SUPPLEMENTARY INFORMATION

Widespread abiotic methane in chromitites

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Supplementary Table 1. Main mineralogical description of the rock samples

| Ophiolite | Location | Sample | Lat. | Long. | Lithotype | Basic Mineralogy |
|-----------|----------|--------|------|-------|-----------|------------------|
| Moschokarya | | MSK1 | 39.017 | 22.265 | Chromitite | Massive chromitite, with interstitial chlorite, hosted in serpentinized harzburgite and lherzolite, along a thrust zone |
| | | MSK2 | 39.018 | 22.265 | Chromitite |
| | | MSK3 | 39.018 | 22.265 | Chromitite |
| | | MSK4 | 39.018 | 22.265 | Chromitite |
| | | MSKB2 | 39.018 | 22.265 | Rodingitized gabbro | Intrusion in MSK chromitite outcrop. The intrusion borders contain disseminated chromitite pods |
| | | MET1 | 39.080 | 22.321 | Chromitite | Massive chromitite with large chromite agglomerates and minor interstitial serpentinite, chlorite and magnetite |
| | | MET2 | 39.080 | 22.321 | Chromitite |
| | | MET3A | 39.080 | 22.321 | Serpentinite | Serpentinite, with mesh texture chloride and magnetite. Rare relic olivine and pyroxene. |
| | | MET3B | 39.080 | 22.321 | Serpentinite |
| | | MET4 | 39.080 | 22.321 | Chromitite | Massive chromitite with fine grained chromite and minor interstitial serpentinite chloride and magnetite. Minor calcite veins. |
| | | MET5 | 39.080 | 22.321 | Chromitite | Massive chromitite with coarse chromite agglomerates and minor interstitial serpentinite chloride and magnetite. Crosscut by serpentinite and rare calcite veins |
| | | MET6 | 39.080 | 22.321 | Chromitite |
| | | MET7 | 39.080 | 22.321 | Chromitite |
| | | MET8 | 39.080 | 22.321 | Serpentinite | Serpentinite with mesh texture, chloride and magnetite. Rare relic olivine and pyroxene |
| Othrys | | AS1 | 39.026 | 22.247 | Serpentinitized peridotite | Relics of pyroxene and accessory spinel crystals. Secondary serpentinite, chlorite and magnetite |
| | | AS2 | 39.026 | 22.247 | Serpentinitized peridotite |
| | | AS3 | 39.026 | 22.247 | Serpentinite | Intensely altered peridotite dominated by serpentinite, chlorite and magnetite. Rare olivine and pyroxene relics |
| | | AS4 | 39.026 | 22.247 | Serpentinite |
| | | AS5 | 39.026 | 22.247 | Serpentinite (cataclasite) |
| | | ARCB4 | 38.942 | 22.116 | Rodingitized gabbro | Highly altered gabbro with relics of plagioclase and clinopyroxene, as well as secondary hydrogrossular, tremolite, minor quartz and chlorite |
| | | ER1 | 39.292 | 22.613 | Chromitite | Massive chromitite hosted randomly in tectonized serpentinites of shear zones |
| | | ER2 | 39.292 | 22.613 | Chromitite |

Google Earth Pro V7.3.1 (14/12/2015). Greece. 28°34’56”N-22°09’14”E, Eye altitude 1422 km (NOAA Image Landsat/Copernicus). DigitalGlobe 2012. http://www.earth.google.com (February 8, 2018).https://earth.google.com/intl/eng/licensepro.html
| Location     | Code | Depth (m) | Rock Type                          | Description                                                                                     |
|--------------|------|-----------|------------------------------------|-------------------------------------------------------------------------------------------------|
| Chalkidiki   |      |           |                                    | Serpentinitized peridotite Dominant serpentinite, chlorite and magnetite, with olivine and orthopyroxene relics |
| Agrilla      |      |           |                                    | Sepertinized dunite Abundant relics of olivine and traces of orthopyroxene altered to serpentinite, chlorite and magnetite |
| Koumovo      |      |           |                                    | Ophiolitic Basalt Highly altered and vesicular pillow lavas with abundant amygdules, calcite and chlorite from the alteration of plagioclase and clinoxyroxene |
| Vourinos     |      |           |                                    | Serpentinized dunite Highly altered basalt including plagioclase and clinoxyroxene surrounded by abundant groundmass devitrified to chlorite. Secondary Fe-oxides are dispersed in the groundmass and calcite fills up amygdules or forms micro-veins |
| Spartia      |      |           |                                    | Flood Basalt Highly altered basalt with rare plagioclase phenocrysts in partly devitrified groundmass. Veins filled with calcite, chlorite and minor quartz. Partially oxidized and impregnated with Fe-oxides. |
| Palaioneraida|      |           |                                    | Flood Basalt Highly altered basalt with only plagioclase phenocrysts in a partially devitrified groundmass. Calcite replaces plagioclases or fills former voids |
| Palaikerasia |      |           |                                    | Pumiceous texture, with plagioclase and clinoxyroxene phenocrysts. Minor secondary quartz filling voids |
| Kozlakas     |      |           |                                    | Basalt with plagioclase and clinoxyroxene phenocrysts, altered to chlorite, amphibole, and pumpellyite. Minor quartz and calcite veins |
| Filira       |      |           |                                    | Plagioclase and clinoxyroxene phenocrysts in a groundmass including chlorite and Fe-oxides. Scarce amygdules are filled with calcite |
| Mouzaki      |      |           |                                    | Ophiolitic Basalt Highly altered basalt with rare plagioclase phenocrysts in partly devitrified groundmass. Veins filled with calcite, chlorite and minor quartz. Partially oxidized and impregnated with Fe-oxides. |
| Xerolivado   |      |           |                                    | Ophiolitic Basalt Highly altered basalt with rare plagioclase phenocrysts in partly devitrified groundmass. Veins filled with calcite, chlorite and minor quartz. Partially oxidized and impregnated with Fe-oxides. |
| Aetorrraches |      |           |                                    | Schlieren Chromitite with transition boundaries and chromite grain size variations. Interstices filled with serpentine and olivine relics |
| Vourinos     |      |           |                                    | Chromite bearing serpentinitic dunite (disseminated chromitite) Intensely serenitized olivine with disseminated coarse chromites |
| Skountsa     |      |           |                                    | Schlieren Chromitite with transition boundaries from coarse massive chromite to totally serpentinitized dunite containing disseminated chrome |
| Mikrokleisoura|      |           |                                    | Schlieren Chromitite altered Mylonitised, schlieren chromite with smooth transition boundaries from coarse massive chromite to totally serpentinitized dunite containing disseminated chromite |
| Edipsos      |      |           |                                    | Ophiolitic Basalt Plagioclase phenocrysts in a chloritized and oxidized groundmass |
| Sithonia     |      |           |                                    | Ophiolitic Basalt Basalt with plagioclase phenocrysts and chloritized, oxidized groundmass with minor calcite |
| Chalkidiki   |      |           |                                    | Serpentinized dunite Relics of olivine and fine grained chromite dispersed in highly serpentinitized matrix |
| Torone (submarine) | |           |                                    | Cumulate (layered) Gabbrro Cumulus plagioclase and clinoxyroxene locally chloritized and oxidised. Rare calcite veins |
|               |      |           |                                    | Microgabбро Fine grained clinoxyroxene and plagioclase, with local chloritization |
|               |      |           |                                    | Basalt Plagioclase phenocrysts surrounded by slightly chloritized and locally oxidised groundmass, with calcite amygdules |
|               |      |           |                                    | Serpentinite Highly altered sample with predominance of mesh serpentine, chlorite and magnetite |
### Supplementary Table 2. Concentration and isotopic data of the gas extracted from the ophiolitic rocks

| ID | Sample | lithology | Analyt. tech. | CH₄ | CH₅ | C₂H₆ | C₂H₅ | C₃H₈ | H₂ | CO₂ | δ¹³C | δ¹²C | δ¹³C | δ¹²C | δ³H | % VPDB | % VSMOW |
|----|--------|-----------|---------------|-----|-----|------|------|------|----|-----|------|------|------|------|------|-------|--------|
|    |        |           | ppmv | µg/g,ppm | ppmv | vol.% | %     | %     |
| 1  | MSK1   | chromitite | TC   | 410 | 0.383 |     |       |       |
|    |        |            | GI   | 3650 | 0.100 | 10.0 | 5.0   | 10.0 | 2   | 0.033 | -6.7 | -5.3 | -29.74 | -13.7 | -380 |
| 2  | MSK2   | chromitite | TC   | 759 | 1.187 |     |       |       |
|    |        |            | GI   | 26780 | 1.000 | 355.0 | 195.0 | <0.5 | 22  | 0.8   | -5.4 | -6.6 | -26.1 | -28   | -646 |
| 3  | MSK3   | chromitite | TC   | 145 | 0.157 |     |       |       |
|    |        |            | GI   | 8250 | 0.270 | 120.0 | 75.0  | <0.5 | 3.7 | 1     | -7.8 | -10  | -26.2 | -26.8 | -546 |
| 4  | MSK4   | chromitite | TC   | 79.7 | 0.121 |     |       |       |
|    |        |            | GI   | 1258 | 0.040 | 19.2  | 12.0  | 5.0  | 2.5 | <0.01 | -15.6 | -17.1 | -27.3 | -28.8 | -14.1 | -377 |
| 5  | MSKB3  | chromitite | TC   | 58  | 0.072 |     |       |       |
|    |        |            | GI   | 1258 | 0.040 | 19.2  | 12.0  | 5.0  | 2.5 | <0.01 | -15.6 | -17.1 | -27.3 | -28.8 | -14.1 | -377 |
| 6  | MET1   | chromitite | TC   | 115 | 0.192 |     |       |       |
|    |        |            | TC   | 60  | 0.008 |     |       |       |
|    | MET1bis |           | TC   | 115 | 0.192 |     |       |       |
| 7  | MET2   | chromitite | TC   | 48  | 0.050 |     |       |       |
|    |        |            | GI   | 3430 | 0.180 | 140.0 | 81.0  | <0.5 | 5.7 | 1.8   | -14  | -20  | -26.6 | -30.2 | -512 |
| 8  | MET4   | chromitite | TC   | 95  | 0.096 |     |       |       |
|    |        |            | GI   | 8500 | 0.280 | 200.0 | 120.0 | <0.5 | 6.3 | 1.3   | -12.8 | -14.1 | -27.1 | -581 |
| 9  | MET5   | chromitite | TC   | 26  | 0.035 |     |       |       |
|    |        |            | TC   | 38  | 0.047 |     |       |       |
| 10 | MET6   | chromitite | TC   | 124 | 0.129 |     |       |       |
|    |        |            | TC   | 6   | 0.008 |     |       |       |
| 11 | MET7   | chromitite | TC   | 124 | 0.129 |     |       |       |
| 12 | ER1    | chromitite | TC   | 48  | 0.050 |     |       |       |
| 13 | ER2    | chromitite | TC   | 196 | 0.225 |     |       |       |
|    |        |            | GI   | 1300 | 0.050 | 90.0  | 40.0  | <0.5 | <0.1 | <0.1 | 1.6   | -0.5  |       |       |
| 14 | ER 3   | chromitite | TC   | 95  | 0.096 |     |       |       |
|    |        |            | GI   | 8500 | 0.280 | 200.0 | 120.0 | <0.5 | 6.3 | 1.3   | -12.8 | -14.1 | -27.1 | -581 |
| 15 | ERB 2  | chromitite | TC   | 26  | 0.035 |     |       |       |
|    |        |            | TC   | 38  | 0.047 |     |       |       |
| 16 | AET1   | chromitite | TC   | 860 | 1.007 |     |       |       |
|    |        |            | GI   | 6907 | 0.100 | 19.0  | 11.1  | <0.5 | <0.1 | 0.12 | -1    |       |       |
| 17 | AET3   | chromitite | TC   | 190 | 0.232 |     |       |       |
|    |        |            | GI   | 1983 | 0.040 | 6.0   | <0.5  | <0.5 | 0.35 | 0.06 | 1.3   | -2.3  |       |       |
| 18 | AET4   | chromitite | TC   | 115 | 0.146 |     |       |       |
|    |        |            | GI   | 1508 | 0.030 | 13.5  | 8.9   | 18.7 | 0.35 | <0.01 | -4    | -5    | -15.1 |       |
| 19 | AET5   | chromitite | TC   | 568 | 0.701 |     |       |       |
|    |        |            | GI   | 6666 | 0.140 | 4.7   | <0.5  | 0.7  | 0.25 | <0.01 | -4    | -4.8  | -10.3 |       |
| 20 | SK1    | chromitite | TC   | 149 | 0.184 |     |       |       |
|    |        |            | GI   | 543  | 0.010 | 3.3   | <0.5  | 1.2  | 0.19 | 0.08 | -6.1  | -7.7  | -8.3  |       |
| 21 | SK2    | chromitite | TC   | 104 | 0.128 |     |       |       |
|    |        |            | GI   | 1379 | 0.030 | 6.2   | <0.5  | 9.1  | 0.34 | 0.05 | -5.4  | -6.5  | -10.3 |       |
| 22 | SK3    | chromitite | TC   | 150 | 0.177 |     |       |       |
|    |        |            | GI   | 1740 | 0.060 | 6     | <0.5  | <0.5 | 0.54 | 0.04 | -5.9  | -7.7  | -16.2 | -7.5  |
| 23 | MSKB2  | chromitite | TC   | 241 | 0.287 |     |       |       |
|    |        |            | GI   | 2700 | 0.040 | 9.0   | <0.5  | <0.5 | 1   | <0.01 | -4.5  |       |       |
| 24 | Si10   | chromitite | TC   | 21  | 0.026 |     |       |       |
|    |        |            | GI   | 406  | 0.010 | 8.0   | <0.5  | 1.0  | 0.5  | <0.01 | -16.4 | -19.1 | -16.7 | -7.2  |
| 25 | XL3    | chromitite | TC   | 30  | 0.037 |     |       |       |
|    |        |            | GI   | 544  | 0.010 | 7.0   | <0.5  | <0.5 | 0.07 | <0.01 | -14.3 | -15.6 | -8.9  |       |
| 26 | ARCB4  | chromitite | TC   | 223 | 0.275 |     |       |       |
|    |        |            | GI   | 2670 | 0.070 | 38.0  | 15.0  | 5.0  | 0.4  | <0.01 | -30.5 | -41.7 | -30.1 | -27.9 | -19.8 | -319 |
| 27 | TE2    | chromitite | TC   | 4045 | 0.133 | 170.0 | 105.0 | <0.5 | 4.8 | 0.97 | -16.5 | -26.1 | -28.5 | -589 |
| 28 | MET3A  | chromitite | TC   | 3   | 0.004 |     |       |       |
|    |        |            | TC   | 3   | 0.004 |     |       |       |
| 29 | MET3B  | chromitite | TC   | 23  | 0.025 |     |       |       |
| Sample | Rock Type | TC | GI | <0.5 | <0.5 | <0.5 | 1.0 | 1.00 | -19.8 | 0.1 | 0.27 | -29.1 | TC | GI | 0.008 | <0.5 | <0.5 | <0.5 | 0.01 | 1.2 |
|--------|-----------|----|----|-------|-------|-------|------|------|-------|------|------|--------|----|----|-------|-------|-------|-------|-------|------|------|
| MET8   | serpentine| 30 |    | 8     | 0.010 |       |      |      |       |      |      |        |    |    |       |       |       |       |       |      |      |
| ERB 1  | serp perid| 31 |    | Gl    | 613   | 0.012 | <0.5 | <0.5 | <0.5 | 1.1  | 1.00 | -19.8  |    |    |       |       |       |       |       |      |      |
| AS1    | serp perid| 32 |    | TC    | 10    | 0.012 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AS2    | serp perid| 33 |    | TC    | 13    | 0.021 |       |      |      |      |      | -15.4  |    |    |       |       |       |       |       |      |      |
| AS3    | serpentine| 34 |    | TC    | 3     | 0.005 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AS4    | serpentine| 35 |    | TC    | 24    | 0.030 |       |      |      |      |      | -21.0  |    |    |       |       |       |       |       |      |      |
| AS5    | serpentine| 36 |    | TC    | 3     | 0.005 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AS5bis | serpentine|    |    | TC    | 4     | 0.006 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| TOR7   | serp perid| 37 |    | TC    | 12    | 0.015 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| TOR3A  | gabbro    | 38 |    | TC    | 9     | 0.009 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| TOR4A  | gabbro    | 39 |    | TC    | 51    | 0.054 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| VR7    | rodingite  | 40 |    | TC    | 9     | 0.011 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| TORME  | basalt    | 41 |    | TC    | 86    | 0.092 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| FIL1   | basalt    | 42 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| SI4    | basalt    | 43 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| SI5    | basalt    | 44 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| MKL4   | basalt    | 45 |    | TC    | 7     | 0.008 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| KRN6   | basalt    | 46 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| KRN7   | basalt    | 47 |    | TC    | 20    | 0.001 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| MZ1    | basalt    | 48 |    | GI    | 65    | 0.001 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| MZ10   | basalt    | 49 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| MZ11   | basalt    | 50 |    | TC    | 5     | 0.006 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AGR1   | basalt    | 51 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AGR6   | basalt    | 52 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| AGR11  | basalt    | 53 |    | TC    | 18    | 0.024 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| MK1    | basalt    | 54 |    | GI    | 223   | 0.005 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| P3     | basalt    | 55 |    | TC    | 4     | 0.005 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| PN4    | basalt    | 56 |    | TC    | 6     | 0.007 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| PK2    | basalt    | 57 |    | IC    | 299   | 0.003 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| LOG6   | basalt    | 58 |    | TC    | 5     | 0.006 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| ED5    | basalt    | 59 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| ED5bis | basalt    | 60 |    | TC    | 3     | 0.004 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| ED6-1  | basalt    | 61 |    | GI    | 13    | 0.0002 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |
| ED6-2  | basalt    | 62 |    | GI    | 10    | 0.0001 |       |      |      |      |      |        |    |    |       |       |       |       |       |      |      |

TC: TDLS-CRDS (INGV lab); GI: GC-IRMS (GEO-data lab). Empty cells mean "not measured"
Tests on gas extraction methods

It is known that C-bearing gas and hydrogen can be artificially produced by mechanical friction during rock crushing or milling in stainless steel devices (Higaki et al., 2006). The presence of rock fragments in the jar of a milling device however minimizes the artificial gas generation (Welhan, 1988). Milling also generates new and clean surfaces, which are chemically active and can adsorb considerable quantities of gas; accordingly, the content of gas extracted and analysed is an underestimation of the actual gas content in the rock. It is also known that gas concentration and isotopic composition may change with milling due to diffusion effects (Zhang et al., 2014), because of the progressive release of gas occluded in smaller pores. Accordingly, a series of tests assessing the effect of milling conditions (time and velocity) on the evolution of the gas yield were carried out.

A first set of tests was done in order to identify the milling parameters leading to the lowest artificial gas production, using blanks (i.e., rocks where CH₄ occluded is not expected) but still effective to mill completely the rocks under investigation. Tests at GEO-data lab were done in dry jar conditions (evacuated and then filled with 20 mL of pure He) and wet conditions (evacuated and then filled completely with salt brine and 20 mL He), with only spheres (empty jar), and with jar filled with alumina oxide, silica gel and washed sea sand. Milling was run from 2 to 16 min. We observed that wet conditions produced in all cases higher gas yields. The salt brine seemed also to induce isotopic fractionation and differential solubility and adsorptions for several gases, especially CO₂. Optimal milling conditions with the lowest artificial gas generation were obtained using 6 spheres, milling velocity of 300 rpm (round per minute), milling duration of 3 minutes, and dry conditions with He filling.

Tests at INGV lab were done using different milling times, velocities and number of spheres with various rock samples (blanks, i.e. granite, quartz, limestone, to assess the lowest artificial gas yield; peridotites, to assess the minimum time for complete crushing). Optimal milling conditions with the lowest artificial gas generation were obtained using 6 spheres, velocity of 300 rpm and 5 minutes.

Specific tests were also performed to understand the effect of milling time on the amount and isotopic composition of gas evolved in the jar from the ultramafic rocks under investigation (this test was actually performed after we realized that chromitites release larger amounts of gas compared to other rocks). GEO-data lab performed a test on chromitite sample MET5, while INGV lab used chromitites MSK1, MSK2 and AET1.

In the MET5 GEO-data test, lasting from 3 to 24 minutes, the concentrations of methane, ethane, propane and H₂ increased over time (Supplementary Table 3). After 24 min the concentration of the hydrocarbons and H₂ was on average 4 times higher than for 3 min milling. The CO₂ concentration had no increase trend. The stable C and H isotope ratios are relatively constant until 12 min, then (at 24 min) the δ¹³C and δ²H values increased. In all cases, the C1-C3 alkanes display an inverse isotope trend (δ¹³C₃> δ¹³C₂> δ¹³C₁).

**Supplementary Table 3: GEO-data test of milling time vs. gas yield for chromitite MET5**

| Mill time (min) | Gas yield (mL/g) | CH₄ (ppmv) | C₂H₆ (ppmv) | C₂H₅ (ppmv) | H₂ (ppmv) | CO₂ (ppmv) | CH₄ (µg/g) | δ¹³C-C₁ (‰) | δ¹³C-C₂ (‰) | δ¹³C-C₃ (‰) | δ¹³C-CO₂ (‰) | δ²H-H₂ (‰) |
|----------------|-----------------|------------|-------------|-------------|---------|-----------|------------|-------------|-------------|-------------|----------------|-------------|
| 3              | 0.11            | 3945       | 144         | 96          | 93000   | 36636     | 0.31       | -19.5       | -26.2       | -26.7       | -17.7          | -482         |
| 6              | 0.11            | 7045       | 256         | 155         | 180000  | 40000     | 0.55       | -20.4       | -25.9       | -26.2       | -16.3          | -437         |
| 12             | 0.17            | 8040       | 390         | 211         | 282083  | 17782     | 0.98       | -20.2       | -27.0       | -27.3       | -18.4          | -470         |
| 24             | 0.08            | 17117      | 695         | 305         | 343079  | 35539     | 0.98       | -14.0       | -25.6       | -25.6       | -1.0           | -216         |

In the INGV tests, lasting from 3 to 20 minutes, the concentrations of methane increased with milling time (Supplem. Table 4; Supplem. Fig 3). The δ¹³C-CH₄ values increased from -7.5 to +9.5‰.

**Supplementary Table 4. INGV test of milling time vs. gas yield for chromitites MSK1, MSK2 and AET1**

| Sample | rock (g) | Mill vel (rpm) | Mill time (min) | CH₄ ppmv | CH₄ µg/g rock | δ¹³C-CH₄ |
|--------|----------|----------------|-----------------|----------|---------------|----------|
| MSK1   | 158      | 300            | 3               | 239      | 0.234         | -7.5     |
| MSK1   | 150      | 300            | 3               | 242      | 0.252         | -7.7     |
| MSK1   | 164      | 300            | 5               | 410      | 0.383         | -6.7     |
| MSK1   | 150      | 300            | 5               | 397      | 0.413         | -4.5     |
| MSK1   | 152      | 300            | 5               | 346      | 0.354         | -5.5     |
| MSK1   | 168      | 300            | 10              | 563      | 0.510         | 4.0      |
| MSK1   | 153      | 300            | 15              | 690      | 0.701         | 7.0      |
| MSK1   | 150      | 300            | 20              | 674      | 0.702         | 9.5      |
| MSK2   | 120      | 400            | 3               | 440      | 0.597         | -6.5     |
| MSK2   | 106      | 300            | 5               | 759      | 1.187         | -4.0     |
| AET1   | 136      | 300            | 5               | 860      | 1.010         | -10.2    |
| AET1   | 134      | 300            | 10              | 1370     | 1.630         | -8.0     |

rpm: rounds per minute
Supplementary Figure 2. Increase of CH4 concentration over milling time for four chromitites

All results are consistent with those of Zhang et al (2014), who observed CH4 concentration and δ13C-CH4 increase over milling time in organic rich mudrocks. The authors explained the phenomenon considering diffusion effects in small pores: small pores retain more 13C-enriched CH4 that is liberated when prolonged milling affects smaller grains.

The assessment of the real concentrations and isotopic composition of the gas occluded in the rocks is not an easy task. Longer milling times seem to provide a more complete release of gas from all types of occlusions, but it may also increase the risk of artificial gas production by mechanical friction. We preferred to keep the milling time as short as possible in order to release the gas that is in secondary and larger occlusions (“free” gas) and compare the relative yields from the several rocks. GEO-data adopted a milling time of 3 minutes. INGV lab run the milling for 5 minutes. Based on the data and discussion above, it is important to remember then, that the gas concentration data measured with our methodology underestimate the actual gas content in the rock. According to Supplem. Fig. 2, the actual methane content may be 3-4 times higher.

Blank analyses

Blank analyses were performed using granite, limestone, quartz, sand and aluminium oxide (alumina, Al2O3) samples, and following the same methodology adopted for the ophiolitic rocks. Granite, quartz and alumina have hardness (6-7 and >8 in the Mohs scale, respectively) higher than that of chromitite and peridotites (5.5-6), therefore the mechanical friction during their crushing should produce higher amounts of gas compared to the investigated rock samples. Tests confirmed that runs in empty ball mill generate much more CH4 and H2 compared with rock-filled jar, as reported by Welhan (1988). Overall, blank analyses showed that the amounts of artificial gas generated during milling is 1 to 3 orders of magnitude lower than the amount of gas observed in chromites (Supplementary Tables 5 and 6).

Supplementary Table 5. Analyses of blanks by GEO-data laboratory

| Type       | time | Weight | Gas yield | CH4 | CH4 | C2H6 | C2H4 | C2H10 | H2 | CO2 | δ13C-CH4 | δ13C-C2H6 | δ13C-C2CO2 |
|------------|------|--------|-----------|-----|-----|------|------|-------|----|-----|----------|-----------|-----------|
|            |      | g      | ppmv      |     | ppmv| ppmv | ppmv | ppmv   | Vol%| Vol%| % VPDB   | % VPDB    | % VPDB    |
| Granite    | 3    | 101.6  | 0.177     | 60.5| 0.007683 | 4.3 | 0.16 |       |     |     | -36.2    | -18.1      |           |
| Limestone  | 3    | 101.1  | 0.010     | 181.6| 0.001279 | 9.2 | 0.4  | 1.8  | 0.87| 0.06| -40.7    | -25.6      | 2.6       |
| Limestone  | 3    | 100.4  | 0.010     | 200.9| 0.001434 | 22.8| 1.8  | 2.9  | 0.01| 0.62|         |            |           |
| Limestone  | 3    | 101.0  | 0.020     | 73.2 | 0.001039 | 18.4| 2.5  | 4    | 0.01| 1.00|         |            |           |
| Limestone  | 3    | 101.0  | 0.030     | 73.9 | 0.001573 | 19.2| 1.6  | 2.8  | 0.02| 1.60| -40.7    | -25.6      | 2.6       |
| Limestone  | 3    | 100.0  | 0.040     | 321.6| 0.009221 | 98.4| 4.26 | -32.9|     |     |         |            |           |
| Sea Sand   | 2    | 20     | 0.025     | 42   | 0.000759 | 6   | 0.013| -30.3|     |     |         |            |           |
| Sea Sand   | 4    | 20     | 0.025     | 56   | 0.001008 | 6   | 0.008| -30.5|     |     |         |            |           |
| Sea Sand   | 8    | 20     | 0.025     | 88   | 0.001583 | 13  | 0.013| -30.3|     |     |         |            |           |
| Sea Sand   | 16   | 20     | 0.025     | 146  | 0.002617 | 24  | 0.019| -29.7|     |     |         |            |           |
| Alum.oxide | 4    | 20     | 0.025     | 33   | 0.000587 | 3   | 0.018|       |     |     |         |            |           |
| Alum.oxide | 4    | 20     | 0.025     | 68   | 0.001226 | 8   | 0.010| -26.7|     |     |         |            |           |
| Quartz     | 4    | 20     | 0.025     | 13   | 0.000236 | 1   | 0.003|       |     |     |         |            |           |
| Quartz     | 8    | 20     | 0.025     | 8    | 0.000134 | 0   | 0.000|       |     |     |         |            |           |
| Alum.oxide | 4    | 20     | 0.025     | 667  | 0.011951 | 7   | 0.059| -23.3|     |     |         |            |           |
| Alum.oxide | 8    | 20     | 0.025     | 2380 | 0.042649 | 24  | 0.040|       |     |     |         |            |           |
| Quartz     | 4    | 20     | 0.025     | 101  | 0.001813 | 4   | 3.729| -24.1|     |     |         |            |           |
| Quartz     | 8    | 20     | 0.025     | 407  | 0.007286 | 9   | 3.928| -24.6|     |     |         |            |           |

*Empty cells mean “not detected” or “below detection limit” (0.5 ppmv). C3H8 was also analysed but it was never detected.*
Supplementary Table 6. Analyses of blanks by INGV laboratory

| Sample | weight (g) | Mill vel (rpm) | Mill time (min) | CH₄ (ppmv) | CH₄ µg/g | δ¹³C-CH₄ (‰) |
|--------|------------|----------------|----------------|------------|----------|----------------|
| quartz | 150        | 300            | 3              | 14.4       | 0.010    | -28.1          |
| quartz | 105        | 300            | 5              | 19.4       | 0.020    | -28.7          |
| quartz | 104        | 300            | 5              | 36.6       | 0.039    | -27.0          |
| quartz | 101        | 300            | 5              | 30.8       | 0.034    | -28.5          |
| quartz | 100        | 300            | 5              | 19.5       | 0.022    | -18.7          |
| quartz | 102        | 300            | 5              | 20         | 0.022    | -28.7          |
| limestone | 120 | 300            | 2              | 6          | 0.005    |                |
| limestone | 125 | 300            | 3              | 2.9        | 0.002    |                |
| limestone | 121 | 300            | 3              | 2.7        | 0.002    |                |
| limestone | 119 | 300            | 5              | 6.6        | 0.006    |                |
| limestone | 120 | 300            | 5              | 3.1        | 0.003    |                |
| limestone | 120 | 400            | 3              | 7.4        | 0.006    |                |
| limestone | 97  | 400            | 3              | 4.1        | 0.005    |                |
| granite | 110       | 300            | 3              | 15         | 0.015    | -30.1          |
| granite | 99        | 300            | 5              | 43         | 0.049    | -11.5          |
| granite | 103       | 300            | 5              | 4.8        | 0.005    |                |
| granite | 104       | 300            | 5              | 10.7       | 0.011    | -29            |
| granite | 113       | 300            | 5              | 11.1       | 0.011    | -28            |

GEO-data analyses showed that maximum methane yields are 0.009 µg/g, for 3 min milling time (carbonate and granite). Higher concentrations up to 0.04 µg/g were obtained for longer milling times (8 min, with alumina). INGV analyses showed maximum methane yields of 0.039 µg/g with quartz and 0.049 µg/g with granite with 5 min milling time. Values one order of magnitude lower were observed for limestone, likely because of the lower hardness of the rock, which implies lower mechanical stress for artificial gas generation. Hydrogen concentration is proportional to that of methane. CO₂ concentrations are higher for carbonates, as expected. Ethane is typically in the range of <0.5 ppmv (detection limit) to 24 ppmv (with an outlier of 98 ppmv in a carbonate), and propane from <0.5 ppmv to 12 ppmv (outlier with 77 ppmv). Isotopic composition of methane, δ¹³C, is generally in the order of -20 to -40‰. δ¹³C-CO₂ values after carbonate milling are positive, suggesting a clear input and fractionation from the calcite. To our knowledge these are the first isotopic data ever reported for artificial gas generated by milling.

Laboratory inter-comparison and uncertainties

With reference to methane concentration data, GEO-data and INGV analyses show comparable results for many samples, but for some samples the results are different (e.g., AET1, AET5, ARCB4). Repeated analyses of the same samples by the same lab show also appreciable differences (e.g., MET1 and MET6 by INGV). This may imply heterogeneity in the occurrence of gas in a given rock, which may vary at small scale from a sample to another. It is important to remember that the samples were collected at or near the surface, and they may have experienced different degree of weathering and degassing. Overall, the results from the two laboratories are consistent, at least for the relative amounts and clear difference between chromitites and all other rocks (and blanks).

Methane isotopic compositions obtained from the two labs are consistent, with more marked differences for samples AS2 and ARCB4 (Supplem. Fig. 3). The δ¹³C values by INGV are generally slightly higher (more ¹³C enriched) than those of GEO-data. Besides possible differences in the calibration, it is likely that the more ¹³C-enriched values by INGV are due to the longer milling time compared to that of GEO-data (5 min vs. 3 min), which may involve the diffusion effects or release of heavier methane in smaller and primary inclusions, as previously discussed.

Supplementary Figure 3. Comparison of δ¹³C of CH₄ obtained by GEO-data and INGV labs for the same type of rock.
Comparison with isotopic composition of CH$_4$ released from serpentinized peridotites worldwide

The $\delta^{13}$C values of methane extracted from the chromitites is within the range observed for dominantly abiotic gas released from gas seeps and hyperalkaline springs in serpentinized peridotites (Suppl. Fig. 4).

Supplementary Figure 4. $\delta^{13}$C-CH$_4$ data observed in chromitites compared to methane from various geological habitats and origins (isotopic diagram with data redrawn after Etiope, 2017). Chromitite CH$_4$ is within the range of the isotopic composition of CH$_4$ observed in surface manifestations (gas seeps and hyperalkaline springs) in serpentinized peridotites (green triangles and white diamonds).

Mineralogical description of MSK2, AET1 and AET5

MSK2 is a massive chromitite sample from Othrys ophiolite. It shows cataclastic texture (Suppl. Fig. 5a) and consists of ~95% subhedral to euhedral mangesiochromite (~100 µm). The interstitial assemblage is pervasively altered to chlorite. Local hydrogarnet fills micro-veins up to 50µm thick among the spinel fragments (Suppl. Fig. 5b). Rare titanite, kammererite and millerite are also spotted along these veins. Few fractures are partially filled with calcite and quartz. AET1 is a schlieren and nodular chromitite sample from Vourinos ophiolite. It has a cataclastic texture, consisting of 70-95% subhedral magnesiochromite (~150µm). Trails of aligned inclusions (<5µm) are observed in some magnesiochromites (Suppl. Fig. 5c). The interstices between the spinels are occupied by intensely serpentinized matrix with mesh texture and local preservation of relics of forsteritic olivine. The cores of the meshes are mainly occupied by richer-in-Fe-serpentinite than the rims. Local, richer-in-Fe serpentine overgrowths are observed in the centers of veins filled with nearly pure in Mg serpentine (Suppl. Fig. 5d). AET5 is a disseminated chromitite and serpentinized dunite representing the host of Vourinos chromitites. It is dominated by mesh and lesser bastitic serpentine. Primary crystal relics include mainly forsteritic olivine porphyroclasts (>100µm) and traces of diopside (<40µm) (Suppl. Fig. 5e). Anhedral chromite grains (~70µm) are highly disseminated in the sample. Late-stage serpentine forms ribbon textures surrounding earlier serpentine. Richer-in-Fe serpentine is overgrown on nearly pure in Mg serpentine. Common pentlandite and rare chlorite are also associated with the serpentine (Suppl. Fig. 5f). Veinlets of calcite are also present. Trails of Fe-oxides are included in olivine as a result of secondary processes.
Supplementary Figure 5. Backscattered electron images of MSK2, AET1, AET5 samples. MSK2 chromitite (a-b), AET1 chromitite (c-d), AET5 disseminated chromitite - serpentized dunite (e-f). (a) Typical cataclastic texture in chromitite, (b) intergranular hydrogarnet formation along magnesiocromite fragments, (c) magnesiocromite with aligned inclusions of secondary origin, (d) interstitial serpentine with richer-in-Fe serpentine cores in meshes and centers of veins along with olivine relics, (e) cataclastic texture in olivine with interstitial serpentine, (f) secondary pentlandite associated with serpentine. Chr: chromite, Chl: chlorite, Grt: hydrogarnet, Srp: serpentine, Fe-Srp: richer-in-Fe serpentine, Ol: olivine, Pn: pentlandite.

Supplementary Table 7. Representative microanalyses (in wt.%) of Cr-spinels (a), olivine (b), serpentine (c), pyroxene (d) and chlorite (e), for the samples AET1, MSK2, AET5 (- means below detection limit)

|(a) Sample | AET1 | MSK2 | AET5 |
|-----------|------|------|------|
| Mineral   | Magnusiocrinite | Magnusiocrinite | Chromite |
| Anal. Nr  | 106  | 108  | 113  | 139  | 343  | 349  |
| Al₂O₃     | 11.90| 11.78| 22.63| 25.04| 12.86| 13.46|
| FeO       | 14.58| 14.24| 16.10| 15.28| 24.61| 24.63|
| MgO       | 14.56| 14.64| 13.97| 14.92| 9.30  | 9.49 |
| Cr₂O₃     | 58.91| 59.32| 47.29| 44.75| 52.58| 51.72|
| Total     | 99.95| 99.98| 99.99| 99.99| 99.35| 99.30|
| Structure formulae (3 cations) |
| Al         | 0.446| 0.453| 0.814| 0.886| 0.477| 0.524|
| Cr         | 1.476| 1.551| 1.140| 1.062| 1.417| 1.354|
| Fe²⁺       | 0.078| 0.015| 0.046| 0.052| 0.196| 0.122|
| Mg         | 0.690| 0.637| 0.635| 0.668| 0.422| 0.427|
| Fe³⁺       | 0.310| 0.363| 0.365| 0.332| 0.578| 0.573|

|(b) Sample | AET1 | AET5 |
|-----------|------|------|
| Mineral   | Olivine |
| Anal. Nr  | 26   | 27   |
| SiO₂      | 40.58| 40.31|
| FeO       | 10.47| 9.34 |
| MgO       | 48.56| 48.86|
| Total     | 99.61| 98.51|
| Structure formulae (4 O) |
| Si         | 1.000| 1.000|
| Fe²⁺       | 0.216| 0.194|
| Mg         | 1.784| 1.807|
Microstructural analysis

AET5: serpentine/chlorite filled veins occupy 43-48 vol.% of the sample, their thickness ranges from 10 to 150 µm and the length is up to 250 µm, but mostly < 50 µm (Supplem. Fig. 6a). The veins follow two, nearly orthogonal preferred strikes and a prevalence of X-type intersection (75 %) with respect to I- and Y-types. The occurrence of two preferred strikes is in agreement with that found by Rigopoulos et al. (2011) on the Vourinos serpentinites. The geometry of the intersections show that the paleo-percolation threshold is exceeded (Manzocchi, 2002). The permeability tensor, indicating the direction along which the permeability related to rock fractures is maximised (Long et al., 1982), is anisotropic.
AET1: the veins are between 29 and 35 vol.% of the rock and follow a preferred strike with a large dispersion (~90°) of values around a maximum (Supplem. Fig. 6b). Vein thickness ranges between few µm and 300 µm and the length, mostly <50 µm, is up to 350 µm. The prevailing interconnections among the veins are of X-type (72%), well above the percolation threshold; the anisotropic permeability tensor (Long et al., 1982) indicates that the paleo-flow was allowed along the average orientation of the veins with the larger hydraulic gradients nearly orthogonal to the vein walls.

MSK2: chlorite filled veins are between 22 and 28 vol.%, and show a maximum length of 480 µm but mostly <70 µm (Supplem. Fig. 6c). They have a weak preferred orientation with a large dispersion of strikes. The geometry of intersections shows that the vein network is above the percolation threshold and the permeability tensor is anisotropic.

**Supplementary Figure 6.** Microstructural analysis of the serpentine and chlorite-filled veins in (a) AET5, (b) AET1, and (c) MSK2. The determined parameters are: distribution of the vein lengths, vein orientation (rose diagram), vein network connectivity, vein network permeability tensor and permeability gradient. These parameters are determined following the procedure reported by Healy et al. (2017). Specifically, to determine the anisotropic permeability tensor we calculated, in a first step, the crack tensor \( P_{ij} = (\pi/4) \rho R_i^2 T_i N_{ij} \), where \( \rho \) is the density of fractures (number per unit area), \( R_i^2 \) is the mean of the squared lengths of fractures, \( T_i \) is the mean of the cubed apertures of the fractures and \( N_{ij} \) is the orientation matrix. In a second step, we estimate the permeability tensor \( k_{ij} \) with the following relation: \( k_{ij} = (\lambda/12) (P_{ij} \delta_{ij} - P_i) \) where \( \lambda \) is a factor between 0 and 1, \( \delta_{ij} \) is the Kronecker delta, and \( P_i \) is the sum of crack tensor’s diagonal component. The anisotropic permeability tensor allow us to detect the direction along which the permeability related to the rock fractures is maximized.
Raman spectroscopy

1. Determination of chemisorbed CH₄

CH₄ has two fundamental Raman active vibrational modes in the gaseous state, (a) the CH symmetrical stretching mode $\nu_1$ at 2917 cm⁻¹ and (b) the out-of-plane degenerate deformation $\nu_2$ at 1526 cm⁻¹. Upon adsorption, the intermolecular interactions between adsorbent and gas alter the intramolecular potential of the gas molecules, causing displacements of the vibrational modes (Siberio-Perez et al. 2007). These shifts may occur either to higher frequency (upshift, negative $\Delta\nu$) or to lower frequency (downshift, positive $\Delta\nu$). The CH peaks observed in chromitite veins-fractures are generally centered on 2917 cm⁻¹ but asymmetrically broadened covering both higher and lower frequencies, with two sub-peaks at about 2908 and 2940 cm⁻¹.

Upon chemisorption, methane dissociates to CH₃ and H on contact with metal surfaces (Han et al., 2013 and references therein). Downshift to lower frequency is also reported for CH₄ adsorbed on zeolites and other porous media (including gas hydrates; Siberio-Perez et al. 2007). Using an external Ne emission lamp (calibration standard) we confirmed that these peaks actually correspond to vibrational modes of CH₂ and CH₃. Neon calibration lamp and deconvolution using ACD labs Spectrus software were used to calibrate the CH region based on Neon peaks at 626.65, 630.48, 633.44 and 638.30 nm.

Our analysis shows the presence of CH₃ functional groups usually associated with CH₂ and on occasion amorphous carbon but the absence of peaks indicative of other organic functional groups such as C=O, C-O or OH etc. The CH₂ group could refer to the downshifted adsorbed CH₄; ethane and propane, found in the chromitites by crushing, could also contribute to the CH₂ vibrational mode. It is interesting that the presence of amorphous carbon may also play a role in the chemisorption process as this type of carbon is not usually associated with aliphatic material.

In the thin sections, contamination by polymer used to polish the sample may produce a peak in the CH field (Fries and Steele, 2010), which could overlap the actual chemisorbed CH₄ peak. However, in thin sections the peaks match the calibrated chemisorbed CH₄ (2938 cm⁻¹) and the peaks observed in chips (not affected by polymer contamination; e.g., Fig. 5 and Supplem. Fig. 7), and occur exclusively in serpentine-filled fractures.

Supplementary Figure 7. Additional example of Raman spectra with C-H (chemisorbed CH₄) stretch detected on chip of AET5 sample.

2. Analysis of solid inclusions

Supplementary Figure 8. Example of solid inclusions and Raman spectra in AET5 sample
Ruthenium and chromium oxide analysis

Supplementary Table 8. Ru and Cr₂O₃ concentrations analysed in 20 ophiolitic rocks (nd: not determined)

| Sample | Lithology          | Ru (ppb) | Cr₂O₃ (wt.%) |
|--------|--------------------|----------|--------------|
| MSK2   | chromitite         | 178      | nd           |
| MSK3   | chromitite         | 73       | 21.6         |
| MSKB3  | chromitite         | <5       | 38.2         |
| MET2   | chromitite         | 152      | 38.3         |
| MET5   | chromitite         | 101      | 42.5         |
| ERB2   | chromitite         | 131      | 30.5         |
| AET1   | chromitite         | 157      | 28.5         |
| SK1    | chromitite         | 115      | 11.3         |
| SK2    | chromitite         | 150      | 23.1         |
| AET5   | dissem. chrom      | 9        | nd           |
| XL3    | serp. dunite       | <5       | 0.3          |
| ERB1   | serp. peridotite   | 37       | 0.38         |
| AS5    | serpentinite       | <5       | 0.44         |
| MSKB2  | gabbro in chromitite| 38 | 0.03       |
| ARCB4  | roding. gabbro     | <5       | 0.107        |
| VR7    | rodingite          | <5       | 0.12         |
| MNL4   | basalt             | <5       | 0.3          |
| AGR11  | basalt             | <5       | 0.093        |
| P3     | basalt             | <5       | 0.095        |
| PN4    | basalt             | <5       | 0.098        |

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