sometimes marked by oxide exsolutions and sometimes curved due to tectonic stress. Clinopyroxene relics often show tremolite alteration rims and in thermometamorphosed rocks it is present as small neoblastic diopside crystals (Gianfagna et al., 1992; Barnes et al., 2006). Serpentine, in assemblage with amphibole, is also present in fine-grained dikes that crosscut metagabbros (Barnes et al., 2006).

The heat flow at the western sector of Elba Island is relatively low, 80–100 mW/m^2 (Della Vedova et al., 2001; Verdoya et al., 2005), equivalent to about 40–50 °C/km local gradient (Cataldi et al., 1998).

2.2. Description of the seep

The gas seeps are located 230 m from the western coast of the island, near the village of Pomonte, at a depth of about 12 m, near the islet Scoglio dell'Ogliera (Figs. 1 and 2). The seafloor is composed of medium-grained sand with sporadic rock outcrops (mainly gabbro) and scattered seagrass meadows (*Posidonia oceanica*). During our field campaign gas was emitted from 6 major seepage spots spread over an area of about 500 m^2. Seep-related macrofaunal assemblages are lacking but filamentous mats of sulfur-oxidizing bacteria are often visible near the seepage spots (Ruff et al., 2016), probably indicating areas of sediment influenced by lower gas fluxes or diffuse non-bubbling seepage. A detailed site description is found in Meister et al. (2018). Wiedling (2010) estimated the areal gas flow to 3 $L\,h^{-1}$ of eight bubble streams within an area of 100 m^2, or 0.72 $L\,m^{-2}{\cdot}d^{-1}$.

3. Methods

3.1. Gas sampling

Gas samples were collected from bubble plumes in June 2017 by SCUBA diving (Fig. 2) using an inverted funnel placed at the bottom of the seafloor. Samples were stored, following water displacement, in 100 mL two-valve glass tubes. Permanent gases (He, H_2, O_2, N_2, CO, CH_4 and CO_2) were measured by means of a gas chromatograph (GC, Agilent 7890 equipped with PPU and MS5A columns) associated with a MicroGC module (equipped with a PPU column) and a double detector (TCD and FID) using argon as carrier gas. Higher hydrocarbons (C_2-C_5) were analysed using a Shimadzu 2010 GC equipped with FID and a capillary CP Poraplot column using helium as carrier gas. Analytical precision for GC analyses is better than ± 5% for trace gases and ± 10% for alkanes. Stable carbon and hydrogen isotope compositions of CH_4 and CO_2 were measured using a Delta Plus XP IRMS equipped with a Thermo TRACE GC interfaced with Thermo GC/C III and Thermo GC/TC. $^{13}C/^{12}C$ ratios are reported as $\delta^{13}C$ values ($1\ \sigma = 0.1‰$) against VPDB standard and $^{2}H/^{1}H$ ratios are reported as $\delta^{2}H$ values ($1\sigma = 1‰$) against VSMOW standard. Helium isotope composition (expressed as R/Ra, which is $^{3}He/^{4}He$ of the sample versus the same $^{3}He/^{4}He$ ratio in atmosphere, $Ra = 1.386 \times 10^{-6}$) and ^{20}Ne content were analysed by a GVI Helix SFT mass spectrometer.

3.2. Water, sediment and rock sampling and analysis

Six water samples (three inside and three outside the seepage zone as control samples) and six sediment samples around the bubble plumes were taken to verify whether the seepage includes water (e.g., hyperalkaline water with $pH > 8$, as generally occurs in serpentinite-hosted gas manifestations). Temperature, pH and electro-conductivity (EC) of

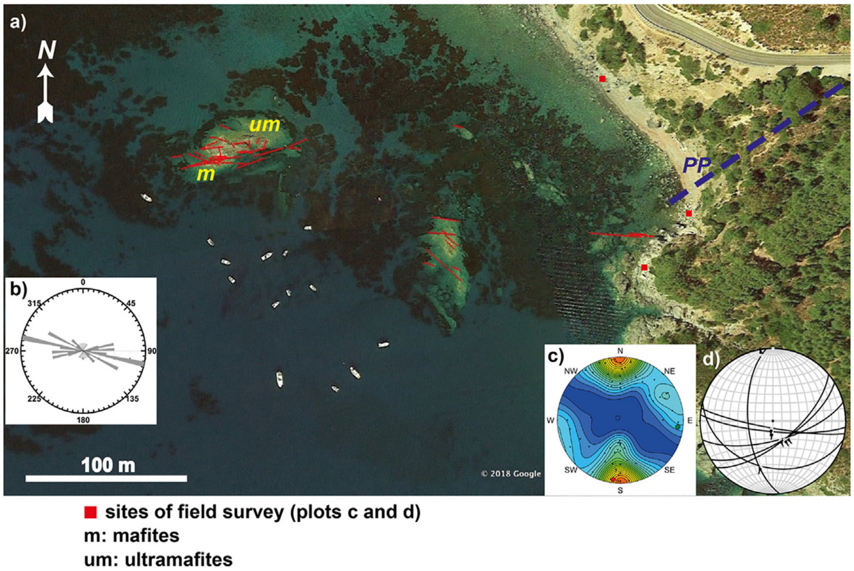

Fig. 3. Geological-structural setting of Scoglio dell'Ogliera. (a) Map of main structural features, red lines: lineaments by satellite image interpretation. Red squares are the sites of field survey, dashed, thick blue line is the morphostructure lineament PP as in Dini et al. (2008). (b) Rose diagram of azimuth distribution of lineaments. (c) Stereonet (lower hemisphere) of main fractures with contours (maximum class > 21 measures). (d) Stereonet (lower hemisphere) of main faults with associated kinematic indicators (arrows). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

water samples were measured on boat by using EUTECH portable Instruments.

Sediment samples were taken using PVC cores driven to a depth of about 20 cm into the sediments by hand, and closed by rubber stoppers. pH and electrical conductivity (EC) of pore-water were measured after a soil-water extraction following a routine protocol (Di Bonito et al., 2008).

Two rock samples were taken with a hammer from an outcrop at the seabed nearby the emission site. Thin sections were prepared and analysed by a polarization microscope to determine the modal percentage of the minerals and define the rock type.

3.3. Geological and structural analysis

A geological field survey was performed along the western coast of Elba Island, around the Monte Capanne pluton, and at the Scoglio dell'Ogliera in order to map in detail the brittle structures (fault and fractures) affecting the mafic and ultramafic rocks in the studied area for comparison with mapped lineaments acquired by analysis of satellite image (Fig. 3). Fracture and fault attitude along with kinematic indicators (slickensides) have been collected to perform fault inversion analysis to derive the possible stress field in the area coherent with the brittle structures (FaultKin software, Marrett and Allmendinger, 1990). Fractures and fault indicate a local N-S extension (trend and plunge of computed σ_3: 187°/3°) affecting the whole inverse ophiolitic sequence.

4. Results

4.1. Gas chemistry

All gas samples collected in the six seeps are enriched in methane, with concentrations between 82.4 and 86.2 vol%. Other gases include nitrogen (up to 16 vol%), carbon dioxide (from 0.09 to 1.48 vol%), ethane (0.049–0.062 vol%), hydrogen (up to 0.0004 vol%) and helium (up to 0.0385 vol%) (Table 1). The isotopic composition of CH_4 varies in a narrow range, from −135 to −143‰ VSMOW for δ^2H-CH_4 and from −18 to −19‰ VPDB for δ^{13}C-CH_4. CO_2 is relatively ^{13}C-depleted (δ^{13}C-CO_2 from −6.95 to −12.42‰), compared to mantle or thermo-metamorphic origin (δ^{13}C-CO_2 from −8 to 0‰ VPDB; Javoy et al., 1986). The helium isotope ratio, ^{3}He/^{4}He, ranges from 0.87 to 0.93 Ra_c.

4.2. Chemico-physical features of seawater and sediment pore-water

Electro-conductivity and pH of the seawater samples at the bubble plumes was 55.1 mS/cm and 7.8, respectively, while values of pore-water samples at the bubbling area were ranging from 19.5 to 28.7 mS/cm, for EC, and from 8.28 to 8.38, for pH. These values are similar to those of seawater and pore-water at the control sites outside the seepage zone (EC, 24.3–28.2 mS/cm; pH, 8.27–8.34), which confirms that there is no hyperalkaline water discharge at the bubbling sites and only gas is released from the seep, as preliminary reported by Ruff et al. (2016).

4.3. Petrographic features of the rock at the seep site

The sampled rock at the seep site is mostly constituted by coarse-grained quite altered gabbros. The microscopic analyses of the two rock samples reveal that the rock is mainly constituted by clinopyroxene of medium to fine grain size, often altered into tremolite. These millimetre-sized crystals seem to be arranged along a preferred orientation and are surrounded by a groundmass of plagioclase (about 60 vol%). Most of the plagioclases are highly altered in sericitic products, or epidote and are allotriomorphic in shape. In very few specimens it is still recognizable Albite and Carlsbad twinning. Opaque minerals are also present, mainly magnetites produced by the serpentinization of olivine. Calcite, chlorite and quartz are widespread both interstitial and

Table 1
Chemical and isotopic composition of gas sampled in the Scoglio dell'Ogliera seeps site.

ID	He ppmv	H_2 ppmv	N_2 vol%	CH_4 vol%	CO_2 vol%	C_2H_6 vol%	$\delta^{13}C_{CO2}$ VPDB	$\delta^{13}C_{CH4}$ VPDB	$\delta^{2}H_{CH4}$ SMOW	R/Ra_c	He/Ne
POM 1	383	4.3	13.9	85.9	0.09	0.049	−8.5	−18.3	−141	0.92	768.3
POM 2	354	2.1	14.4	85.2	0.25	0.061	−11.15	−18.6	−142	0.89	2404.7
POM 3	385	4.2	16.0	82.4	1.48	0.057	−6.95	−18.0	−135	0.88	193.1
POM 5	346	1.0	14.5	85.3	0.14	0.062	−12.42	−19.0	−142	0.87	1994.7
POM 6	316	4.1	13.5	86.2	0.16	0.049	−17.6	−18.4	−143	0.93	986.6

Propane (C_3H_8) and CO are below detection limits in all samples.

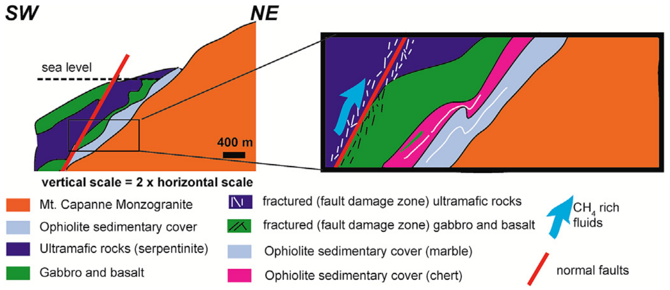

Fig. 4. Reconstruction of the Elba ophiolite geometry and faulting at the seepage site. The reverse limb of the antiform in the host is dissected by normal faulting that brings ultramafic rocks (deep blue) into contact with mafic intrusives (gabbro, green). Inset: an expanded view of the fault zone from ultramafic rocks in the hanging wall to the granite in the footwall of the fault and more detail in the structure of the ophiolite sedimentary sequence (marble and cherts) where asymmetric folds (white lines) and gabbro dikes occur. Damage and fault core are the preferred pathways gas release. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

in veins, due to the presence of strong fracturing.

4.4. *Geological and structural reconstruction*

In the southwestern side of Monte Capanne, adjacent to the seepage zone, the granite pluton is hosted by preserved HT-LP methamorphic rocks (hornefels, calcschist, marble and quartzite) representing the former sedimentary cover of the ophiolitic mafic and ultramafic rocks, i.e. basalt, gabbro and peridotite. The contact between the host rocks and the granite dips toward west and southwest of about 45–50° and the ophiolitic sequence is cut by ENE-WSW and NNW-SSE normal faults associated with E-W to ENE-WSW fractures. The E-W trending faults and fractures system continues offshore up to the Scoglio dell'Ogliera where the ultramafites (serpentinites) of the reverse limb are in contact by fault with gabbro (Fig. 3). The ophiolite sequence appears to be the reverse limb of a northeast verging antiform (with ultramafic rocks at its nucleus; Fig. 4). The seepage occurs just in correspondence with the reverse limb, which is faulted and fractured at the contact between ultramafic and mafic rocks. Clearly, the gas found its migration pathway along this faulted contact. Considering that, (a) the estimated pluton thickness is about 3 km (Dini et al., 2008), (b) the pluton emplacement level is within the Ligurian units, (c) the actual thickness of exposed reverse limb in Elba is about 1.5 km (Fig. 1) and (d) large bodies of ultramafic rocks occur southwards offshore, as evidenced by magnetic anomalies (Eriksson and Savelli, 1989), we estimate that the thickness of the Elba ophiolitic sequence does not exceed 1–1.5 km.

5. Discussion and conclusions

5.1. *CH_4 origin*

The combined stable C and H isotope composition of CH_4 ($\delta^{13}C$ and δ^2H) of the Elba gas seep is within the range typically observed in ophiolite and peridotite massifs (Fig. 5; Etiope, 2017). This type of methane is considered to have a dominant abiotic origin, related to Fischer-Tropsch Type reaction (Sabatier reaction; e.g., Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014), with variable, generally minor, biotic components. Ethane, frequently observed in continental serpentinized systems, is considered to be abiotically originated via methane polymerization (e.g., Sherwood Lollar et al., 2008; Etiope and Sherwood Lollar, 2013). The presence of minor microbial CH_4 components, as observed in similar cases (e.g. Etiope et al., 2017; Miller et al., 2016) cannot be excluded.

The H_2 concentration is relatively low, in analogy with other continental serpentinization sites, such as Ronda in Spain, Othrys in Greece (Etiope et al., 2013, 2016) and, in particular, Genova in Liguria (Boschetti et al., 2013), located only 200 km north of Elba Island. The paucity of H_2 in seeps related to serpentinization could be due to complete H_2 consumption by CO_2 reduction in a limited H_2 production system (due, for example by an increase of the silica activity) and/or microbial consumption (e.g., Boulart et al., 2013; Etiope et al., 2013).

The Elba seep appears to release only a gas-phase, without water emission. In serpentinized ophiolites or peridotite massifs the water, bearing the gas, is typically hyperalkaline, with $pH > 9$ (Etiope, 2017). Our analyses of the seawater and sediment pore-water at the seep site did not reveal any sign of such alkalinity. The Elba gas seepage system is therefore analogue to the prevailing gas-phase discharge systems of Chimaera (Turkey; Etiope et al., 2011), Kurtbagi (Turkey; D'Alessandro et al., 2018) or Los Fuegos Eternos at Zambales (Philippines; Abrajano et al., 1990). This is also confirmed by the combined stable C and H isotope composition of CH_4 ($\delta^{13}C$ and δ^2H), which is close to that of the other gas-phase vents (Fig. 5). Such a gas-phase venting group has ^2H-enriched CH_4 compared to CH_4 dissolved in hyperalkaline waters (e.g., Oman, Bosnia, Spain, Portugal), where CH_4 and H_2O may have more extensively interacted (but not necessarily attaining isotopic equilibrium; Etiope et al., 2017). However, the δ^2H-CH_4 values depend also on the original isotopic composition of H_2 and isotopic fractionations during Sabatier reactions (Whiticar and Etiope, 2014). The CH_4 of Elba is not very dissimilar from the gas of Genova springs (Italy; Boschetti et al., 2013). Actually, Elba and Eastern Liguria ophiolites have many similarities as they are considered to belong to the same tectonic Vara Group (Principi et al., 2004). In particular, the Ligurian Bracco ophiolite hosts cromitites rich in Platinum Group Elements, including ruthenium (Ru) (Baumgartner et al., 2013). Chromitites or chromite-rich lenses are not outcropping on Elba Island but, given their presence in the Vara Group, they likely occur at depth, within the submersed ultramafic unit offshore, as depicted in Fig. 4. It is worth noting that PGE-rich rocks also occur in the Monte Maggiore ophiolite in the Corsica Island, just 60 km east of Elba (Ohnenstetter, 1992). Ru-bearing chromitites may represent the source rocks of abiotic methane, as recently observed in Greece (Etiope et al., 2018). The hypotheses for a CH_4 source from fluid inclusions in the mafic-ultramafic rocks, as proposed by Wang et al. (2018) for submarine hot springs, is unlikely in the case of continental ophiolite systems such as Elba, where the gas formation temperatures are quite low (as discussed in detail below) and this is inconsistent with post-magmatic high temperature processes related to fluid inclusion formation.

5.2. *Origin of other gases*

The low amounts of CO_2 as those found in the Elba seep bubbles are quite common in other gas seeps from ophiolites (e.g., Abrajano et al., 1990; D'Alessandro et al., 2018; Etiope et al., 2017). The low CO_2 concentrations in these settings are generally due to its consumption for CH_4 production via Sabatier reaction, and to the hyperalkaline conditions of water, where the main C form is HCO_3^-. Although hyperalkaline water is not discharged in the Elba seep, it could exist in the subsurface as an effect of serpentinization, as observed in other peridotite settings, including the Ligurian site (Bruni et al., 2002; Cipolli et al., 2004). The concentrations of helium up to 350 ppmv are, however, higher than those expected (a few ppmv) in non-sedimentary settings. Such an enrichment could suggest a chemical fractionation induced by partial dissolution of CO_2 in water. In fact, since CO_2 is highly soluble in water, a marked gas-water interaction, under favorable conditions, may lead the residual gas phase being progressively enriched in less soluble species (such as N_2, CH_4 and He) as CO_2 dissolution proceeds. The same dissolution process could also be responsible for ^{13}C-depletion of the $\delta^{13}C_{CO2}$ with respect to a deep inorganic CO_2 originated from the mantle with $\delta^{13}C$ values from -8 to 0‰ (Javoy et al., 1986) or from a thermo-metamorphic reaction

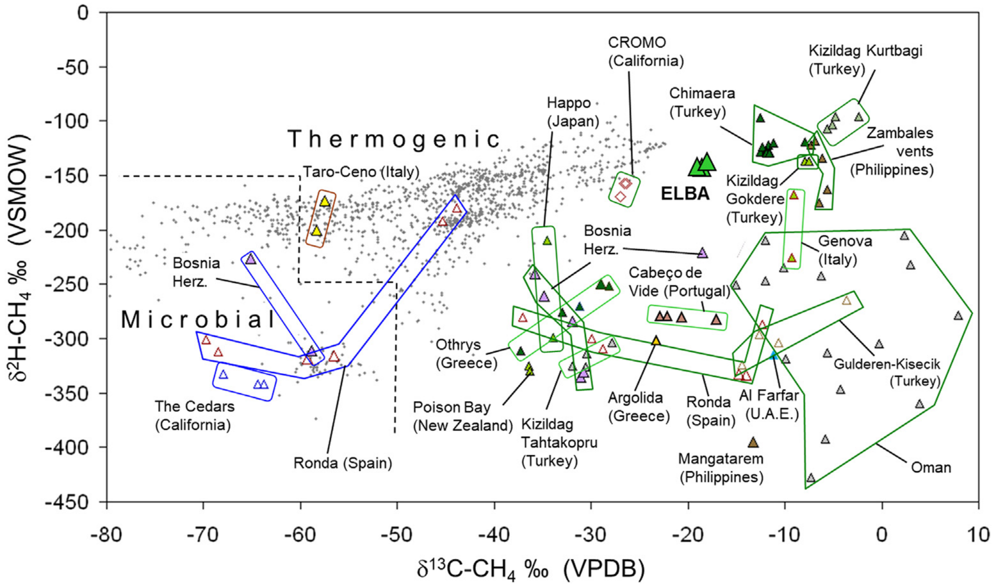

Fig. 5. $\delta^{13}C$ vs $\delta^{2}H$ diagram of methane in the Elba samples compared to abiotic methane from other continental serpentinized ultramafic rocks. Grey points refer to biotic (microbial and thermogenic) gas in sedimentary basins (from Etiope, 2017; Etiope et al., 2017 and references therein, with additional data from Vacquand et al., 2018).

involving carbonate rocks with $\delta^{13}C$ values from −1 to +2‰ (Faure, 1986).

Atmospheric helium can be considered negligible as indicated by $^{4}He/^{20}Ne$ ratios generally ranging from 193 to 2404 (Table 1), exceeding the atmospheric air ratio (0.318) and air-saturated water ratio (ASW 0.24). Therefore, the helium in the Elba ophiolitic gas seeps can be a two-component mixture between crustal and mantle helium. A simple mass balance calculation allowed to estimate the mantle-derived helium contribution in the range between 10 and 15% assuming as representative of the mantle beneath Elba Island a typical MORB composition (R/Ra = 8; Kurz et al., 1982). The mantle-derived component increases up to about 30% if we assume the deep endmember having a composition similar to the Larderello geothermal field (R/Ra = 3.2; Gherardi et al., 2005). Therefore, a mantle-derived ^{3}He-rich component is present in the ophiolitic seeps offshore Elba Island.

Another possible explanation for the high helium concentrations is that the noble gas derives from remnant magmatic sources in the mantle rocks, as suggested for ophiolitic gases in the Philippines (Abrajano et al., 1990) and Oman (Sano et al., 1993). In this respect, we recall that the Monte Capanne pluton at the western sector of Elba Island (described in section 2.1) may play an important role, representing a potential additional source of remnant magmatic helium. Furthermore evaluation on CO_2 origin based on $CO_2/^{3}He$ ratios (e.g., Marty and Jambon, 1987) cannot be indicative as CO_2 in the seep is likely residual from abiotic methanation processes, as discussed above.

5.3. *Relationships among gas origin, seepage and local geology*

It is generally observed that gas seeps and springs in ophiolites or peridotite massifs occur along a fault bordering or cutting the ultramafic rocks (e.g., Etiope et al., 2017). Our geological and structural reconstruction of the seepage area revealed that the Elba seep is actually along a fault at the contact between mafic and ultramafic rocks. At the seepage site the ophiolite sequence appears to be folded, with ultramafic rocks continuing at depth towards offshore. Considering that the ophiolite nappe has likely a maximum thickness of about 1.5 km and the local geothermal gradient is 40–50 °C/km, we estimate that the maximum temperature at the base of the ophiolite is about 60–80 °C. These temperatures are also confirmed from two deep exploration wells, located ~30 km south and ~50 km north of the Scoglio dell'Ogliera (Martina 001 and Maria 001 exploratory wells drilled in 1975), with measured temperatures of 93 °C at 2900 m of depth and ~57 °C at 2000 m of depth, respectively (ViDEPI, 2009–2018). The low temperature of methane production is consistent with the temperatures generally estimated in other continental serpentinization sites with abiotic methane, also based on CH_4 clumped-isotope analyses (Young et al., 2016). The lack of considerable CO_2 degassing confirms that the area is not affected by active geothermal circulation systems, as in the onshore Tuscan region, but magmatic intrusions (e.g. Monte Capanne pluton) may have contributed to a mantle C feedstock. Clumped-isotope CH_4 analyses of Elba gas shall however be performed to define more exactly the gas formation temperature.

Acknowledgments

This work is a contribution to the Deep Energy Community of the Deep Carbon Observatory. We are thankful to Johanna Wiedling and Andreas Eich from the HYDRA team for their assistance during field work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.10.025.

References

Abrajano, T.A., Sturchio, N.C., Kennedy, B.M., Lyon, G.L., Muehlenbachs, K., Bohlke, J.K., 1990. Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. Appl. Geochem. 5, 625–630.

Barboni, M., Schoene, B., 2014. Short eruption window revealed by absolute crystal growth rates in a granitic magma. Nat. Geosci. 7, 524–528.

Barboni, M., Annen, C., Schoene, B., 2015. Evaluating the construction and evolution of upper crustal magma reservoirs with coupled U/Pb zircon geochronology and thermal modeling: a case study from the Mt. Capanne pluton (Elba, Italy). Earth Planet Sci. Lett. 432, 436–448. https://doi.org/10.1016/j.epsl.2015.09.043.

Barnes, J.D., Selverstone, J., Sharp, Z.D., 2006. Chlorine isotope chemistry of serpentinites from Elba, Italy, as an indicator of fluid source and subsequent tectonic history. G-cubed 7, Q08015. https://doi.org/10.1029/2006GC001296.

Baumgartner, R.J., Zaccarini, F., Garuti, G., Thalhammer, O.A.R., 2013. Mineralogical and geochemical investigation of layered chromitites from the Bracco-Gabbro complex, Ligurian ophiolite, Italy. Contribut. Mineral. Petrol. 165, 477–493.

Bortolotti, V., Fazzuoli, M., Pandeli, E., Principi, G., Babbini, A., Corti, S., 2001. Geology of central and eastern Elba island, Italy. Ofioliti 26, 97–150.

Boschetti, T., Etiope, G., Toscani, L., 2013. Abiotic methane in the hyperalkaline springs of Genova. Italy. Procedia Earth Plan. Sci. 7, 248–251.

Boschi, C., Fruh-Green, G.L., Delacour, A., Karson, J.A., Kelley, D.S., 2006. Mass transfer and fluid during detachment faulting and development of an oceanic core complex, Atlantis Massif (MAR 30°N). G-cubed 7, Q01004. https://doi.org/10.1029/2005GC001074.

Boulart, C., Chavagnac, V., Monnin, C., Delacourt, A., Ceuleneer, G., Hoareau, G., 2013. Difference in gas venting from ultramafic-hosted warm springs: the example of Oman and Voltri ophiolites. Ofioliti 38, 143–156.

Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., Marini, L., Ottonello, G., Zuccolini, M.V., 2002. Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg-HCO_3 and high-pH, Ca-OH spring waters of the Genova province, Italy. Appl. Geochem. 17, 455–474. https://doi.org/10.1016/S0883-2927(01)00113-5.

Caratori Tontini, F., Stefanelli, P., Giori, I., Faggioni, O., Carmisciano, C., 2004. The revised aeromagnetic anomaly map of Italy. Ann. Geophys. 47. https://doi.org/10.4401/ag-3358.

Cassano, E., Anelli, L., Cappelli, V., Giori, I., La Torre, P., 2001. The Island of Elba - northern Tyrrhenian sea aeromagnetic and gravity data. Ofioliti 26, 153–160.

Cataldi, R., Mongelli, F., Squarci, P., Taffi, L., Zito, G., Calore, C., 1988. Geothermal ranking of Italian territory. Geothermics 24, 115–129.

Chavagnac, V., Monnin, C., Ceuleneer, G., Boulart, C., Hoareau, G., 2013. Characterization of hyperalkaline fluids produced by low-temperature serpentinization of mantle peridotites in the Oman and Liguria ophiolites. G-cubed 14, 2496–2522. https://doi.org/10.1002/ggge.20147.

Cipolli, F., Gambardella, B., Marini, L., Ottonello, G., Vetuschi Zuccolini, M., 2004. Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modelling of CO_2 sequestration in serpentinite aquifers. Appl. Geochem. 19, 787–802.

D'Alessandro, W., Yüce, G., Italiano, F., Bellomo, S., Gülbay, A.H., Yasin, D.U., Gagliano, A.L., 2018. Large compositional differences in the gases released from the Kizildag ophiolitic body (Turkey): evidences of prevailingly abiogenic origin. Mar. Petrol. Geol. 89, 174–184.

Della Vedova, B., Bellani, S., Pellis, G., Squarci, P., 2001. Deep temperatures and surface heat flow distribution. In: Vai, G.B., Martini, L.P. (Eds.), Anatomy of an Orogen: the Apennines and Adjacent Mediterranean Basins. Kluwer Academic Publishers, pp. 65–76.

Deville, E., Prinzhofer, A., 2016. The origin of N_2-H_2-CH_4-rich natural gas seepages in ophiolitic context: a major and noble gases study of fluid seepages in New Caledonia. Chem. Geol. 440, 139–147.

Di Bonito, M., Breward, N., Crout, N., Smith, B., Young, S., 2008. Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils: operational and technical aspects. In: Book: Environmental Geochemistry, Site Characterization, Data Analysis and Case Histories, Chapter Ten, pp. 213–249. https://doi.org/10.1016/B978-0-444-53159-9.00010-3.

Dick, H.J.B., Lin, J., Schouten, H., 2003. An ultraslow-spreading class of ocean ridge. Nature 426, 405–412.

Dini, A., Innocenti, F., Rocchi, S., Tonarini, S., Westerman, D.S., 2002. The magmatic evolution of the late Miocene laccolith-pluton-dyke granitic complex of Elba Island, Italy. Geol. Mag. 139, 257–279.

Dini, A., Westerman, D.S., Innocenti, F., Rocchi, S., 2008. Magma emplacement in a transfer zone: the Miocene mafic Orano dyke swarm of Elba Island, Tuscany, Italy. In: In: Thomson, K., Petford, N. (Eds.), Structure and Emplacement of High-level Magmatic Systems, vol. 302. Geological Society, London, Special Publications, pp. 131148 (1)10.1144SP302.10.

Eriksson, L., Savelli, C., 1989. Magnetic anomalies and magmatic events in and around the island of Elba (Northern Tyrrhenian Sea). In: In: Makris, J. (Ed.), Geological Aspects and Tectonic Evolution of Mediterranean Seas, vol. 87. Mar. Geol, pp. 85–93.

Etiope, G., 2017. Abiotic methane in continental serpentinization sites: an overview. Procedia Earth Planet. Sci. 17, 9–12.

Etiope, G., Schoell, M., 2014. Abiotic gas: atypical but not rare. Elements 10, 291–296.

Etiope, G., Sherwood Lollar, B., 2013. Abiotic methane on Earth. Rev. Geophys. 51, 276–299.

Etiope, G., Schoell, M., Hosgormez, H., 2011. Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. Earth Planet Sci. Lett. 310, 96–104.

Etiope, G., Tsikouras, B., Kordella, S., Ifandi, E., Christodoulou, D., Papatheodorou, G., 2013. Methane flux and origin in the Othrys ophiolite hyperalkaline springs, Greece. Chem. Geol. 347, 161–174.

Etiope, G., Vadillo, I., Whiticar, M.J., Marques, J.M., Carreira, P.M., Tiago, I., Benavente, J., Jiménez, p., Urresti, B., 2016. Abiotic methane seepage in the Ronda peridotite massif, southern Spain. Appl. Geochem. 66, 101–113.

Etiope, G., Samardžić, N., Grassa, F., Hrvatović, H., Miošić, N., Skopljak, F., 2017. Methane and hydrogen in hyperalkaline groundwaters of the serpentinized Dinaride ophiolite belt, Bosnia and Herzegovina. Appl. Geochem. 84, 286–296.

Etiope, G., Ifandi, E., Nazzari, M., Procesi, M., Tsikouras, B., Ventura, G., Steele, A., Tardini, R., Szatmari, P., 2018. Widespread abiotic methane in chromitites. Sci. Rep. 8, 8728. https://doi.org/10.1038/s41598-018-27082-0.

Faure, G., 1986. Principles of Isotope Geology, second ed. Wiley, New York, pp. 589.

Frassi, C., Musumeci, G., Zucali, M., Mazzarini, F., Rebay, G., Langone, A., 2017. The Cotoncello Shear Zone (Elba Island, Italy): the deep root of fossil oceanic detachment fault in the Ligurian ophiolites. Lithos 278–281, 445–463. https://doi.org/10.1016/j.lithos.2017.02.015.

Gherardi, F., Panichi, C., Gonfiantini, R., Magro, G., Scandiffio, G., 2005. Isotope systematics of C-bearing gas compounds in the geothermal fluids of Larderello, Italy. Geothermics 34, 442–470.

Gianfagna, A., Grubessi, O., Massera, S., 1992. Cr-rich spinel chemistry of the serpentinites from the island of Elba, Tuscany, Italy: note I. Atti Soc. Tosc. Sci. Nat. Mem. 99, 175–194.

Ildefonse, B., Blackman, D.K., John, B.E., Ohara, Y., Miller, D.J., MacLeod, C.J., and the IODP Expedition 304/305 Scientists, 2007. Oceanic core complexes and crustal accretion at slow-spreading ridges. Geology 35 (7), 623–626.

Javoy, M., Pineau, F., Delorme, H., 1986. Carbon and nitrogen isotope in the mantle. Chem. Geol. 57, 41–62.

Kurz, M.D., Jenkins, W.J., Schilling, J.G., Hart, S.R., 1982. Helium isotopic variations in the mantle beneath the central North Atlantic Ocean. Earth Planet Sci. Lett. 58, 1–14.

Marrett, R.A., Allmendinger, R.W., 1990. Kinematic analysis of fault-slip data. J. Struct. Geol. 12, 973–986.

Marty, B., Jambon, A., 1987. C/^{3}He in volatile fluxes from the solid Earth: implication for carbon geodynamics. Earth Planet Sci. Lett. 83, 16–26.

Massa, G., Musumeci, G., Mazzarini, F., Pieruccioni, D., 2017. Coexistence of contractional and extensional tectonics during the northern Apennines orogeny: the late Miocene out-of-sequence thrust in the Elba Island nappe stack. Geol. J. 52, 353–368. https://doi.org/10.1002/gj.2761.

McCollom, T.M., 2013. Laboratory simulations of abiotic hydrocarbon formation in Earth's deep subsurface. Rev. Mineral. Geochem. 75 (1), 467–494.

Meister, P., Wiedling, J., Lott, C., Bach, W., Kuhfuß, H., Wegener, G., Böttcher, M.E., Deusner, C., Lichtschlag, A., Bernasconi, S.M., Weber, M., 2018. Anaerobic methane oxidation inducing carbonate precipitation at abiogenic methane seeps in the Tuscan Archipelago (Italy). PLoS One 13. https://doi.org/10.1371/journal.pone.0207305.

Miller, H.M., Matter, J.M., Kelemen, P., Ellison, E.T., Conrad, M.E., Fierer, N., Ruchala, T., Tominaga, M., Templeton, A.S., 2016. Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and implications for microbial habitability. Geochem. Cosmochim. Acta 179, 217–241.

Miranda, E.A., Dilek, Y., 2010. Oceanic core complex development in modern and ancient oceanic lithosphere: baggro-localized versus peridotite-localized detachment models. J. Geol. 118. https://doi.org/10.1086/648460.

Musumeci, G., Mazzarini, F., Cruden, R., 2015. The Zuccale Fault, Elba Island, Italy: a new perspective from fault architecture. Tectonics 34, 1195–1218. https://doi.org/10.1002/2014TC003809.

Oehler, D., Etiope, G., 2017. Methane seepage on Mars: where to look and why. Astrobiology 17, 1233–1264.

Ohnenstetter, M., 1992. Platinum group element enrichment in the upper mantle peridotites of the Monte Maggiore ophiolitic massif (Corsica, France): mineralogical evidence for ore-fluid metasomatism. Mineral. Petrol. 46, 85–107.

Piccardo, G.B., 2008. The Jurassic Ligurian Tethys, a fossil ultraslow-spreading ocean: the mantle perspective. In: In: Coltorti, M., Grégoire, M. (Eds.), Metasomatism in Oceanic and Continental Lithospheric Mantle. Geol. Soc., vol. 293. Special Publications, London, pp. 11–34.

Principi, G., Bortolotti, V., Chiari, M., Cortesogno, L., Gaggero, L., Marcucci, M., Saccani, E., Treves, B., 2004. The pre-orogenic volcano-sedimentary covers of the western Tethys Oceanic Basin: a review. Ofioliti 29, 177–211.

Principi, G., Bortolotti, V., Pandeli, E., Benvenuti, M., Fanucci, F., Chiari, M., Dini, A., Fazzuoli, M., Menna, F., Moretti, S., Nirta, G., Reale, V., 2015. Note Illustrative Della Carta Geologica D'Italia Alla Scala 1:50.000, Foglio 316, 317, 328, 329. Isola d'Elba. Selca, Firenze.

Ruff, S.E., Kuhfuss, H., Wegener, G., Lott, C., Ramette, A., Wiedling, J., Knittel, K., Weber, M., 2016. Methane seep in shallow-water permeable sediment harbor high diversity of anaerobic methanotrophic communities, Elba, Italy. Front. Microbiol. 7, 374. https://doi.org/10.3389/fmicb.2016.00374.

Russell, M.J., Hall, A.J., Martin, W., 2010. Serpentinization as a source of energy at the origin of life. Geobiology 8, 355–371.

Saccani, E., Principi, G., 2016. Petrological and tectono-magmatic significance of ophiolitic basalts from Elba island within alpine corsica-northern apennine system. Mineria Pet. 110, 713–730. https://doi.org/10.1007/s00710-016-0445-3.

Sano, Y., Urabe, A., Wakita, H., Wushiki, H., 1993. Origin of hydrogen–nitrogen gas seeps, Oman. Appl. Geochem. 8, 1–8.

Sherwood Lollar, B., Lacrmpe-Couloume, G., Voglesonger, K., Onstott, T.C., Pratt, L.M., Slater, G.F., 2008. Isotopic signatures of CH_4 and higher hydrocarbon gases from Precambrian Shield sites: a model for abiogenic polymerization of hydrocarbons. Geochem. Cosmochim. Acta 72, 4778–4795.

Silantyev, S.A., Krasnova, E.A., Bortnikov, N.S., Beltenev, V.E., Kononkova, N.,N., Cannat, M., 2011. Peridotite-gabbro-trondhjemite association of the mid-Atlantic Ridge between 12°58' and 14°45'N: ashadze and logachev hydrothermal vent fields. Translated from Geokhimiya, 2011. Geochem. Int. 49 (4), 339–372. 49(4), 323-354. https://doi.org/10.1134/S0016702911040070.

Snow, J.E., Edmond, H.N., 2007. Ultraslow-spreading ridges:rapid paradigm changes. Oceanography 20, 90–101.

Vacquand, C., Deville, E., Beaumont, V., Guyot, F., Sissmann, O., Pillot, D., Arcilla, C., Prinzhofer, A., 2018. Reduced gas seepages in ophiolitic complexes: evidences for multiple origins of the H_2-CH_4-N_2 gas mixtures. Geochem. Cosmochim. Acta 233, 437–461.

Verdoya, M., Pasquale, V., Chiozzi, P., 2005. Thermo.mechanical evolution and rheology of the northern sector of the Tyrrhenian-Apennines system. J. Volcanol. Geoth. Res. 148, 20–30.

ViDEPI, 2009-2018. Progetto ViDEPI - Visibilità dei dati afferenti all'attività di esplorazione petrolifera in Italia Ministero dello sviluppo economico DGRME. Società Geologica Italiana - Assomineraria. http://unmig.sviluppoeconomico.gov.it/videpi/pozzi/dettaglio.asp?cod=3524.

Wang, D.T., Reeves, E.P., McDermott, J.M., Seewald, J.S., Ono, S., 2018. Clumped isotopologue constraints on the origin of methane at seafloor hot springs. Geochem. Cosmochim. Acta 223, 141–158.

Whiticar, M.J., Etiope, G., 2014. Hydrogen isotope fractionation in land-based serpentinization systems. Comment on “Origin of methane in serpentinite-hosted hydrothermal systems: the CH_4–H_2–H_2O hydrogen isotope systematics of the Hakuba Happo hot spring” by Suda et al. [Earth Planet. Sci. Lett. 386 (2014) 112–125]. Earth Planet Sci. Lett. 401, 373–375.

Wiedling, J., 2010. Biogeochemical Investigations on a Shallow-water Methane Seep in the Mediterranean Sea. Bachelor thesis, Universität Greifswald, Germany.

Young, E.D., Kohl, I.E., Sherwood Lollar, B., Etiope, G., Rumble III, D., Li, S., Haghnegahdar, M.A., Schauble, E.A., McCain, K.A., Foustoukos, D.I., Sutclife, C., Warr, O., Ballentine, C.J., Onstott, T.C., Hosgormez, H., Neubeck, A., Marques, J.M., Pérez-Rodríguez, I., Rowe, A.R., LaRowe, D.E., Magnabosco, C., Yeung, L.Y., Ash, J.L., Bryndzia, L.T., 2017. The relative abundances of resolved $^{12}CH_2D_2$ and $^{13}CH_3D$ and mechanisms controlling isotopic bond ordering in abiotic and biotic methane gases. Geochem. Cosmochim. Acta 203, 235–264.