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Short communication

Methane in serpentinized ultramafic rocks in mainland Portugal

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ABSTRACT

We report a new case of methane (CH_4) of apparent abiotic origin in continental serpentinized ultramafic rocks. Multiple analytical techniques, on-site and in the laboratory, revealed methane and ethane degassing from hyperalkaline (pH > 11) $Ca^{2+}-OH^-$ mineral waters in boreholes drilled in the Alter-do-Chão igneous intrusion, at Cabeço de Vide, in mainland Portugal. The C and H isotopic composition of CH_4 ($\delta^{13}C \sim -20‰$; δ^2H: $-283‰$) suggests a dominant abiotic origin, although minor thermogenic contributions cannot be excluded. Similarly, low methane-to-ethane ratios suggest a predominantly non-microbial source, consistent with previous microbiological data showing the lack of methanogenic archaea in these waters. Heavier hydrocarbons, CO_2 and H_2 are below detection limits. This case study confirms that CH_4 from serpentinized ultramafic rocks can be transported by hyperalkaline fluids linked to deep circulation of meteoric waters. Maximum depth of Cabeço de Vide serpentinized rocks is less than 1 km, and present temperatures are likely lower than 50 °C. Serpentinization and related gas formation may have occurred at any time during thermal evolution of the igneous intrusion, so gas formation temperature cannot be easily determined. This case is an opportunity to test thermometry provided by CH_4 isotopologue analyses. The existence of methane in continental serpentinized igneous rocks is more widespread than previously thought and petroleum systems with similar serpentinized ultramafics in reservoir rocks may have traces of the observed ^{13}C-enriched CH_4.

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1. Introduction

Although natural gas of abiotic origin (i.e., formed by chemical reactions not directly involving organic matter) has never been found in commercial quantities, new field data suggest it may occur regularly in geologic settings with serpentinized (i.e., hydrated) mafic and ultramafic rocks. Considerable amounts of methane (CH_4) of mostly abiotic origin have been typically found in continental igneous rocks, such as ophiolites—ultramafic rocks obducted on continents—where CH_4 is likely produced after serpentinization of peridotite by CO_2 hydrogenation following Fischer—Tropsch Type (FTT) reactions (Abrajano et al., 1988; Fritz et al., 1992; Lyon and Giggenbach, 1994; Etiope et al., 2011b; Suda, 2013; Boschetti et al., 2013; Etiope et al., 2013). In some cases, gases observed in surface manifestations (i.e., seeps, springs) may be mixed with minor amounts of thermogenic or microbial gas.

Mafic (e.g., diorite, gabbro) and ultramafic rocks (e.g., peridotite) with varying degrees of serpentinization can act as hydrocarbon reservoirs in atypical and deep petroleum systems (Farooqui et al., 2009; Schutter, 2003, and references therein). The permeability of peridotites is comparable to that of shales, but serpentinization induces secondary permeability via expansion and fracturing (Macdonald and Fyfe, 1985; O'Hanley, 1992). Serpentinized rocks, for example, form competent reservoirs for many oil fields in Texas and Cuba (Smith et al., 2005). Therefore, it is possible that abiotic gas may contribute in a subsidiary way to hydrocarbon pools in serpentinized igneous reservoir rocks (Szatmari, 1989; Sherwood Lollar et al., 2002; Szatmari et al., 2011). Serpentinized olivine-rich rocks also occur on Mars (e.g., Ehlmann et al., 2009; Michalski et al., 2013), which may imply an abiotic source of CH_4 to

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the Martian atmosphere (e.g., Etiope et al., 2012, and references therein).

Here we report the discovery of a new case of methane in continental serpentinized rocks. The gas has been detected, through multiple analytical techniques including sensors adopted for gas exploration on Earth and Mars, in water boreholes drilled in the igneous intrusive massif of Alter-do-Chão, at Cabeço de Vide, within the Iberian Hercynian belt (Portugal). We present first molecular and CH_4 isotopic data and discuss the difficulty of assessing gas formation temperature, proposing this case for thermometric determination by the newly developed technology of isotopologue analyses (Ma et al., 2008).

2. Geologic setting

Cabeço de Vide mineral waters issue from boreholes and natural springs at the intrusive contact between the Alter-do-Chão massif (a mafic-ultramafic pluton) and Cambrian carbonate metasediments of Elvas, associated with a main regional NE–SW trending fault crossing the Portuguese mainland through the NE Alentejo region, in the tectonic Ossa Morena zone (Fig. 1). The Alter-do-Chão pluton has an NW–SE elongated shape (following the Variscan orientation) and is a ring-like intrusion, with mafic rocks surrounding the ultramafic core. This pluton has been faced as a cumulate-type structure of Ordovician age (Ribeiro da Costa et al., 1993), comprising ultramafic (dunites, serpentinized dunites to serpentinites and peridotites) and mafic rocks (mainly gabbros). Serpentinized peridotites are distributed vertically to depths of several hundreds meters, likely up to 1 km (Pinto et al., 2006). Most commonly, they contain predominantly serpentine minerals (lizardite, antigorite and chrysotile), magnetite and residual chromite, plus brucite and carbonates. The serpentinization is driven by meteoric water infiltration (present-day serpentinization), according to models by Barnes et al. (1967, 1972), Bruni et al. (2002),

Marques et al. (2008), producing the hyperalkaline (pH > 11) Ca^{2+}–OH^- type waters, today released by natural springs and boreholes at Cabeço de Vide. Two boreholes, AC3 and AC5, about 170 m far apart, discharge the same type of water as indicated by hydrochemical and isotopic parameters (Marques et al., 2008). No conventional gas or oil fields are known around the igneous massif.

3. Methods

Water samples were collected in 2012 from two boreholes (AC3 and AC5, ≈150 m depth), and stored in high-density polyethylene bottles fixed with $HgCl_2$ to prevent microbial oxidation. AC3 is the main borehole, with continuous pumping and output of mineral water; AC5 is a secondary well, used only periodically; two water samples, AC5a and AC5b, were collected at different times after pump activation.

Dissolved gas was analysed, after air-equilibration head-space extraction procedures (e.g., Etiope, 1997) using seven instruments: (1) on site, by a tunable diode laser absorption spectrometer (TDLAS) developed by the Jet Propulsion Laboratory (JPL) and adapted to be hand-carried and measure methane and ethane (C_2H_6) (CH_4 sensitivity 10 ppbv, accuracy 1%; C_2H_6 20 pptv, 5%; additional 25% uncertainty from gas/liquid handling; Christensen et al., 2010), and in the laboratory by (2) a commercial TDLAS CH_4 detector (West Systems, Italy; precision 0.1 ppmv, lower detection limit 0.1 ppmv) coupled with (3) a double beam infrared CO_2 sensor (Licor; accuracy 2%, repeatability ±5 ppmv and full scale range of 2000 ppmv), (4) by a semiconductor H_2 detector (Hydrotech Huberg, Italy; detection limit of 5 ppmv), (5) by Cavity Ring-Down Spectroscopy (CRDS) for $\delta^{13}C$–CH_4, and CH_4 and CO_2 concentration analyses (Picarro G2112-I CH_4 isotope analyser; precision <0.7‰ at 1.8 ppmv CH_4, 5 min), (6) by gas chromatography for hydrocarbon and trace gas composition (Shimadzu 2010 TCD-FID GC; accuracy 2%; lower detection limits: HCs: 1 ppmv; He and H_2: 10 ppmv; CO_2:
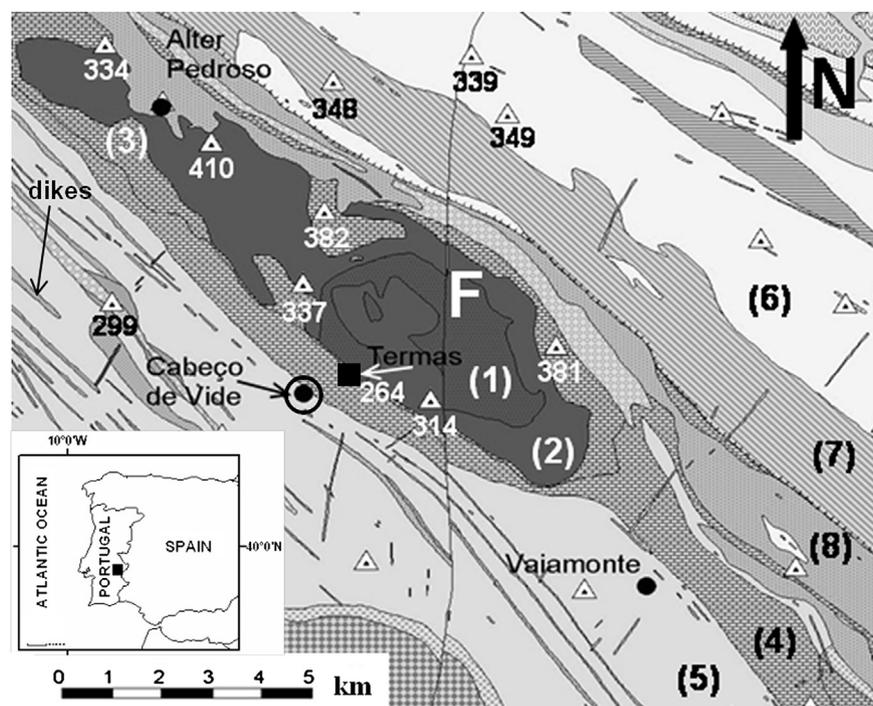

Figure 1. Location and geologic map of Cabeço de Vide area; (1) serpentinized ultramafic rocks; (2) mafic and ultramafic rocks; (3) hornfels; (4) carbonate rocks, displaying contact metamorphism; (5) Cambrian rocks: schists, quartzites and greywackes; (6) Precambrian rocks: metamorphic schists and greywackes; (7) orthogneisses and (8) orthogneisses and hyperalkaline syenites. "Termas" stands for Cabeço de Vide spa and boreholes. F stands for the main regional NNE–SSW trending fault. Altitude (m a.s.l.) is given through the geodetic marks (△). Adapted from Marques et al. (2008) and Fernandes, J. (pers. comm.).

50 ppmv), and (7) by isotope ratio mass spectrometry (IRMS) for C and H isotopic composition (Finnigan Delta Plus XL mass spectrometer, precision $\pm$ 0.1‰ for ^{13}C and ±2‰ for ^2H). On site methane and ethane measurements by JPL instrumentation were performed to rapidly assess presence of dissolved hydrocarbons and field test technologies and science strategies for future planetary science (Webster and Mahaffy, 2011). The other analytical methods were widely used in gas seepage studies both in igneous and sedimentary rocks (e.g., Boschetti et al., 2013; Etiope et al., 2011b, 2013, and references therein).

4. Results and discussions

Methane and ethane were found in both AC3 and AC5 borehole waters with concentrations up to 1.2 and 0.03 mg/L, respectively (Table 1). On site measurements using JPL instrumentation provided immediate recognition of the presence of both methane and ethane, showing a consistent C_1/C_2 ratio at both AC3 and AC5b, in the range 30–40, which was then confirmed by GC analysis for AC3. The lower CH_4 concentration and C_1/C_2 ratio in the AC5a water sample were probably due to higher water degassing or dilution with shallower fresh water (as also suggested by a slightly higher CO_2 concentration) since the sample was collected shortly after pump activation. Sample AC5b, showing CH_4 and C_2H_6 values similar to AC3, appears to be less diluted. The CH_4 concentration in AC3 and AC5b is comparable to those reported in hyperalkaline waters in Italy and Greece (Bruni et al., 2002; Boschetti et al., 2013; Etiope et al., 2013) and is almost one order of magnitude higher than that found in hyperalkaline springs in Canada (Szponar et al., 2012). With a flow rate of 1.3 L per second, the AC3 borehole continuously brings to the surface about 0.1 kg of CH_4 per day. As documented in similar cases (Boschetti et al., 2013; Etiope et al., 2013), gas evolves from the water into the atmosphere once at the surface. CO_2 concentration was lower than the equilibrium with

atmospheric air, and elemental hydrogen (H_2) was not detected by the semiconductor sensor nor by gaschromatography. Propane and heavier alkanes were below the detection limits (<1 ppmv).

CH_4 is ^{13}C-enriched ($\delta^{13}C \sim -20$‰ VPDB; Table 1) with an isotopic composition substantially different from that of typical microbial or thermogenic gas; in the $\delta^{13}C$ vs. δ^2H diagram (Fig. 2) Cabeço de Vide methane plots in the middle of the typical "abiotic" gas field, where all other gases from serpentinized igneous rocks are graphically located. The $\delta^{13}C$ vs. δ^2H diagram is poorly sensitive to mixing, and the paucity of CO_2 (for which we could not analyse the isotopic composition) and other hydrocarbons prevents evaluation of possible mixing of gases from different sources. The low C_1/C_2 ratio suggests a predominantly non-microbial source and the existence of microbial CH_4 is likely precluded by the lack of methanogenic archaea, as recently observed by Tiago and Verissimo (2012). We cannot exclude, however, the presence of minor amounts of thermogenic gas produced, for example, by thermal cooking of organic matter in the surrounding carbonate rocks. The position of the Cabeço de Vide CH_4 data in the $\delta^{13}C$ vs. δ^2H diagram suggests little or no contribution from microbial oxidation or diffusion of biotic gas. Considering the fractionation slopes typical of microbial oxidation and gas diffusion ($\Delta H/\Delta C$: 8.6 and 4.5, respectively, shown by the red arrows in Fig. 2), it appears that Cabeço de Vide CH_4 cannot be a fractionated biotic gas unless there is some microbial CH_4 enriched in ^{13}C and extremely depleted in ^2H, i.e., outside the traditional isotopic range of microbial gas observed in sedimentary rocks. But the waters host only a scarce population of methanotrophs and do not have methanogens (Tiago and Verissimo, 2012).

H_2 is the primary gas produced by serpentinization. We have not detected H_2, however, as also observed in serpentinized rocks in Italy (Boschetti et al., 2013), Greece (Etiope et al., 2013) and in inclusions in India (Sachan et al., 2007) and Oman (Miura et al., 2011). The apparent lack of H_2 could be due to complete consumption by CO_2 hydrogenation in a system where H_2 production was reduced or interrupted due to increased silica activity, or decreased temperature or water–rock ratio (Etiope et al., 2013; Okland et al., 2012). Solubility effects due to pressure and temperature changes may also play a role. Detailed mineralogical analyses shall be performed to evaluate these hypotheses.

Unlike other cases of continental present-day serpentinization (e.g., Turkey, Oman, Philippines, Canada, Italy and Greece) Cabeço de Vide is not in an ophiolite but in a large igneous intrusion complex. The maximum depth of the serpentinized peridotites, which would have been the gas production "kitchen", is today maximum 1 km. Assuming the local present-day geothermal gradient of $\sim$30 °C/km (IGM, 1998), this corresponds to temperatures below 50 °C, compatible with the low temperatures of the Cabeço de Vide spring waters ($\sim$20 °C), and the typical temperatures associated with other continental gas-bearing serpentinization systems (Etiope et al., 2011b, 2013). In the case of Cabeço de Vide, however, serpentinization and related gas production may have occurred at any time during the Myr thermal evolution (cooling) of the igneous intrusion, so the actual gas formation temperature could be higher. We believe that the earliest serpentinization may have begun soon after the emplacement of the Alter do Chão ultramafic massif, given inherent rock fracturing that favoured the infiltration of meteoric waters at great depths. Geothermometers based on water and gas chemistry or mineralogical assemblages (e.g., Ribeiro da Costa et al., 1993) could be tested, but a more precise answer concerning the gas formation temperature may come from the novel geothermometer based on CH_4 isotopologue (or clumped-isotope) analysis. CH_4 in natural gas forms doubly-substituted isotopologues, $^{13}CH_3D$, whose abundance depends only on temperature (Ma et al., 2008).

Table 1
Molecular and isotopic composition of gas dissolved in the Cabeço de Vide waters.

Parameter	Method	AC3	AC5a	AC5b
CH_4	On site TDLAS-JPL	1.1	nd	1.2
	Lab TDLAS-INGV	0.9	0.2	nd
	CRDS	0.7	0.15	nd
	GC	0.7	0.13	nd
C_2H_6	On site TDLAS-JPL	0.028	nd	0.034
	GC	0.03	0.002	nd
C_1/C_2	On site TDLAS-JPL	40	nd	35
	GC	42	105	nd
ΔCO_2	IR	−180	−27	nd
	CRDS	−165	−44	nd
	GC	−130	0	nd
C_{3+}	"	bdl	bdl	nd
He	"	15	bdl	nd
H_2	"	bdl	bdl	nd
	SC	bdl	bdl	nd
$\delta^{13}C_{CH4}$	CRDS	−18.6	−19.8	nd
	IRMS	−20.7	−23.0	nd
δ^2H_{CH4}	"	−283	−282	nd

Methane and ethane concentrations in mg/L; C_1/C_2 is the methane/ethane ratio measured in the extracted head-space; CO_2 is expressed as the difference with the background concentration measured in air (780 ppmv) in the head-space; helium is in ppmv in the head-space; isotopic composition in ‰ VPDB for C, ‰ VSMOW for H. AC5a sample collected shortly after pumping; AC5b was collected after prolonged water flushing. bdl: below detection limit, see text; nd: not determined; TDLAS: Tunable Diode Laser Absorption Spectroscopy (at Istituto Nazionale di Geofisica e Vulcanologia or Jet Propulsion Laboratory); CRDS: Cavity Ring-Down Spectroscopy; IR: Infrared CO_2 sensor; GC: gas chromatography; IRMS; isotope ratio mass spectrometry; SC: Semiconductor. CH_4 depletion from TDLAS-INGV to GC reflects inevitable sample dilution and air contamination during gas transfer from head-space (TDLAS) to gas bags (CRDS) and glass vials (GC).
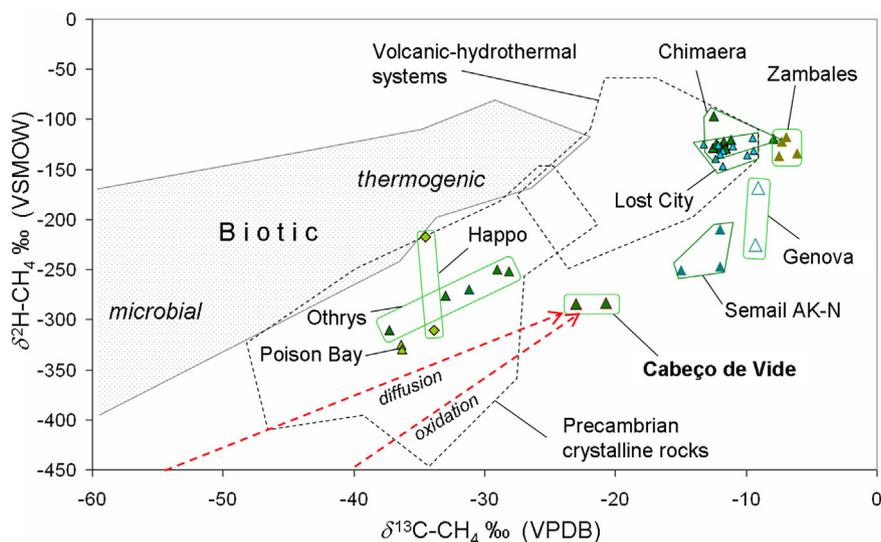
Figure 2. Methane $\delta^{13}C$ vs. $\delta^{2}H$ diagram of Cabeço de Vide (hyperalkaline waters in serpentinized igneous intrusion) compared with all gases so far documented in serpentinized ultramafic rocks, in submarine environment (Lost City hydrothermal fields, Proskurowski et al., 2008) and continental setting (Chimaera-Turkey, Etiope et al., 2011b; Zambales-Philippines, Abrajano et al., 1988; Poison Bay-New Zealand, Lyon and Giggenbach, 1994; Semail-Oman Al-Khoud and Nizwa; Fritz et al., 1992; Othrys-Greece, Etiope et al., 2013; Genova-Italy, Boschetti et al., 2013; Happo-Japan, Suda, 2013). Isotopic fields of methane in Precambrian crystalline shields (South Africa, Canada and Scandinavia) and volcanic-hydrothermal systems (e.g., East Pacific Rise, Southwest Indian Ridge, Socorro, Milos) are also shown for comparison (data from Etiope et al., 2012; Etiope and Sherwood Lollar, 2013 and references therein). The biotic isotopic field encompasses a global dataset (Etiope et al., 2012) of microbial and thermogenic natural gases in sedimentary basin petroleum fields. Isotopic fractionation slopes (red dashed arrows) due to microbial oxidation and diffusion (residual gas) are from Etiope et al. (2011a), Schoell (1983), and references therein. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Serpentinization typically produces two main types of waters: moderately alkaline (pH ~7–9) Mg-rich bicarbonate type waters, due to a shallow open-system weathering of serpentinized rocks, and hyperalkaline (pH > 10) calcium–hydroxide (Ca^{2+}–OH^{-}) waters, resulting from hydration of olivine and pyroxenes in a deeper and closed-system. Etiope et al. (2013) noted that CH_4 from serpentinized ultramafic rocks in Greece and all over the world was found only in hyperalkaline waters. Moderately alkaline and Mg-rich waters, at least on the basis of what has been documented so far, do not show CH_4. The present work confirms this relationship between gas occurrence and water type, which implies that CH_4 production is intimately related to the depth and residence time of the circulating meteoric waters described, among others, by Barnes et al. (1972), Bruni et al. (2002), and Marques et al. (2008). The circulation depth of the Cabeço de Vide hyperalkaline water circuit still remains unclear, however. The hyperalkaline Ca^{2+}–OH^{-} waters and the local shallow immature Mg^{2+}–HCO_3^{-} waters have similar $\delta^{2}H$ and $\delta^{18}O$ values (~ −27‰ vs. VSMOW and −4.5‰ vs. VSMOW, respectively; Marques et al., 2008), indicating that they are meteoric waters with similar local recharge areas (at rather low altitudes within the ultramafic massif) but different underground flow paths. The underground flow paths of the hyperalkaline waters must be deep enough to explain the absence of ^{3}H and the apparent "*age*" (3.6 ± 2.3 ka BP − AC5 borehole waters) based on ^{14}C and $\delta^{13}C$ values (Marques et al., 2008). Radiocarbon and isotopologue analyses of CH_4 will permit estimation of gas formation age and temperature, and thus of the maximum hyperalkaline water circulation depth.

5. Conclusions

The existence of methane in continental serpentinized igneous rocks is more widespread than previously thought. We have documented the 8th case of this gas after those, documented with complete C and H isotopic composition, in the Philippines, Oman, Turkey, New Zealand, and only since 2012, in Italy, Greece and Japan (Abrajano et al., 1988; Fritz et al., 1992; Etiope et al., 2011b;

Lyon and Giggenbach, 1994; Boschetti et al., 2013; Etiope et al., 2013; Suda, 2013). As in these other localities, the CH_4 isotopic composition at Cabeço de Vide suggests a dominant abiotic origin, likely due to Fischer–Tropsch type reactions (see a review by Etiope and Sherwood Lollar, 2013). Similar serpentinized igneous rocks can form reservoirs of atypical petroleum systems (see examples in Schutter, 2003; Smith et al., 2005); it might be possible, then, that such reservoirs may contain minor amounts of abiotic gas. The present work confirms that, whereas underground water can be sampled (via springs or boreholes) in serpentinized rocks, methane occurs only in hyperalkaline Ca^{2+}–OH^{-} type waters, while moderately alkaline and Mg-rich waters do not release gas. Finally, this work is a further example of the gas-bearing potential of hydrated olivine-rich rocks, which are similar to those occurring on Mars, and that, therefore, can be considered as a potential source of methane for the Martian atmosphere (Etiope et al., 2012).

Further investigations at Cabeço de Vide will involve more detailed compositional and isotopic determinations, including helium isotope, and clumped-isotope analyses for the assessment of the gas formation temperature. Maturity of organic matter in the metacarbonates surrounding the pluton shall be evaluated (e.g., by TOC analysis and Rock-Eval pyrolysis) to assess potential thermogenic sources. On site analyses of a wider range of gases, including heavier alkanes, can be performed with a modified version of the TDLAS by JPL, and by portable Fourier Transform Infrared spectrometry (as used in Etiope et al., 2013), for a complete test of instrumentation that might be used in future exploration of Mars. Flux measurements shall also be carried out to verify the presence of diffuse seepage of gas from the ground, as was observed in Turkey and Greece (Etiope et al., 2011b, 2013). It is likely, in fact, that at Cabeço de Vide the gas reaches the surface not only via water springs, but also though diffuse and invisible microseepage, similar to what is frequently observed in conventional petroleum systems. The gas emission rate characterizes the potential of the gas source and it may suggest the existence of pressurized gas pools. Flux measurements will also contribute to our understanding of

geologic methane emissions to the atmosphere, now considered a major source of greenhouse gas, but which do not include continental serpentinization sources (Etiope, 2012).

Acknowledgements

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