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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.

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:

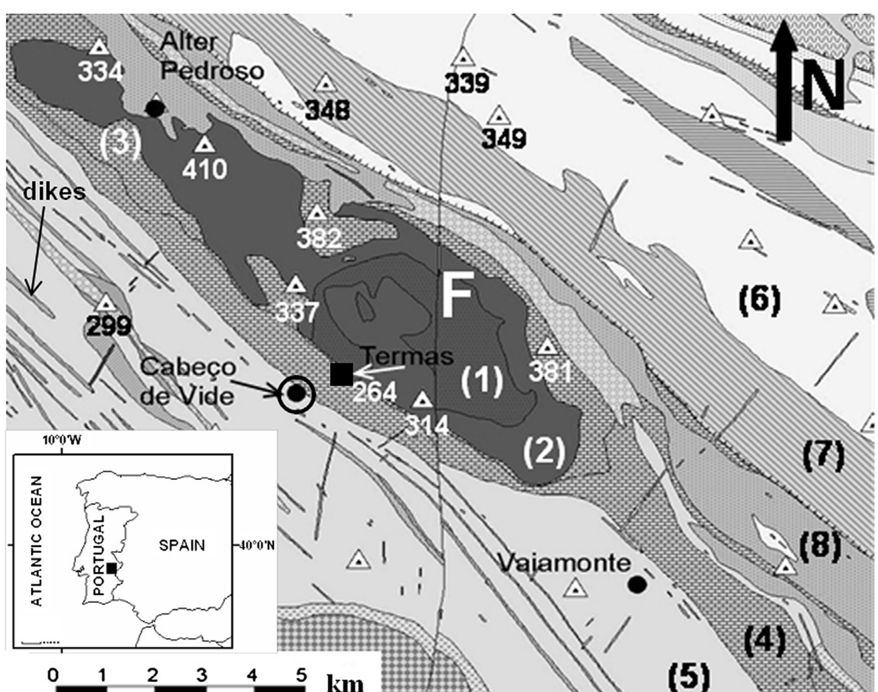

Figure 1. Location and geologic map of Cabeço de Vide area; (1) serpentinized ultramafic rocks; (2) mafic and ultramafic rocks; (3) hornfels; (4) carbonate rocks, displaying contact metamorphism; (5) Cambrian rocks: schists, quartzites and greywackes; (6) Precambrian rocks: metamorphic schists and greywackes; (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.).