

## Manuscript Details

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### Abstract

Sediment-Hosted Geothermal Systems (SHGSs) are hybrid geological systems, where geothermal and sedimentary domains interact, leading to mixtures of inorganic and organic gases. Typically characterized by geothermal (thermomorphogenic or mantle-derived) CO<sub>2</sub> and biotic (microbial or thermogenic) CH<sub>4</sub>, SHGSs occur in sedimentary basins crossed by magmatic intrusions or involved in volcanic plumbing systems. These systems can be of considerable interest for petroleum exploration and natural greenhouse-gas emission studies, but systematic studies for their characterization and worldwide distribution are missing. Here, we provide a review of SHGSs identified so far, and propose methodological criteria for their definition and identification, based on integrated geological and gas-geochemical parameters. We find that SHGSs are typically characterized by: (a) fluids dominated by mantle or decarbonation-metamorphic CO<sub>2</sub> (>50 vol.%); (b) considerable amounts of CH<sub>4</sub> and heavier hydrocarbons (at least 1.5 vol.%, generally up to 30-40 vol.%), produced by microbial or thermogenic degradation of organic matter hosted in sedimentary rocks; (c) tectonically active sedimentary basins (back-arc, rift zones and foredeep), generally hosting petroleum fields and within ~300 km from recent or ancient volcanic centers. This analysis resulted in a global map including a first set of 33 SHGSs located in North America, Central and Eastern Europe, Far East, Eastern Oceania and Northern New Zealand, and a second set of potential SHGS prone areas, occurring also in South America, North Africa, Middle East and Kamchatka. The present SHGS map can evolve on the basis of more detailed geological analysis and new gas-geochemical data.

**Keywords** Sediment-Hosted Geothermal Systems; carbon dioxide; methane; sedimentary basins; volcanoes; geothermal systems; hydrocarbons; mapping

**Corresponding Author** Monia Procesi

**Corresponding Author's Institution** Istituto Nazionale di Geofisica e Vulcanologia

**Order of Authors** Monia Procesi, Giancarlo Ciotoli, Adriano Mazzini, Giuseppe Etiope

**Suggested reviewers** Yunyan Ni, Rick Allis, Henrik Svensen, Maciej Kotarba

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*July 13th, 2018*

Dear Editor,

I am pleased to submit to *Earth Science Reviews* the manuscript entitled “**Sediment-Hosted Geothermal Systems: review and first global mapping**” by Procesi M., Ciotoli G., Mazzini A. & Etiope G.

The work reports a global review of the Sediment-Hosted Geothermal Systems (SHGS), namely, hybrid geological systems where geothermal and sedimentary domains interact, and proposes methodological criteria for their definition and identification, based on integrated geological and gas-geochemical parameters.

We tried to cover all the main aspects and uncertainties dealing with the problem of the hybrid systems, clarifying the terminology and proposing a methodological approach.

Specifically, we provide a review of previously identified SHGSs (Chapter 3) and propose geochemical and geological criteria for their identification and characterization (Chapter 4). We conclude outlining their specific environmental and energy resource implications (Chapter 5). Moreover, future directions for potential specific research are introduced - with clumped isotopes as a specific example.

We believe that our review is of interest for a wide scientific community including volcanologists, geochemists, petroleum geologists and sedimentologists.

Thanks for handling this manuscript.

On the behalf of all the Authors

Sincerely,

*Monia Procesi*

*Istituto Nazionale di Geofisica e Vulcanologia  
via Vigna Murata 605 00143 Roma  
monia.procesi@ingv.it*

# Sediment-Hosted Geothermal Systems: review and first global mapping

Procesi M.<sup>1</sup>, Ciotoli G.<sup>2,1</sup>, Mazzini A.<sup>3</sup>, Etiope G.<sup>1,4</sup>

<sup>1</sup> Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 605, 00143 Roma, Italy

<sup>2</sup> Istituto di Geologia Ambientale e Geoingegneria—CNR-IGAG, Roma, Italy Centre for Earth

<sup>3</sup> Centre for Earth Evolution and Dynamics (CEED), University of Oslo, Norway

<sup>4</sup> Faculty of Environm. Science and Engineering, Babes Bolyai University, Cluj-Napoca, Romania

## Abstract

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**Keywords:** *Sediment-Hosted Geothermal Systems; carbon dioxide; methane; sedimentary basins; volcanoes; geothermal systems; hydrocarbons; mapping.*

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## **Contents**

### **1. Introduction**

### **2. Definitions**

### **3. Previously identified SHGSs**

*3.1 Guaymas Basin (Gulf of California)*

*3.2 Salton Sea (California)*

*3.3 Lusi (East Java)*

*3.4 Tiber Delta - Fiumicino (Italy)*

*3.5 Songliao Basin-Xujiaweizi Depression (China)*

### **4. Preliminary criteria for SHGS identification and characterization**

#### **4.1 Constraints**

*4.1.1 Gas-geochemical constraints*

*4.1.2 Geological constraints*

#### **4.2 Identification of new SHGSs**

*4.2.1 A new list of potential SHGSs*

*4.2.2 Spatial analysis and mapping of SHGS prone areas*

### **5. Environmental and energy implications of the SHGSs**

### **6. Conclusions**

### **Acknowledgments**

### **References**

## 1. Introduction

The release of carbon-bearing gases from the Earth is generally classified considering two distinct and broad geological domains: (a) the high temperature volcano-geothermal systems, releasing inorganic carbon dioxide (CO<sub>2</sub>) rich gases, typically produced by thermometamorphism of limestones or magma-mantle degassing, and (b) the low temperature sedimentary basins, releasing mainly biotic methane (CH<sub>4</sub>) and other hydrocarbons, produced by microbial or thermogenic degradation of organic matter or oil in sedimentary rocks. A wide body of literature exists about geochemistry and geology of such degassing processes, which have considerable implications for the environment, geo-hazards, global climate changes and energy resource exploration (e.g., relevant case-histories and reviews are reported by [Klusman et al. 1998](#); [Kerrick, 2001](#); [Etiope and Klusman, 2002](#); [Morner and Etiope, 2002](#); [Chiodini et al. 2004](#); [Burton et al. 2013](#); [Etiope, 2015](#)). In many cases, however, geothermal and sedimentary domains can partially overlap, leading to hybrid geological systems with mixtures of inorganic and biotic gases. These hybrid systems are known as *Sediment-Hosted Geothermal Systems* (SHGSs), or *Sediment-Hosted Hydrothermal Systems* (SHHS). We will use the first term, SHGS, discussing the reasons in Chapter 2. These systems refer to sedimentary basins perturbed by magmatic intrusions or involved in volcanic plumbing systems, and characterized by CO<sub>2</sub>-rich geothermal fluids and biotic (microbial or thermogenic) CH<sub>4</sub>, sourced from the organic-rich sediments. Inorganic CO<sub>2</sub> concentrations generally exceed 50 vol.%. CH<sub>4</sub> (and heavier alkanes, such as ethane and propane) concentrations are generally higher (roughly >1-2 vol.%) than those occurring in pure volcanic-geothermal fluids (typically in the order of ppbv or ppmv; [Taran and Giggenbach, 2003](#); [Capaccioni et al, 2004](#); [Etiope et al, 2007](#); [Fiebig et al, 2015](#)). SHGSs are common, as palaeo-systems, in the large igneous provinces as those of South Africa, Australia, Siberia and the North Atlantic province ([Jamtveit et al., 2004](#); [Holford et al., 2013](#); [Svensen et al., 2004](#); [Svensen et al., 2007](#); [Svensen et al., 2009](#); [Jones et al., 2016](#); [Reynolds et al., 2017](#)). Active SHGSs are recognized in the Guaymas Basin Rift Zone-Gulf of California (Pacific Ocean; [Welhan and Lupton, 1987](#); [Berndt, C., et al., 2016](#)), in the Salton Sea geothermal field in California (e.g., [Helgeson, 1968](#); [Mazzini et al., 2011](#)), in Java, Indonesia (Lusi eruption; [Mazzini et al 2012](#)), within the Tiber Delta, at Fiumicino, in central Italy ([Ciotoli et al. 2016](#)) and in the Songliao Basin ([Shuai et al., 2018](#)). Their surface manifestations, like muddy craters or bubbling pools, may be similar to, and thus may be confused with, pure sedimentary gas manifestations (hydrocarbon seeps), such as mud volcanoes ([Etiope, 2015](#); [Mazzini and Etiope, 2017](#)), or mere geothermal/volcanic manifestations (e.g., mofettes, bubbling pools, muddy geysers). The distinction between SHGSs, pure sedimentary systems and geothermal-volcanic complexes is not only a semantics problem. The attribution of SHGS implies, in fact, the

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180 recognition of specific geological and geochemical processes that can have peculiar implications for  
181 petroleum exploration and global climate change studies. SHGSs, in fact, (1) may lead to  
182 production of hydrocarbons resulting from enhanced thermal maturity of sedimentary source rocks;  
183 (2) can be significant natural sources of greenhouse gas (CO<sub>2</sub> and CH<sub>4</sub>) emissions to the atmosphere  
184 (Etiope, 2015), and (3) are potential driver of past climate changes (Svensen et al., 2004; Aarnes et  
185 al., 2010; Iyer et al., 2013; Polozov et al., 2016). Nevertheless, systematic studies for SHGS  
186 characterization and worldwide distribution are missing.

187  
188 Here we provide a review of previously identified SHGSs (Chapter 3) and propose geochemical and  
189 geological criteria for their identification and characterization (Chapter 4). In particular gas genetic  
190 diagrams will show fundamental differences among classic CO<sub>2</sub>-dominated (volcanic,  
191 hydrothermal) systems, CH<sub>4</sub>-dominated (sedimentary) seepage systems, and SHGSs. These criteria  
192 are then used to identify and map other potential SHGSs on the globe (Chapter 4). We conclude  
193 outlining their specific environmental and energy resource implications (Chapter 5). The sequence  
194 of the logical flow chart of this approach is schematized in figure 1. It is important to highlight that  
195 most of the SHGSs identified so far (Guaymas Basin, Salton Sea, Lusi, Fiumicino Tiber-Delta)  
196 have been recognized based on the occurrence of surface gas manifestations. Nevertheless, the  
197 concept of SHGS is independent of surface gas discharges, which act only as “vehicle” of  
198 subsurface information. Obviously, deep-seated SHGSs may exist also without any surface  
199 expression, and they can be identified through deep boreholes, as in the case of the Songliao Basin.  
200 Accordingly, in this work, we have addressed the potential SHGSs revealed by both surface  
201 manifestations and borehole data.  
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## 220 **2. Definitions**

221 The peculiarity of hybrid geological systems, with volcano-hydrothermal and sedimentary  
222 components, was recognized in early works in California, at the Salton Sea geothermal field  
223 (Helgeson, 1968), in the Gulf of California, at the Guaymas Basin (Von Damm et al., 1985; Welhan  
224 and Lupton, 1987) and, more recently, at Lusi in East Java (Mazzini et al., 2012), in central Italy  
225 within the Tiber Delta (Ciotoli et al., 2013; 2016) and in the Songliao petroliferous Basin in China  
226 (Shuai et al. 2018). These works noted that deep sedimentary basins crossed by magmatic fluids or  
227 igneous intrusions, may result in the migration of a combination of fluids, hot water and gases,  
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239 different from the one observed in classic volcanic-geothermal systems or classic sedimentary  
240 basins.

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242 Several terms, such as sediment-hosted mineral deposits (Von Damm et al., 1985), sediment-  
243 dominated hydrothermal systems (Jamtveit et al., 2004), sediment-hosted low temperature systems  
244 (Nicholson, 1993), sediment-hosted hydrothermal systems (Mazzini et al., 2011) or sediment-hosted  
245 geothermal systems (Alt, 2009; Mazzini et al., 2011; Ciotoli et al., 2013; Di Pippo, 2016; Ciotoli et  
246 al., 2016; Mazzini and Etiope, 2017; Shuai et al., 2018) have been used to define this kind of  
247 geological setting; but a clear and univocal definition of these terms is still lacking.

248  
249 The above Authors used the term *sediment*, referring to systems hosted in sedimentary rocks;  
250 whereas they often used “geothermal” or “hydrothermal” referring to emission of hot fluids.  
251 However, “geothermal” and “hydrothermal” have a different meaning as proposed by Jackson  
252 (1997). *Geothermal* refers to any system that transfers heat from within the Earth towards the  
253 surface, while *hydrothermal* is a subset of *geothermal*, implying that the heat transfer is mainly  
254 operated by water (convection), in liquid or steam state. This is also defined as *Conventional*  
255 *Geothermal System (CGS)* to indicate a classic high heat flow hydrothermal system that typically  
256 includes the circulation of meteoric water that infiltrates and migrates to depths of several  
257 kilometers generating convective transport mechanisms (Heasler et al., 2009). Nevertheless,  
258 hydrothermal circulation is not always present in medium-high temperature (geothermal) areas and  
259 in sedimentary basins. For these reasons, we prefer to use the term “Sediment-Hosted *Geothermal*  
260 *System*” instead of “*Hydrothermal*”.

261  
262 Some authors recently introduced the term “*Sedimentary Geothermal Resources*” referring to  
263 relatively “hot” sedimentary systems where geothermal energy can be exploited (for direct and/or  
264 indirect use; Jiachao, 2012; Porro et al., 2012; Anderson et al., 2013). In this framework, Rybach  
265 (1981) highlighted that the geothermal *resource* is formed by an economically sufficient amount of  
266 heat concentration at drillable depth of the Earth's crust, whereas the geothermal *system* is generally  
267 classified by its geological, hydrogeological and heat transfer characteristics. Therefore, the  
268 *Sedimentary Geothermal Resources* may lack the hybrid fluid features and, as a consequence, may  
269 exclude the SHGSs described in this review.

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271 To better clarify the gas-geochemical and geological factors characterizing a SHGS, we briefly  
272 describe the active SHGSs identified so far (Guaymas Basin, Gulf of California; Salton Sea,  
273 California; Lusi, Indonesia; Tiber Delta – Fiumicino, Italy; Songliao Basin, China) (Fig. 2a-e),  
274 focusing on their strong analogies. These analogies will be used as reference for setting the  
275 geochemical-geological criteria for a general characterization and a first SHGS global screening  
276 (Chapter 4).

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*Proposed approximate-location for Figure 2*  
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### 3. Previously identified SHGSs

#### 3.1 Guaymas Basin (Gulf of California)

The Guaymas Basin is located in the central part of the Gulf of California (N27°03'; W111°07'). It is an actively spreading oceanic basin that is part of the system of spreading axes and transform faults extending from the East Pacific Rise to the San Andreas fault (Curry et al., 1982; Lonsdale and Becker, 1985) (Fig. 2a). The basin has a maximum depth of ~2000 m and consists of two NE oriented sub-basins that are 30 and 50 km long, respectively (Lonsdale and Becker, 1985). The lithology of the basin was assessed through a Deep Sea Drilling Project (Curry et al., 1982). Seismic studies indicate the presence of a magmatic chamber in the basin, below a sedimentary column, 700-1000 m thick (Curry et al., 1982), which rapidly covered the rift floor (sedimentation rate >2m/1000yr). The sequence includes basaltic sills in contact with diatomaceous, calcareous deposits rich in organic matter and detritic clay minerals (Von Damm et al., 1985 and references therein). The estimated geothermal reservoir temperature is 315°C (Von Damm et al., 1985) and the computed mean heat flow is 453 mW/m<sup>2</sup> (Curry et al., 1982). The chemical composition of the Guaymas fluids is typical of deep submarine “hot” vents, dominated by CO<sub>2</sub> (~90 vol.%) followed by CH<sub>4</sub> (~10 vol.%) (Simoneit and Galimov, 1984; Galván et al., 2015). In addition to the “magmatic” influence of the basaltic sills, the fluids also show effects of interaction with organic matter within the sediments (German and Von Damm, 2003; Berndt et al, 2016). Thermal stress caused rapid maturation of the organic matter with concomitant generation of oil and thermogenic hydrocarbon gas (Simoneit, 1988, Teske et al., 2016), as indicated by δ<sup>13</sup>C-CH<sub>4</sub> data, ranging between -51 and -15‰ VPDB (Welhan and Lupton, 1987; Berndt et al, 2016). The fossil source of CH<sub>4</sub> is confirmed by radiocarbon measurements (<sup>14</sup>C-CH<sub>4</sub>) that show values of 0.2 ± 0.1 pMC (Kessler et al., 2008). The CO<sub>2</sub> carbon isotope data (ranging between -6 and +2.7‰ VPDB) suggest a source related to thermo-metamorphic reactions on carbonates and magma-mantle degassing (Welhan and Lupton, 1987).

### 3.2 Salton Sea (California)

The Salton Sea geothermal system is situated in the Salton Trough in southern California (N33°12'; W115°34'), an area with abundant surface hydrothermal manifestations (bubbling mud pools, gryphons and gas vents) (Svensen et al., 2007; Svensen et al., 2009; Mazzini et al., 2011). Salton Sea occurs in a pull-apart basin, filled by sedimentary rocks and intruded by quaternary basalt and rhyolite bodies, inducing high heat flow (up to 600 mW/m<sup>2</sup>) (Svensen et al., 2007; Mazzini et al., 2011; Onderdonk et al., 2011) (Fig. 2b). The intrusions can cause a temperature increase exceeding 350°C at the depth of 1400m, diffuse CO<sub>2</sub> degassing and alteration of organic matter (Svensen et al., 2007). The chemical composition of gas discharged to the surface is dominated by CO<sub>2</sub> with concentrations up to 98 vol.%, followed by CH<sub>4</sub> (up to 1.9 vol.%) and heavier hydrocarbons (C<sub>2+</sub><0.5 vol.%). The δ<sup>13</sup>C-CO<sub>2</sub> (ranging from -5.4 to +0.4 ‰) is within the range of magmatic sources and thermal decarbonation reactions (Mazzini et al., 2011 and references therein), while δ<sup>13</sup>C-CH<sub>4</sub> (from -32 to -17.6 ‰) suggests a mixing of thermogenic and abiotic sources (Mazzini et al., 2011 and references therein).

### 3.3 Lusi (East Java)

The 29<sup>th</sup> of May 2006 boiling mud breccia, gas and water suddenly erupted in the Regency of Sidoarjo, along the Watakosek fault system in north east of Java, Indonesia (S7°44'; E112°34') (Mazzini et al., 2007). This eruption site was named Lusi, a contraction of Lumpur Sidoarjo wherein “Lumpur” is the Indonesian Bahasa word for mud. More than 12 years later, Lusi is still active erupting with a flow rate of ~80.000 m<sup>3</sup>/day (early 2018; Miller and Mazzini, 2018). Lusi is located in a Tertiary-aged back-arc basin of NE Java (Kusumastuti et al., 2002), where the sedimentary sequences are characterized by high sedimentation rates of organic-rich deposits often capped by sealing units of tuffaceous or volcanoclastic sands. Mud volcanoes (= sedimentary volcanism) are widespread in this part of the island (Satiana 2008, Mazzini et al., 2009, Istadi et al., 2012) but Lusi has been recognized to have different characteristics from a mud volcano (Mazzini et al., 2012). Unlike the other classic mud volcanoes of Java, Lusi is situated in the proximity of the large Arjuno-Welirang volcanic complex. Here the geothermal gradient is relatively high (42°C/km) and the fluids erupted from the main crater are characterized by high concentrations of water vapour. Besides the water vapour, CO<sub>2</sub> is the main gas (>58 vol.% dry phase), and, with δ<sup>13</sup>C-CO<sub>2</sub> values between -2.2 and -12.8 ‰, is mostly associated to mantle-magma degassing and/or decarbonation processes, whereas methane, with concentration up to 40% (Mazzini et al., 2017) is related to thermogenic origin with δ<sup>13</sup>C-CH<sub>4</sub> from -31 to 51.8‰ (Mazzini et al., 2012; Mazzini et

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416 *al.*, 2017). Early isotopic data, collected soon after the eruption started, indicated the presence of an  
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418 organic CO<sub>2</sub> component (Mazzini *et al.*, 2012), interpreted as initial degassing contribution from the  
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420 shallower sedimentary layers pierced by the active conduit. The thousands of satellite seeps  
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422 scattered over kilometres around the crater (e.g. Sciarra *et al.*, 2018) typically have higher CH<sub>4</sub>  
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424 concentrations (up to 99 vol.%). Also in this case, methane has a biotic (thermogenic, mixed with  
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426 microbial) origin ( $\delta^{13}\text{C-CH}_4$  from -41 to 66 ‰) and CO<sub>2</sub> has inorganic origin ( $-8.2\text{‰} \leq \delta^{13}\text{C-CO}_2 \leq$   
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428 4.12‰; Sciarra *et al.*, 2018). Integrated geochemical geological and geophysical data are consistent  
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430 with a SHGS scenario where deep seated (> 4000 m) magmatic intrusions and hydrothermal fluids  
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432 migration are responsible for the enhanced heat that altered source rocks and/or gas reservoirs  
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434 (Mazzini *et al.*, 2012; Fallahi *et al.*, 2017; Mazzini *et al.*, 2018; Inguaggiato *et al.*, 2018). (Fig. 2c).

### 435 436 **3.4 Tiber Delta-Fiumicino (Italy)**

437 The Tiber Delta, along the Tyrrhenian Sea margin in Central Italy (N12°26'; 41°76'), is located  
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439 within the youngest back-arc basin of the Mediterranean region. It developed since the Miocene as a  
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441 consequence of rifting and back arc extension associated with the west-dipping and “easterly”  
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443 retreating Apennine subduction zone (Bigi *et al.*, 2015 and references therein). Here the heat flow  
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445 shows anomalous values, ranging from 100 to 200 mW/m<sup>2</sup> due to mantle uplift and/or crustal  
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447 thinning (Scrocca *et al.*, 2003). In 2013, a sudden eruption of CO<sub>2</sub>-rich gas occurred in this area,  
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449 near Fiumicino town and very close to the Rome’s international airport (Ciotoli *et al.*, 2013;  
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451 Giordano *et al.*, 2016). CO<sub>2</sub> vents and anomalous CO<sub>2</sub> and CH<sub>4</sub> concentrations in the soil have also  
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453 been discovered at several sites within the delta (Ciotoli *et al.*, 2016) (Fig. 2d). The gas is  
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455 dominantly composed by inorganic/geothermal CO<sub>2</sub> (up to 98 vol.%;  $-2\text{‰} \leq \delta^{13}\text{C-CO}_2 \leq -0.7\text{‰}$ )  
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457 and by minor amounts (up to 3.7 vol.%) of biotic (mainly thermogenic) CH<sub>4</sub> ( $-54\text{‰} \leq \delta^{13}\text{C-CH}_4 \leq -$   
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459 37‰). While CO<sub>2</sub> has the same origin of the geothermal gas of the adjacent Alban Hills volcano,  
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461 CH<sub>4</sub> likely sourced from Meso-Cenozoic petroleum systems overlying deep magmatic fluids.  
462  
463 Inorganic and biotic gases originated in different systems and depths, but follow the same migration  
464  
465 pathways defined by active faults of a half-graben (Ciotoli *et al.*, 2016).

### 466 467 **3.5 Songliao Basin, Xujiaweizi Depression (China)**

468 The Songliao Basin is a large intracontinental Mesozoic-Cenozoic sedimentary basin in  
469  
470 northeastern China (N47°43'; E127°34') (Fig. 2e). The evolution of the basin can be divided into  
471  
472 four stages: mantle upwelling, rifting, post-rifting thermal subsidence and structural inversion. More

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475 than 30 rift depressions, such as the Xujiaweizi depression, developed during the late Jurassic to  
476 early Cretaceous period (Feng, 2008). These isolated rift systems are characterized by volcanic and  
477 coal-bearing clastic rocks. The Xujiaweizi rift depression is located near the center of the Songliao  
478 Basin and is characterized by over mature hydrocarbon source rocks due to the high geothermal  
479 gradient of this rift system (37 to 46 °C/km, with a mean of 40°C/km; Liu et al., 2016). The  
480 abundant and mature source rocks, and the favorable structural conditions for the formation of  
481 reservoir and cap-rocks, lead to the formation of prolific petroleum systems with mixing between a  
482 CO<sub>2</sub>-poor, relatively high maturity coal gas and a CO<sub>2</sub>-dominated gas typical of geothermal systems  
483 (up to 91 vol.%; δ<sup>13</sup>C-CO<sub>2</sub> -4.4‰). Based mainly on <sup>13</sup>C-enrichments in alkanes (e.g. δ<sup>13</sup>C-CH<sub>4</sub> -  
484 26.9 ‰), several authors proposed that in the Xujiaweizi sub-basin, considerable amounts of  
485 hydrocarbons have an abiogenic origin (Guo et al., 1997; Wang et al., 2009; Liu et al., 2016; Huang et  
486 al., 2004; Feng et al., 2008; Mi et al., 2010). More recent studies, based on CH<sub>4</sub> clumped-isotopes  
487 have suggested a methane formation temperature (167<sup>±18</sup> °C to 213<sup>±22</sup> °C) that is much lower than  
488 that of magmatic gas generation processes, and therefore compatible with the high maturity of local  
489 source rocks (Shuai et al. 2018). The inorganic origin of CO<sub>2</sub> is confirmed, suggesting the existence  
490 of a migration pathway related to deep faults and fractures, which allows for the uprising of the  
491 magmatic-mantle fluids (CO<sub>2</sub> and He) towards hydrocarbon reservoirs. Accordingly, the deep  
492 formations of the Songliao Basin have been suggested to represent a typical case of SHGS (Shuai et  
493 al., 2018).  
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#### 509 **4. Preliminary criteria for SHGS identification and characterization**

##### 510 **4.1 Constraints**

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512 The SHGSs previously described have important analogies and recurring features. All systems are  
513 in sedimentary basins characterized by the following factors:  
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- 515 (a) gas emissions to the surface, or gas reservoirs (as in the case of Songliao Basin) dominated by  
516 inorganic CO<sub>2</sub> associated with variable amounts of biotic CH<sub>4</sub>, usually higher than 1.5 vol.%.  
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- 518 (b) basin located within a tectonically active region;  
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- 520 (c) anomalous heat flux (>50 mW/m<sup>2</sup>);  
521
- 522 (d) presence of sills and/or deep magma intrusions related to geothermal or volcanic systems;  
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- 524 (e) organic matter rich sediments with thickness exceeding 700 m;  
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526 These recurring features, which may represent the preliminary constraints to identify potential  
527 SHGSs, are discussed in more detail below.  
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#### 4.1.1 Gas-geochemical constraints

The CO<sub>2</sub> carbon isotope signature,  $\delta^{13}\text{C-CO}_2$ , related to magma and mantle degassing, is generally between -8 ‰ and -4 ‰, and the one related to decarbonation reactions (thermomethamorphism) at high temperatures (> 250 °C) varies from -2 ‰ to +2 ‰ (e.g., [Hoefs, 2015](#)). The CO<sub>2</sub> produced by bacterial or thermal degradation of organic matter or hydrocarbon oxidation in sedimentary rocks has, instead,  $\delta^{13}\text{C-CO}_2$  values typically  $\leq -10$  ‰ (e.g., [Jenden et al., 1993](#); [Hunt, 1996](#)). Basically, a geothermal system is characterized by  $\delta^{13}\text{C-CO}_2$  values ranging between -8 ‰ and +2 ‰. Sedimentary (petroleum-related) gas may also have CO<sub>2</sub> with positive  $\delta^{13}\text{C-CO}_2$  values due to biodegradation of hydrocarbons and secondary methanogenesis ([Pallasser, 2000](#)), but their CO<sub>2</sub> concentration is relatively low (<20-30 vol.%; and obviously lower than CH<sub>4</sub> concentration). The SHGSs recognized so far have actually a CO<sub>2</sub> compatible with the inorganic origin ( $-8.9$  ‰  $\leq \delta^{13}\text{C-CO}_2 \leq +2.7$  ‰). Accordingly, we will consider as a first constraint for SHGSs, a gas which is dominated by CO<sub>2</sub> (concentration above 50 vol.%) and  $\delta^{13}\text{C-CO}_2$  between -8 and +2 ‰. We will consider also those sites where inorganic CO<sub>2</sub> is identified (and clearly discussed in the reference work) but mixed with a minor organic component, leading to slightly lower  $\delta^{13}\text{C-CO}_2$  values.

Typically, volcanic sources, as well as the hydrothermal/geothermal systems (or conventional geothermal systems), discharge methane of dominant abiotic origin, generated by magmatic, post-magmatic high-temperature processes and Fischer-Tropsch Type (FTT) reactions ([Fiebig et al 2007](#); [Etioppe and Sherwood Lollar, 2013](#)). In particular, methane in pure and active magmatic, sediment-free systems, is characterized by isotopic signature ( $\delta^{13}\text{C-CH}_4$ ) typically between -10 ‰ and -18 ‰ (e.g., [Welhan, 1988](#); [Botz et al. 2003](#)) and a concentration generally ranging from 10<sup>-4</sup> and 0.5 vol.%. Geothermal fluids from hydrothermal systems have methane concentrations between 0.01 and 1 vol.% and  $\delta^{13}\text{C-CH}_4$  values between -17 ‰ and -29 ‰. Nevertheless, hydrothermal geothermal systems can also release variable amounts of biotic methane, generally thermogenic, leading the total CH<sub>4</sub> concentration to exceed 1 vol.%. Thermogenic methane has  $\delta^{13}\text{C-CH}_4$  values typically ranging from -55 to -30 ‰, even though highly mature gas may reach values of -20 ‰ ([Schoell, 1988](#); [Shuai et al., 2018](#)) and low maturity gas can have  $\delta^{13}\text{C-CH}_4$  values down to -75 ‰ ([Milkov and Etioppe, 2018](#)). Microbial methane is normally characterized by  $\delta^{13}\text{C}$  values lower than -55 ‰ ([Whiticar, 1999](#)). Thermogenic methane is also associated with higher gaseous hydrocarbons (ethane to butane) and oil, whose concentrations are variable according to the maturity of the source rock.

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593 The SHGSs recognized so far have actually CH<sub>4</sub> concentrations exceeding 1 vol.% with isotopic  
594 composition compatible with a biotic (thermogenic) origin ( $-54 ‰ \leq \delta^{13}\text{C-CH}_4 \leq -24 ‰$ ), produced  
595 by thermal maturation of organic matter or oil cracking in the sediments.  
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600 Combining in Normal Probability Plots (NPP) CH<sub>4</sub> concentration and  $\delta^{13}\text{C-CH}_4$  data of known  
601 SHGSs and those of geothermal-volcanic sites (Supplementary Material) (Fig. 3a-b), we verified  
602 the presence of two populations divided by threshold values of 1.5 vol.% and approximately -30 ‰,  
603 respectively. These thresholds can be considered as statistical constraints of hypothetical SHGS  
604 population and will be taken into account for further identification of SHGSs, although in particular  
605 cases, as discussed above,  $\delta^{13}\text{C-CH}_4$  of SHGSs can be higher than -30 ‰. For these systems,  
606 detailed geochemical studies are necessary to investigate the source of methane and the generation  
607 mechanisms, as done for the case of the Songliao Basin, whose thermogenic gas identification was  
608 possible thanks to clumped-isotope analyses (Shuai et al. 2018).  
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616 *Proposed location for Figure 3a-3b*  
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#### 620 4.1.2 Geological constraints

621 SHGSs have a hybrid geological and geochemical configuration, and are therefore half-way  
622 between a hydrothermal (conventional) geothermal system *sensu strictu* and a hydrocarbon-bearing  
623 sedimentary system. Such a configuration can occur within sedimentary basins in geodynamically  
624 active regions, especially those related to extensional domains as rift, back-arc and forearc basins,  
625 both onshore and offshore. SHGSs may be characterized by the presence of magma chambers or  
626 igneous intrusions (sills and/or dikes), in proximity of active volcanoes or close to hydrothermal  
627 areas characterized by medium-high temperatures and anomalous heat flux. The sedimentary  
628 domain, hosting the “geothermal” system, can be characterized by rocks rich in organic matter,  
629 more or less evolved into mature source rocks, or by complete petroleum systems, including source,  
630 reservoir and cap-rocks. The simultaneous occurrence of such “geothermal” and “sedimentary”  
631 features, in variable combinations, is a requisite for the identification of a SHGS (Fig. 4).  
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639 Accordingly, it is expected that those gas-geochemical features defined in Section 4.1.1 actually  
640 occur in the above described geological settings.  
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## 4.2 Identification of new SHGSs

### 4.2.1 A new list of potential SHGSs

According to what has been discussed above, the identification of potential SHGSs has been carried out starting from a global selection of the CO<sub>2</sub> dominant gas discharges, in surface manifestations and boreholes, with <sup>13</sup>C-depleted CH<sub>4</sub> ( $\delta^{13}\text{C} \leq -30 \text{ ‰}$ ) exceeding 1.5 vol.%. More than 200 published works have been examined. The works that report complete CO<sub>2</sub> and CH<sub>4</sub> composition and isotopic data, fulfilling the constraints established above, are listed in Table 2. For the sites that had more than one data set acquired in different times, the mean values have been considered.

In addition to the previously described SHGSs (Guaymas Basin, Salton Sea, Lusi, Tiber Delta-Fiumicino and Songliao Basin), 33 new sites have been identified (Tab.2; Fig. 5).

The newly identified SHGSs are located in the USA (California, Wyoming, Colorado, West Virginia; n. 2, 3, 13, 14, 15, 16, 24, 25, 36, 37, 38), Italy (7, 8), Hungary (26, 27), Slovenia (28), Poland (33), Taiwan (6, 34), Thailand (17, 18, 19, 35), China (21, 22, 23), Australia (29, 30, 31) and New Zealand (11, 12, 32) (Fig. 5).

#### *Proposed location for Figure 5*

The gas-geochemistry features of the 38 selected SHGSs (newly and previously identified) are shown in the molecular and isotopic composition diagrams of Fig.6 a-d, where they are compared with volcanoes, conventional geothermal systems (CGS) and hydrocarbon systems. Volcanic-geothermal gas data are reported in *Supplementary Material*.

Figures 6a and 6b clearly highlight the hybrid geochemical characteristics of the SHGSs compared to volcanoes, CGS and hydrocarbon systems. It is worth noting that about 15 volcanic-geothermal sites have high CH<sub>4</sub> concentrations, exceeding 1.5 vol% (Fig. 6a). Isotopic data from these sites, however, are not available and we could not label them as SHGSs. Therefore, these sites would deserve further investigations. The inorganic origin of CO<sub>2</sub> (with possible minor organic component in some cases) is mainly related to magma degassing (Fig. 6c). The biotic origin of CH<sub>4</sub> is mainly related to high-maturity source rocks (Fig. 6d), as expected because of the influence of the relatively high temperatures. Salton Sea and Songliao Basin (n. 4, 20) gases are the systems with more <sup>13</sup>C-enriched thermogenic CH<sub>4</sub>, corresponding to high maturity source rocks. In Songliao the hydrocarbon generation temperatures reached 230 °C (Shuai et al., 2018). A few low maturity (T<sub>LM</sub>) gases, related to the first stages of catagenesis and to mixing of thermogenic and microbial gas, occur (e.g., Laghi del Vescovo, n. 10). Three SHGSs seem to involve methane of dominant



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711 microbial origin (Australian sites n. 29-30-31, Colliery, Darkes Forest and Collinsville,  
712 respectively).  
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717 *Proposed location for Figure 6a-6d*  
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#### 720 **4.2.2 Spatial analysis and mapping of SHGS prone areas**

721 To identify additional potential SHGS prone areas, we spatially and statistically analysed the  
722 peculiar geological features characterizing the identified SHGSs described above, i.e. (a) heat flow,  
723 (b) sediment thickness of the basins, (c) distance from volcanic systems and (d) distance from  
724 hydrocarbon fields.  
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727 Spatial analysis of all collected data were conducted in GIS environment by using ArcGIS-10.5  
728 version (copyright © 1999-2016 ESRI Inc.). The point layer relative to the identified SHGSs was  
729 overlaid on the geological features listed above and pointed out with the letters (a), (b), (c) and (d).  
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732 The sources of these geological layers, in raster and vector format, are:  
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- 734 a) Heat flux map (1°x 1° grid resolution), obtained from the Global Heat Flow Database of the  
735 International Heat Flow Commission ([Global Heat Flow Database](#));  
736  
737 b) Sediment thickness, derived from the Global Sediment Map (1°x 1° grid resolution) by [Laske](#)  
738 [and Masters \(1997\)](#);  
739  
740 c) Volcanoes of the World Geodatabase ([Global Volcanism Program, 2013](#));  
741  
742 d) Hydrocarbon fields, from PETRODATA Dataset ([Päivi et al., 2007](#)).  
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744 The *extract multivalued to points* tool in ArcGIS was used to assign the values of the grid layers (a)  
745 and (b), to the SHGS point layer. Whereas, the *near distance* tool was used to calculate the distance  
746 of each SHGS from the nearest volcano and from the boundary of the nearest hydrocarbon field.  
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748 Obtained data are presented in Table 3.  
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750 In order to define the range of population variability of each parameter (a), (b), (c) and (d), the 95%  
751 confidence limits for the mean were calculated (Table 4). These limits were used to categorize the  
752 variables (a), (b), (c) and (d) adopting a binary code “0” and “1”, outside and within the 95%  
753 confidence limit, respectively. The categorization was necessary to apply a multiple correspondence  
754 analysis (MCA) to define the association among the variable categories and to recognize those with  
755 similar profile. In particular, MCA highlights that (a), (c) and (d) with code “1” are correlated,  
756 while (b) is an independent variable (Fig. 7). Therefore, the co-existence of the three factors (a), (c)  
757 and (d) within the 95% confidence interval represents a first important diagnostic constraint for the  
758 occurrence of SHGS prone areas. In these areas, the existence of fluids, in seeps or reservoirs, with  
759 the geochemical characteristics discussed above, is probable but shall be investigated successively.  
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770 In order to map prone SHGS areas, the geological layers (a), (c) and (d) were classified, by Raster  
771 Calculator tool in ArcGIS, into binary grids using “0” and “1” codes, outside and within the 95%  
772 confidence limit, respectively. The binary grids were then summed to obtain a map of potential  
773 SHGS areas (Fig. 8). Since the SGHS are by definition within in a sedimentary basin, the obtained  
774 output raster was back-transformed in a vector polygon layer and intersected with Sedimentary  
775 Basins of the World Map (Robertson Basins and Plays - Tellus TM).  
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780 The resulting intersection map represents the global distribution of the SHGS prone areas. These  
781 areas are located in:  
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- 783 - western regions of North America, especially in the Great Plain Basin, and in the fore-arc  
784 and back-arc basins of the western part of South America, (i.e. Arauco Lebu, Linares  
785 Temuco, san Jorge, Magallanes and Ucayali);
- 786 - Europe, in the Italian neogenic basins (i.e. southern Po Plain, Ripi, Gela and Hyblean  
787 foreland), in the divergent basins around the Massif Central (i.e. basin of Paris, Rhine,  
788 Aquitaine and Bresse), in the Pannonian Basin, in part of the Southern and Northern Aegean  
789 Basin and in Central Turkey (Adana basin);
- 790 - Northern Africa and in particular in the intracratonic basins of Illizi Ghadames, Douela, Rio,  
791 central Atlas and western Sahara;
- 792 - Middle East, in the divergent basins of Sana, Tabuk and central Iran;
- 793 - part of the Far East, in particular in the divergent chinese basin of Shauxi and Subei, in the  
794 malaysian retro-arc basins of Greater Sorawak and Pamusian Tarakan, in the fore-arc  
795 Visayan Basin (Philippines), in the back and fore-arc basins of northern Japan (Niigata-  
796 Akita basins);
- 797 - back-arc basin of Western Kamchatka;
- 798 - Eastern Oceania and Northern New Zealand, in particular in the Otway and Taranaki basin.

800 The occurrence in these areas of fluids with SHGS characteristics (defined in section 4.1.1) shall be  
801 investigated in future detailed research.  
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813 *Proposed location for **Figure 7***

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816 *Proposed location for **Figure 8** (The Authors request full page image)*  
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## 5. Environmental and energy resource implications of SHGSs

As anticipated in Introduction (chapter 1), SHGSs may have implications for energy resource exploration, and global climate change studies. SHGSs can in fact host source rocks with enhanced thermal maturity. In certain cases, it is possible that the development of hydrocarbons in the sedimentary rocks is facilitated by anomalous thermal regimes. These hydrocarbon systems may not occur in conventional petroleum system settings, and as such they may not be considered within the standard target areas of petroleum exploration. Therefore, SHGSs can represent frontier resources for natural gas exploration. The over-mature source rocks, induced by anomalous thermal status, typically release dry gas, characterized by high methane/ethane+propane ratios. Such high ratios could be misinterpreted as due to microbial origin but isotopic analyses shall be always performed to determine the gas origin. In addition, the exploitation of the SHGSs could open new energy scenarios such as the development of the co-produced system that use water-waste from oil gas fields for indirect and direct geothermal application. The co-produced systems for direct geothermal uses (i.e. district heating) have been successfully employed in some basins as the Pannonian (Hungary) and Paris Basin (France), which actually have been identified as potential SHGS areas in our analysis (see Fig.8), whereas for the indirect applications (power production) this technology is yet scarcely developed.

Moreover, SHGSs can be a significant natural source of greenhouse gas ( $\text{CO}_2$  and  $\text{CH}_4$ ) for the atmosphere. The importance and meaning of these gases, and their natural sources, in climate studies are discussed in a wide body of literature (e.g., [Ciais et al., 2013](#)). Surface manifestations of hydrocarbons (seepage) are today recognized as a major natural source of atmospheric methane (e.g., [Ciais et al., 2013](#); [Etioppe, 2012](#); [Schwietzke et al. 2016](#)). These sources, however, included only mere sedimentary (gas-oil seeps, mud volcanoes) and geothermal-volcanic manifestations (mofettes, fumaroles, volcano-crater degassing), and SHGSs have not been specifically considered. SHGS degassing dynamics may have a peculiar role in this respect.  $\text{CH}_4$  occurring within the sedimentary sequences may not have sufficient pressure to migrate autonomously but it can reach the surface thanks to the occurrence of  $\text{CO}_2$  flows, which is typical of SHGSs. Therefore, the  $\text{CH}_4$  “stripping” process operated by  $\text{CO}_2$  is a peculiar feature of SHGSs. Gas flux surveys in SHGSs worldwide may contribute to better estimate the global geological  $\text{CH}_4$ - $\text{CO}_2$  emissions to the atmosphere.

We note, then, that SHGSs can represent specific hazardous sites due to the explosive properties of methane. Methane can lead to explosions when its concentration is in a range of approximately 5–10 vol.% in the presence of oxygen. A level of 5 vol.% is referred to as the Lower Explosive Limit (LEL). A concentration of 0.5 vol.%  $\text{CH}_4$ , (i.e., 10% of the LEL), should be considered the limit

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888 above which mitigation measures must be taken (Etiopie, 2015). In many instances (see Table 2,  
889 Fig. 6a-6b), the concentrations of CH<sub>4</sub> in SHGSs may approach the explosive range, whereas CH<sub>4</sub>  
890 concentration in pure geothermal and petroliferous (oil or gas) seeps is generally outside this range.  
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## 896 **6. Conclusions**

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898 This work provides a review of Sediment-Hosted Geothermal Systems (SHGSs), and proposes  
899 methodological criteria for their definition and identification, based on integrated geological and  
900 geochemical factors. SHGSs are hybrid systems where geothermal and sedimentary domains  
901 interact, leading to mixtures of inorganic and biotic gases, with relevant environmental and energy  
902 resource implications (Fig. 9). A few SHGSs recognized in previous works resulted to have  
903 important analogies and recurring features, which have been used as preliminary constraints to  
904 identify new potential SHGSs. The analogies include the existence of gas flows dominated by  
905 inorganic CO<sub>2</sub> associated with variable amounts of biotic (microbial or thermogenic) CH<sub>4</sub>, usually >  
906 1.5 vol.%, occurring within sedimentary basins in tectonically active regions, with anomalous heat  
907 flow (mainly between 80 and 160 mW/m<sup>2</sup>) due to the presence of geothermal or volcanic systems,  
908 sills and/or deep magma intrusions. Examining CO<sub>2</sub>-rich systems known in the literature, the  
909 peculiar gas-geochemical features (isotopic and molecular) of SHGSs previously recognized have  
910 been used as first diagnostic tool to identify 33 new SHGSs in Northern America, Europe, Asia and  
911 Oceania. Statistical and spatial analysis of geological data related to the 33 SHGSs, including heat-  
912 flow, sediment thickness and geographic distances from volcanic centers and petroleum fields,  
913 allowed to map additional, potential SHGS areas in all continents.  
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923 The potential SHGS areas mapped in this work can represent zones of significant emission of  
924 methane to the atmosphere, potential sites with gas-hazard, and new targets for petroleum and  
925 geothermal exploration. This SHGS map can be refined on the basis of more detailed geological  
926 analysis and new gas-geochemical data. CH<sub>4</sub> clumped-isotopes, in particular, can be beneficial in  
927 the assessment of methane origin, which is still ambiguous in several cases, distinguishing between  
928 thermogenic gas (produced up to 250°C) and magmatic or post-magmatic gas (produced at T>300-  
929 400°).  
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936 *Proposed location for Figure 9*

## 937 **Acknowledgements**

938  
939 This work is a contribution to the Deep Energy Community of the Deep Carbon Observatory.  
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## Figure captions

**Figure 1:** Sketch of the sequence of SHGS identification criteria. Examining CO<sub>2</sub>-rich systems known in the literature, the peculiar gas-geochemical characteristics (isotopic and molecular) of previously recognized SHGSs, have been used as a first diagnostic tool to identify new SHGSs. Statistical and spatial analysis of geological data related to the new SHGSs, including heat-flow, sediment thickness and geographic distances from volcanic centers and petroleum fields, has allowed to map additional, potential SHGS areas in all continents.

**Figure 2.** Location and simplified cross-sections (not to scale) of the previously identified SHGSs. (a) Guaymas Basin (modified after [Lizarralde et al., 2007](#)) (b) Salton Sea (modified after [Bennett, 2011](#)); (c) Lusi (modified after [Satyana, 2008](#)). (d) Tiber Delta-Fiumicino SHGS (modified after [Carminati and Doglioni 2012](#)). (e) Songliao Basin (modified after [Wang et al., 2016](#)), HTB: Hai Tan Basin, Tanlu G-H-R: Graben and horst range of the northern Tanlu Strike-Slip Fault System, SA Belt: Sikhote-Alin Orogenic Belt.

**Figure 3.** Normal Probability Plots (NPP) of methane concentration (a) and  $\delta^{13}\text{C-CH}_4$  (b) in SHGS, volcanoes and conventional geothermal systems. The deviation from a normal distribution is recorded at 1.5 vol.% and around -30 ‰, respectively.

**Figure 4.** Conceptual sketch of a SHGS (hybrid system) and relationship with the endmembers, volcano-geothermal and hydrocarbon systems. The sketch is not to scale.

**Figure 5:** Global distribution of the newly identified SHGSs (brown dots) in North America (a), Europe (b) and, Eastern Asia and Oceania (c). Black dots refer to SHGSs identified in previous works. Numbers refer to Table 2.

**Figure 6:** Gas molecular and isotopic geochemical diagrams of CO<sub>2</sub> and CH<sub>4</sub> in SHGSs and comparison with volcano, conventional geothermal (CGS) and hydrocarbon systems. Volcanic-geothermal data are described in *Supplementary Material*. Hydrocarbon gas data are from [Sherwood et al. \(2017\)](#) and [CGG \(2015\)](#). a) CH<sub>4</sub> vs CO<sub>2</sub> concentration. Some CGSs and volcanoes have relatively high CH<sub>4</sub> concentrations (> 1.5 vol.%, dashed line), these samples lack isotopic data or have  $\delta^{13}\text{C-CH}_4$  values higher than the SHGS threshold (-30 ‰, see diagram 6b) so that the SHGS attribution is not possible at this stage. b)  $\delta^{13}\text{C-CH}_4$  vs CH<sub>4</sub> concentration; c)  $\delta^{13}\text{C-CO}_2$  vs CO<sub>2</sub> concentration; isotopic CO<sub>2</sub> genetic fields are from [Jenden et al., \(1988\)](#) and [Etiope et al., \(2009\)](#). Tm thermomethamorphism; M-M magma-mantle degassing; SM secondary methanogenesis; OB oil biodegradation; O organic; d)  $\delta^{13}\text{C-CH}_4$  vs  $\delta^2\text{H-CH}_4$  (redrawn after [Etiope, 2017](#)). M microbial; T thermogenic; A abiotic; MCR microbial carbonate reduction; MAF microbial acetate fermentation; ME microbial in evaporitic environment; T<sub>H</sub> thermogenic high maturity; T<sub>LM</sub> thermogenic low maturity; GM geothermal and magmatic; S serpentized rocks; PC Precambrian shields. The legend is the same for all diagrams, the green areas in diagrams a, b and c are relative to hydrocarbon systems.

**Figure 7:** Multiple Correspondence diagram among the variable a) HF heat flow; b) ST Sediment thickness; c) dV distance from nearest volcano; d) dH distance from nearest hydrocarbon field. Code “0” and “1” are relative to values (rounded-up) outside and within the 95% confidence limit, respectively (see Tab. 4). In particular, for a) and b) the range values were considered, whereas for the variables c) and d) the maximum confidence limit values were considered. The light orange area shows the correlation among the variables a), c) and d).

**Figure 8:** Workflow relative to the mapping of SHGS prone areas. Top: input raster dataset; Bottom: resulting global map. The location of palaeo-SHGS is from [Svensen et al., 2003](#); [Svensen et al., 2015](#); [Jones et al., 2016](#); [Jamtveit et al., 2004](#).

**Figure 9:** SHGS conceptual geological sketch (introduced in figure 4) integrated with geological and geochemical parametrization resulting from the present study. In particular, the main gas-geochemical features are summarised for the SHGSs (hybrid system) and for the endmembers, volcano-geothermal and hydrocarbon systems. Related CO<sub>2</sub> and CH<sub>4</sub> genetic processes are also specified (from [Etiope and Sherwood, 2013](#)). The sketch is not to scale.

**Chapter 3**

Literature review on SHGS

**Subch. 4.1**

Definition of geochemical and geological constrains

**Subch. 4.2.1**

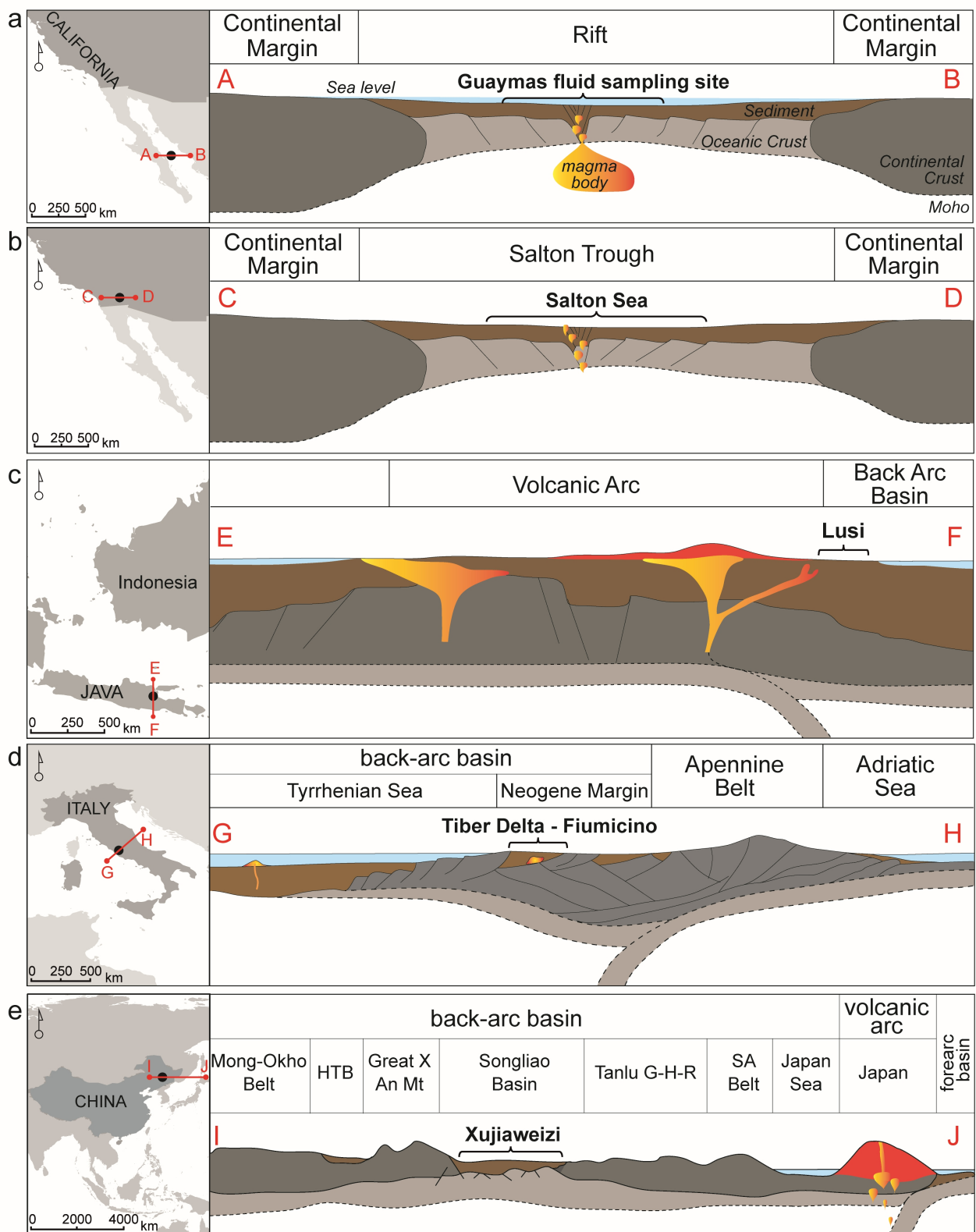
Review of worldwide CO<sub>2</sub>- rich gas occurences and identification of new SHGSs

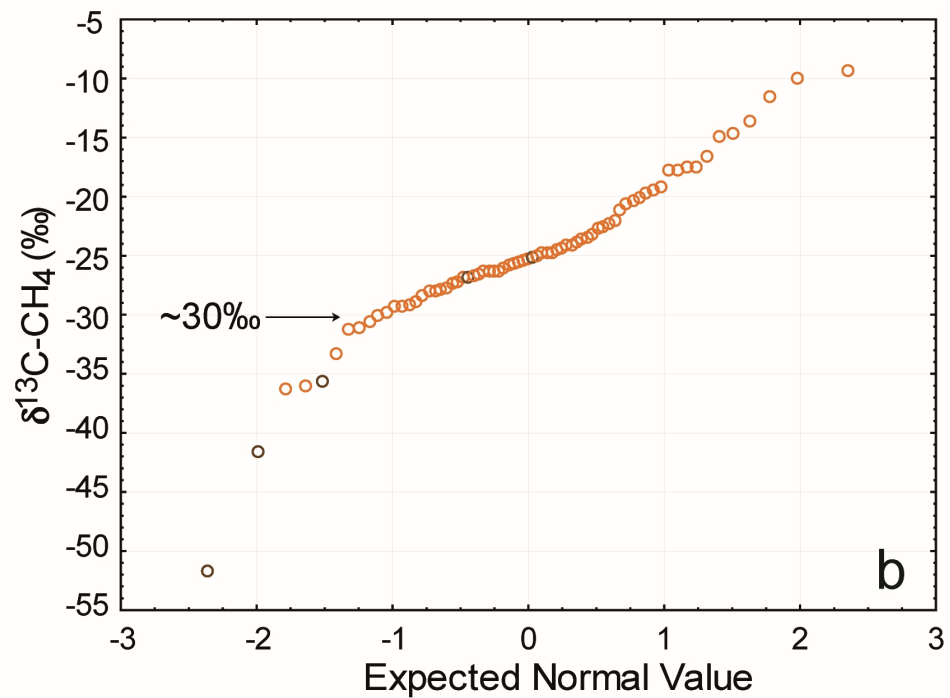
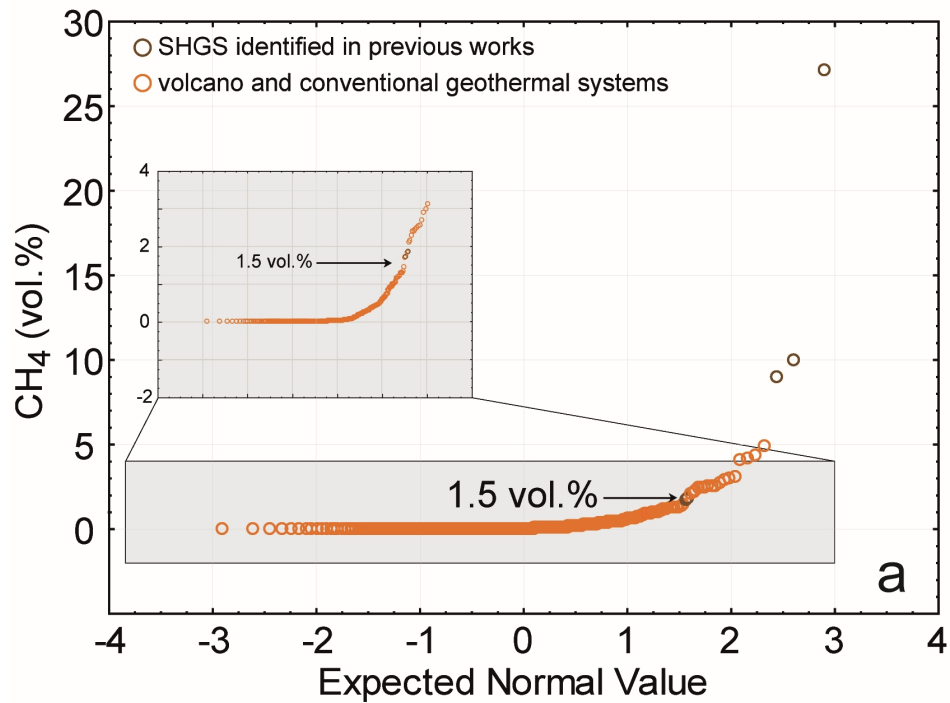
**Subch. 4.2.2**

Statistical and spatial analysis of identified SHGSs

**Subch. 4.2.2**

Mapping of SHGS prone areas

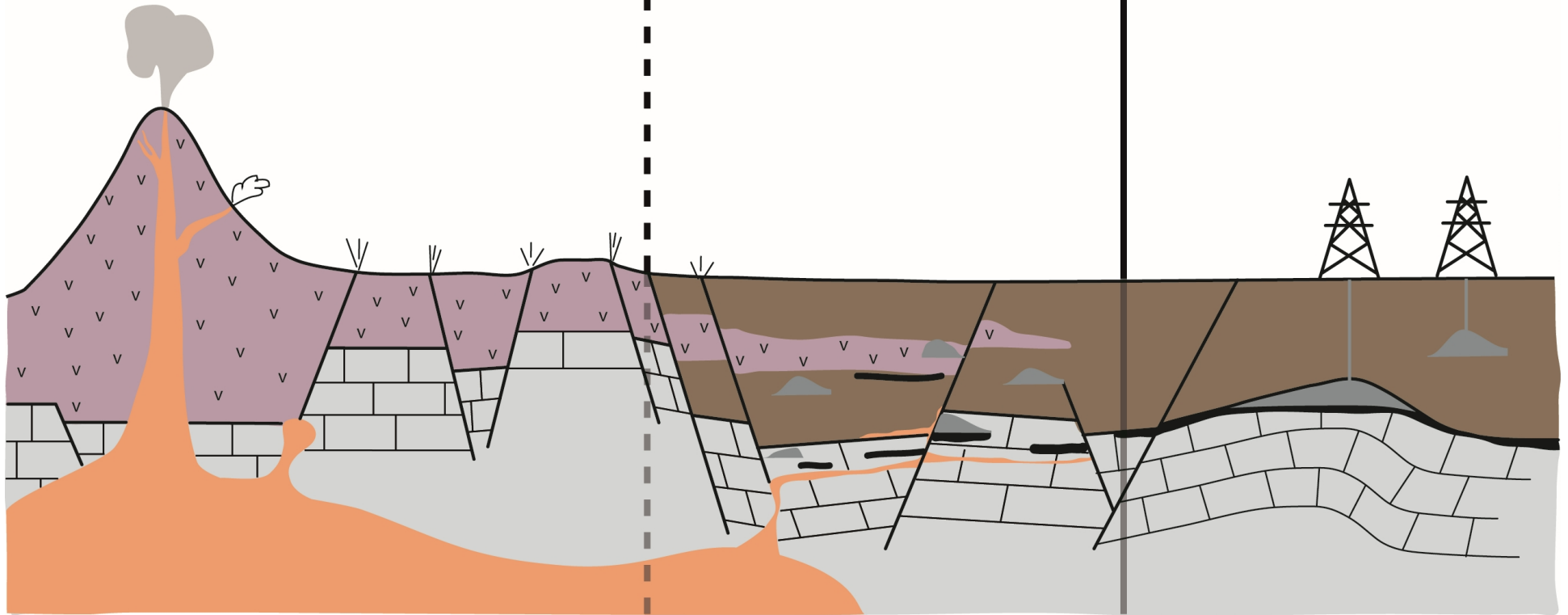




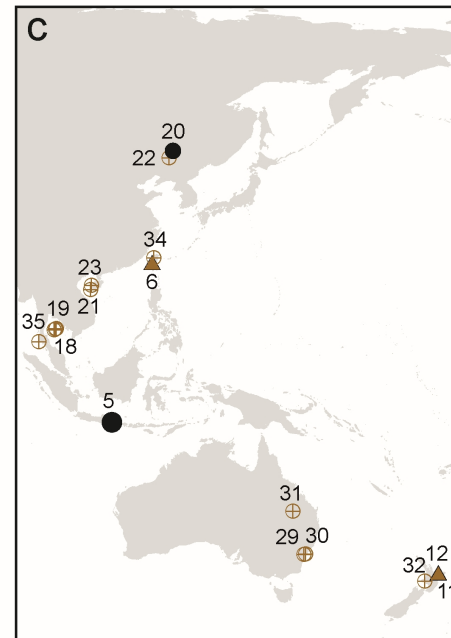
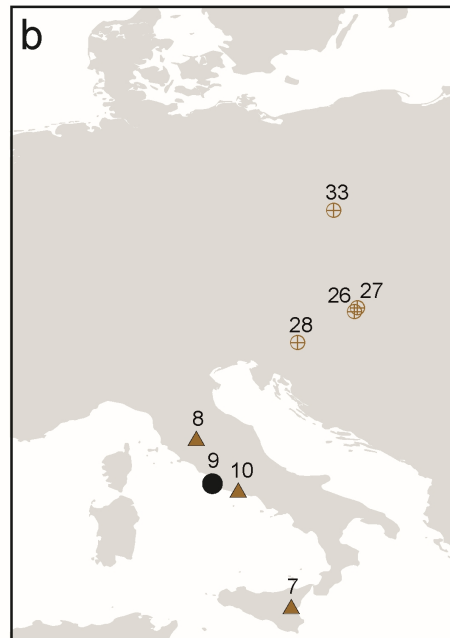
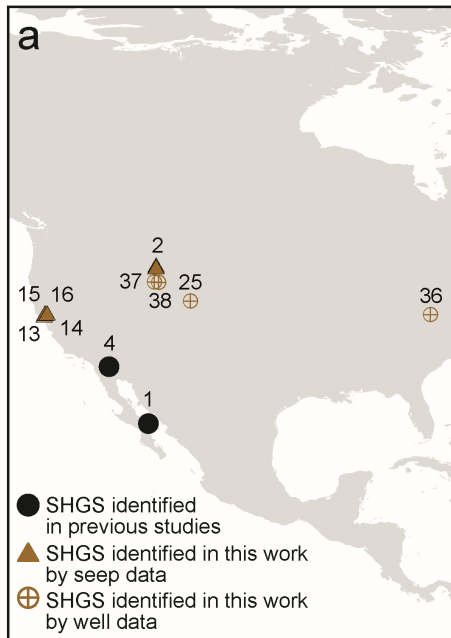
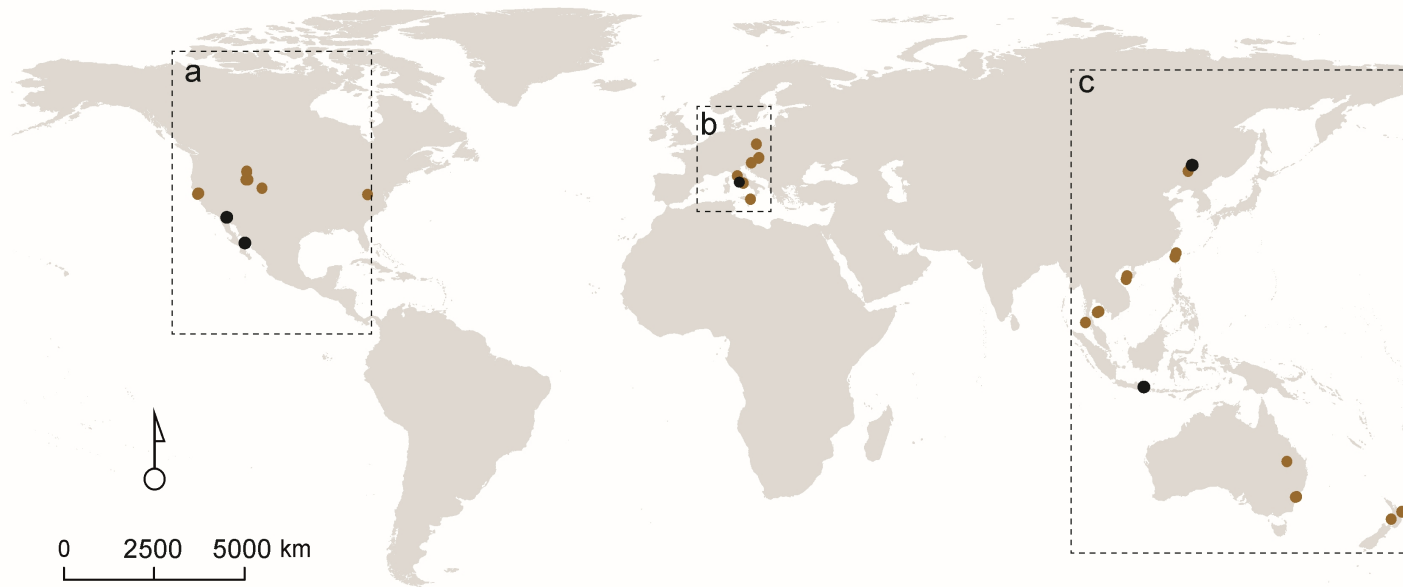
# Volcano & Hydrothermal Geothermal System

# SHGS (Hybrid system)

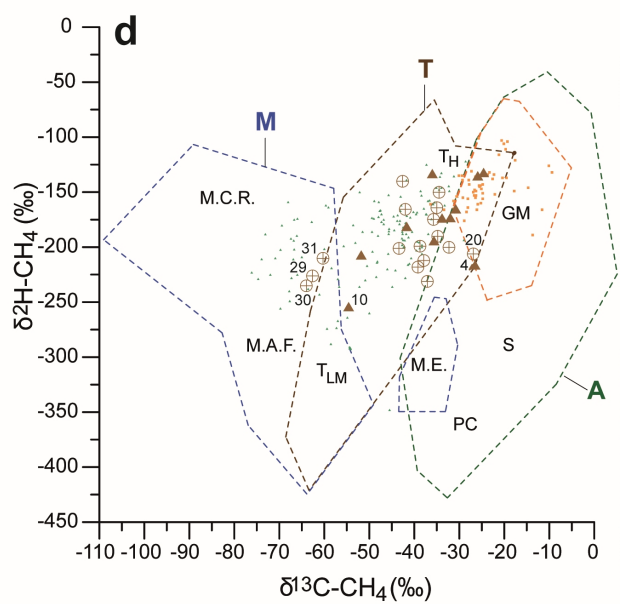
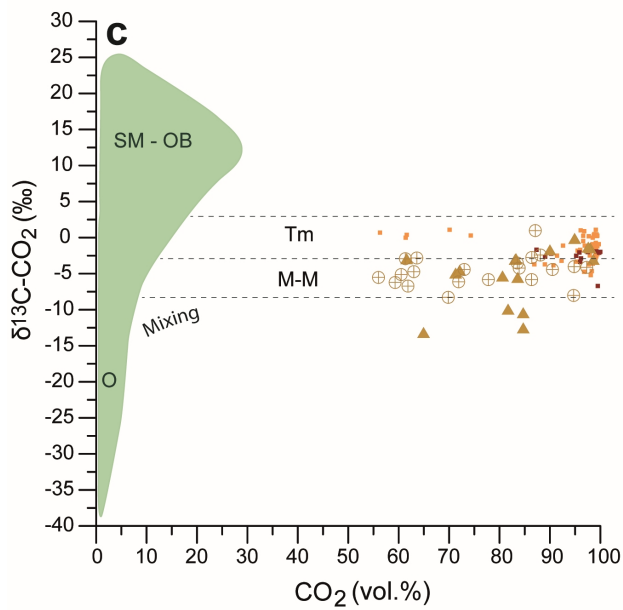
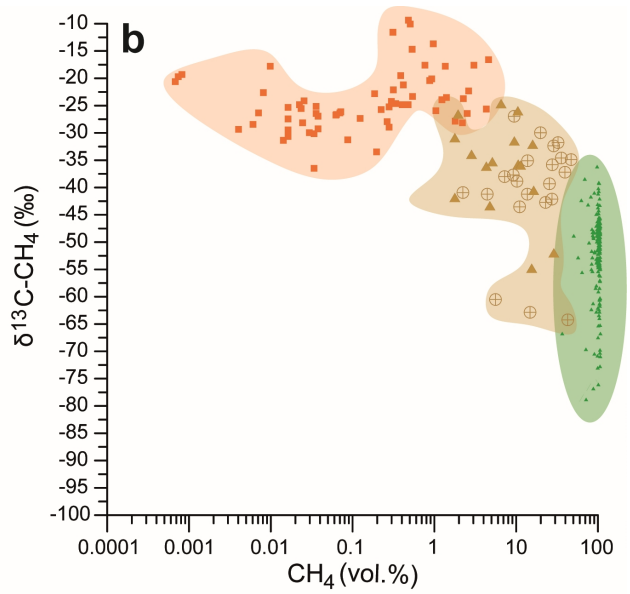
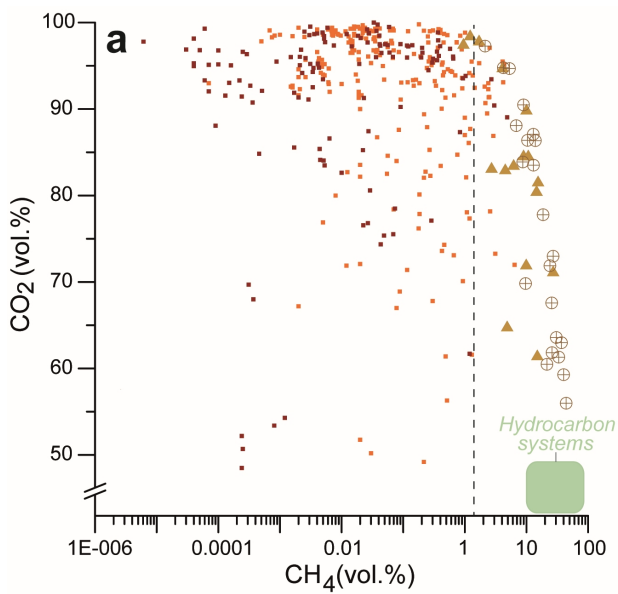
# Hydrocarbon Sedimentary System



- magma bodies
- volcanic deposits
- sedimentary clastic deposits
- crystalline basement
- volcanic plume
- limestones
- natural gas
- oil
- well
- surface manifestation
- fumarole







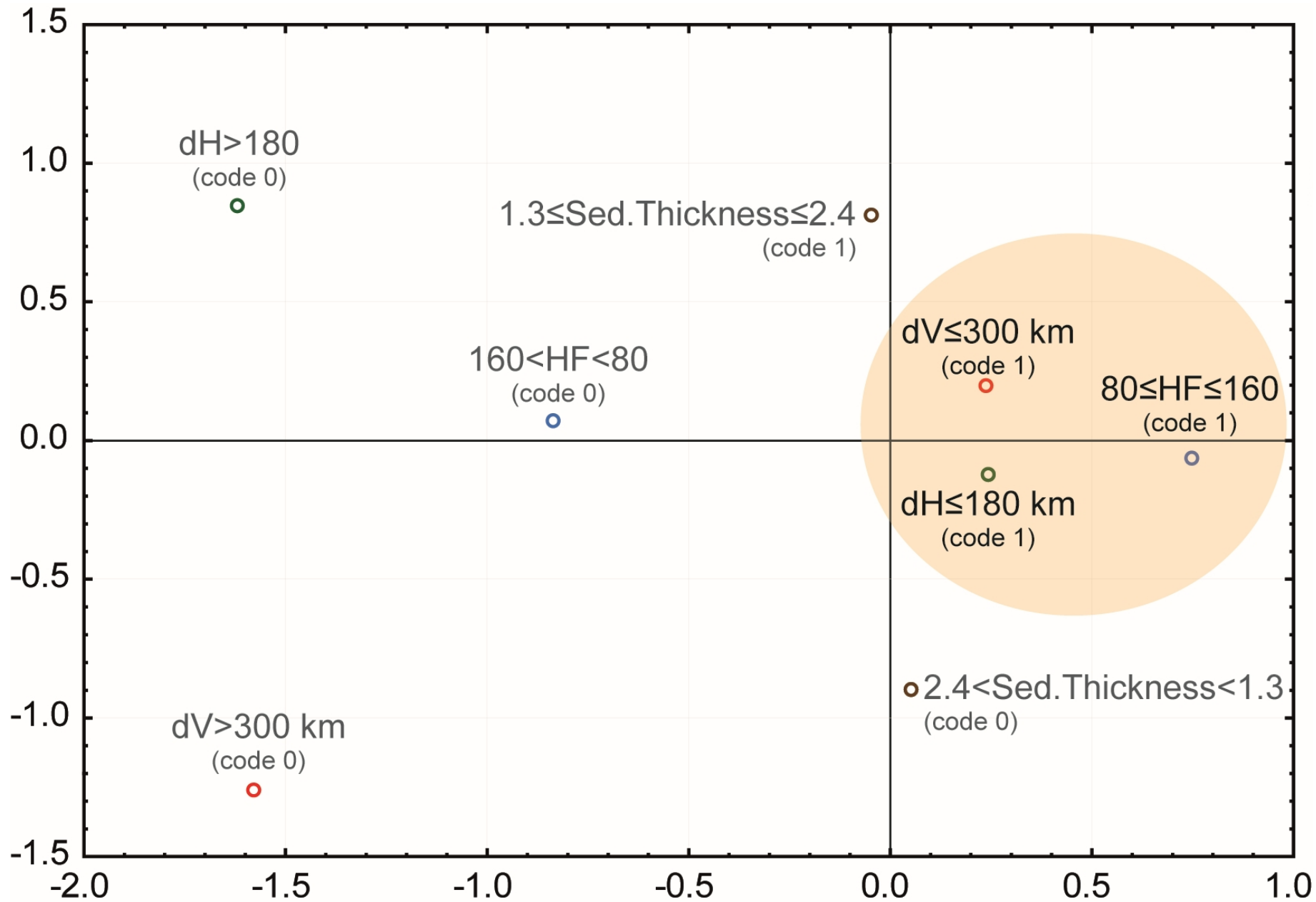
▲ SHGS (seep)

⊕ SHGS (well)

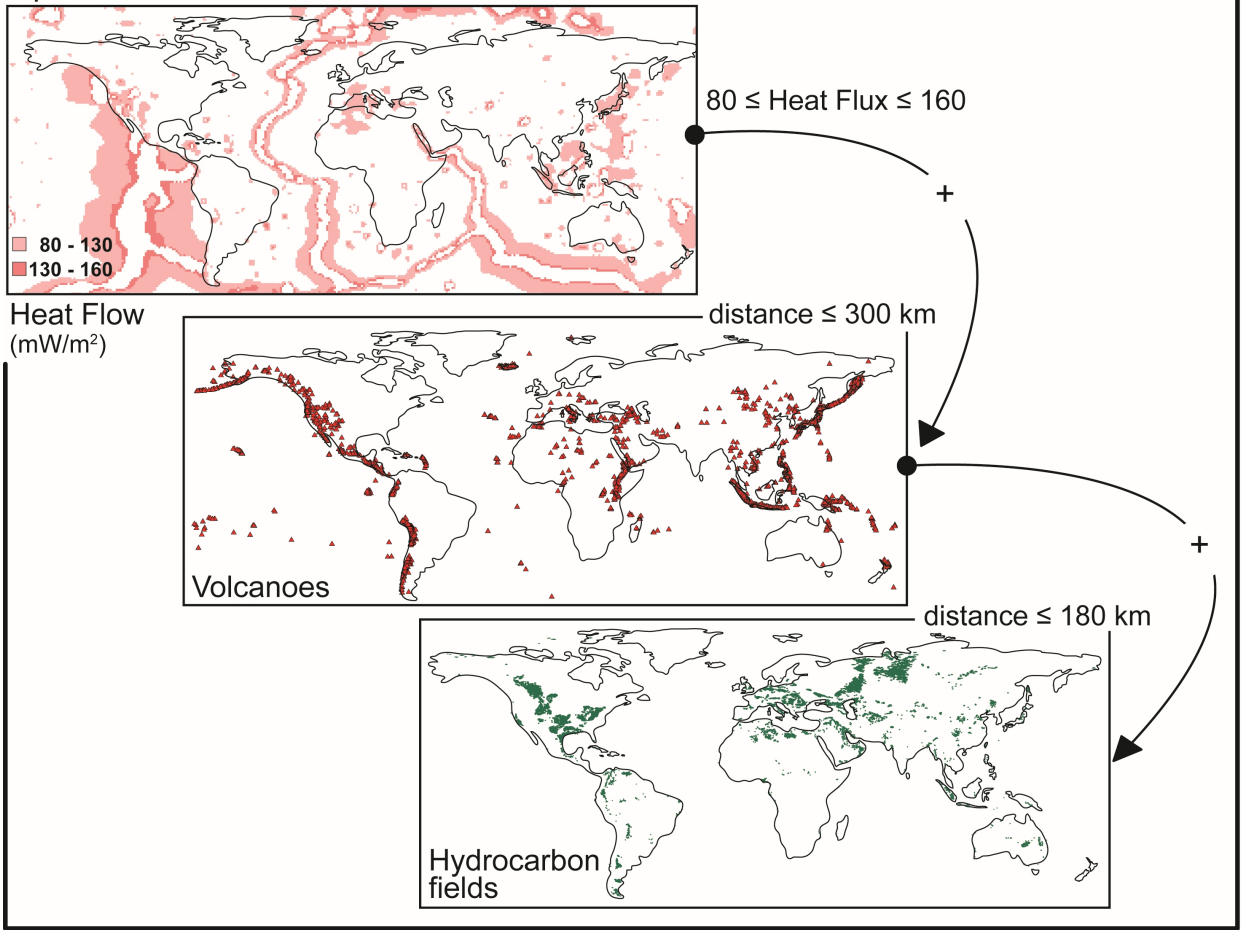
■ CGS

■ Volcano

▲ Hydrocarbon seep

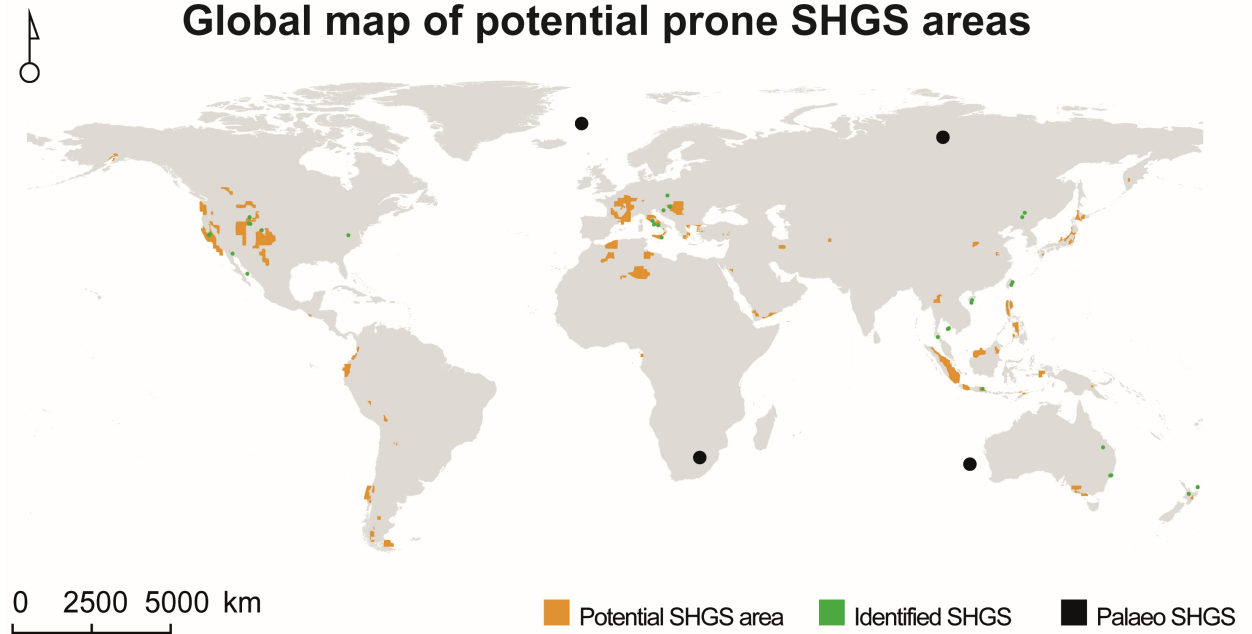


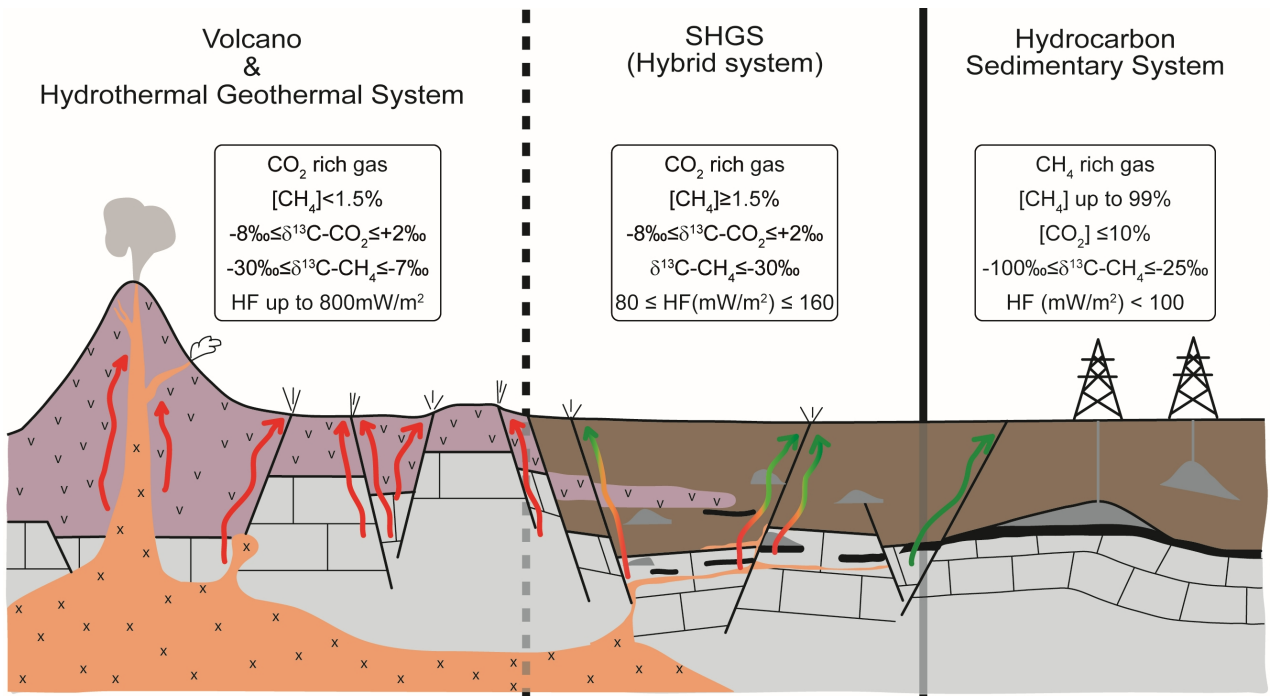
### Input Raster



### Output Raster

## Global map of potential prone SHGS areas





CO<sub>2</sub> rich gas  
 [CH<sub>4</sub>] < 1.5%  
 -8‰ ≤ δ<sup>13</sup>C-CO<sub>2</sub> ≤ +2‰  
 -30‰ ≤ δ<sup>13</sup>C-CH<sub>4</sub> ≤ -7‰  
 HF up to 800 mW/m<sup>2</sup>

CO<sub>2</sub> rich gas  
 [CH<sub>4</sub>] ≥ 1.5%  
 -8‰ ≤ δ<sup>13</sup>C-CO<sub>2</sub> ≤ +2‰  
 δ<sup>13</sup>C-CH<sub>4</sub> ≤ -30‰  
 80 ≤ HF (mW/m<sup>2</sup>) ≤ 160

CH<sub>4</sub> rich gas  
 [CH<sub>4</sub>] up to 99%  
 [CO<sub>2</sub>] ≤ 10%  
 -100‰ ≤ δ<sup>13</sup>C-CH<sub>4</sub> ≤ -25‰  
 HF (mW/m<sup>2</sup>) < 100

**Gas Origin**

<b>CO<sub>2</sub></b>	<b>inorganic</b>	<b>organic</b>	
	Magma-mantle degassing and thermometamorphism reactions		Thermogenesis (e.g. kerogene decarboxilation)
<b>CH<sub>4</sub></b>	<b>abiotic</b>	<b>biotic</b>	
	Magmatic and post-magmatic high T reaction	<i>Thermogenic</i> Thermal cracking of organic matter (catagenesis) or oil at high T (70-250°C)	<i>Microbial</i> Diagenesis of sediments (up to 60-80 °C)

- Magma body
- Sedimentary clastic deposits
- CO<sub>2</sub>- dominated gas
- Volcanic plume
- Volcanic deposits
- Cristalline basement
- CH<sub>4</sub>- dominated gas
- Fumarole
- Limestones
- Natural gas
- CO<sub>2</sub>-CH<sub>4</sub> gas
- Surface manifestation
- Oil
- Hydrocarbon well

SITE	COUNTRY	DOMAIN	GAS DISCHARGE						BASIN		OIL TRACE/ GAS FIELD	HEAT FLUX (mW/m <sup>2</sup> )	REFERENCE
			Type	CO <sub>2</sub> vol.%	CH <sub>4</sub> vol.%	δ <sup>13</sup> C-CO <sub>2</sub> ‰	δ <sup>13</sup> C-CH <sub>4</sub> ‰	δ <sup>2</sup> H-CH <sub>4</sub> ‰	Thickness Sediment (km)	Main lithology			
Tiber-Delta	Italy	back arc basin	bp	98*	1.0* up to 1.7	-2.1 ÷ -0.7	-54.1 ÷ -37	-205 ÷ -162	2	Limestones to clay-sandstones	✓	100 ÷ 250	[1-4]
Salton Sea	California	pull-apart basin	bp+v+g	99*	1.2* up to 1.9	-5.4 ÷ 0.2	-32.7 ÷ -17.6	-270 ÷ -150	0.7 ÷ 4	carbonate	✓	up to 600	[5, 6]
Guaymas Basin	Gulf of California	rift	sv	~90	~10	-6 ÷ 2.7	-50.8 ÷ -43.2	-265 ÷ -123	0.7 ÷ 1	diatomaceous calcareous	✓	up to 453	[7-9]
Lusi	Indonesia	back arc basin	bp+v	71* up to 99	27.1* up to 35	-12.8 ÷ -2.2	-51.8 ÷ -31	-207	2 ÷ 4	clay volcanoclastic- sand, limestone	✓	60 ÷ 100	[10-12]
Songliao Basin	China	retro-arc basin	well	90.5	8.94	-4.4	-26.9	-206	1 ÷ 5	volcanic rocks	✓	50 ÷ 100	[13]

**Tab.1:** Features of the SHGSs characterized in previous works. bp: bubbling pool; v: vent; sv: submarine vent; g: gryphon. \* mean value; [1] Ciotoli et al., 2016; [2] Carapezza et al., 2015; [3] Della Vedova et al., 2001; [4] Northern Petroleum (2002); [5] Mazzini et al., 2011; [6] Younker et al., 1982; [7] Simoneit & Galimov, 1984; [8] Welhan, 1987; [9] Welhan, 1988; [10] Mazzini et al., 2012; [11] Mazzini & Lusi Lab Team, 2017; [12] Tanikawa et al., 2010; [13] Shuai et al., 2018.

ID	LOCATION	COUNTRY/STATE	TYPE	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CH <sub>4max</sub>	C <sub>2+</sub>	H <sub>2</sub>	H <sub>2</sub> S	He	R/Ra <sup>o</sup>	δ <sup>13</sup> C-CO <sub>2</sub>	δ <sup>13</sup> C-CH <sub>4</sub>	δ <sup>2</sup> H-CH <sub>4</sub>	Reference
1*	Guaymas Basin	California	v	90.0	-	10.00	-	-	-	-	-	-	-1.7	-35.6	-194	[1, 2]
2	Heart Lake	Wyoming	v	83.1	10.500	4.53	-	0.015	0.023	0.660	0.067	1.1	-3.0	-43.2	-	[3]
3	Johnson Spring	Wyoming	bp	83.3	12.850	2.71	-	-	-	-	-	0.1	-2.9	-33.8	-173	[4]
4*	Salton Sea	California	bp	98.1	-	1.86	-	0.03	-	-	-	6.5	-1.6	-26.5	-216	[5]
5*	Lusi Crater	Indonesia	bp	73.3	-	24.92	39.85	1.449	-	-	-	5.5	-3	-51.8	-207	[6, 7]
6	Chukou Fault	Taiwan	bp	61.6	-	15.00	33.60	0.290	-	-	-	-	-2.9	-32.0	-173	[8]
7	Salinelle Paternò	Italy	bp	94.9	0.900	4.10	-	0.004	-	-	-	6.5	-0.4	-36.0	-133	[9-11]
8	Torrite di Siena	Italy	bp	98.0	0.330	1.70	-	0.009	-	-	-	-	-1.4	-30.8	-165	[10]
9*	Fiumicino	Italy	bp	98.3	-	1.70	-	0.001	-	-	-	0.2	-1.3	-41.7	-181	[12-14]
10	Laghi del Vescovo	Italy	bp	80.6	4.700	14.60	-	0.002	-	0.016	-	-	-5.3	-54.6	-254	[10]
11	Calypso North	New Zealand	v	83.6	9.370	6.20	-	0.006	-	0.820	-	-	-5.5	-24.6	-132	[15]
12	Calypso North	New Zealand	v	72.1	16.920	9.90	-	0.074	-	1.030	-	-	-4.5	-25.9	-135	[15]
13	The Geysers	Northern California	v	64.9	11.484	4.86	9.39	-	11.860	3.879	0.002	-	-13.1	-35.2	-	[16]
14	Clear Lake	Northern California	v	84.7	-	8.98	53.00	-	-	-	-	-	-12.5	-31.4	-	[17]
15	Sulphur Bank	Northern California	v	84.7	-	10.70	18.20	-	-	-	-	-	-10.4	-35.8	-	[17]
16	Wilbur Spring	Northern California	v	81.7	-	15.40	49.90	-	-	-	-	-	-9.9	-40.4	-	[17]
17	Gulf of Thailand	Thailand	w	55.0	-	43.00	-	2.000	-	-	-	-	-5.5	-34.8	-190	[18]
18	Gulf of Thailand	Thailand	w	63.0	-	33.00	-	4.000	-	-	-	-	-4.7	-37.1	-231	[18]
19	Gulf of Thailand	Thailand	w	71.0	-	27.00	-	2.000	-	-	-	0.18	-4.4	-32.3	-200	[18]
20*	Songliao Basin	China	w	90.5	0.450	8.94	-	0.090	-	-	-	2.2	-4.4	-26.9	-206	[19]
21	Yingqiong Basin	China	w	83.9	6.600	8.70	-	0.700	-	-	-	-	-4.2	-37.6	-	[20]
22	Changling Basin	China	w	77.8	3.200	18.60	-	0.440	-	-	-	-	-5.8	-29.9	-	[20]
23	Dongfang	China	w	63.6	4.700	30.50	-	1.200	-	-	-	-	-2.8	-31.7	-	[20]
24	Sheep Mountain	Colorado	w	97.3	0.666	2.13	-	-	-	-	-	-	-4.1	-40.8	-	[21]
25	Sheep Mountain	Colorado	w	94.8	1.540	4.21	-	-	-	-	-	-	-4.0	-41.1	-	[21]
26	Pannonian System	Hungary	w	88.1	5.090	6.82	-	-	-	-	-	-	-2.4	-37.9	-212	[22]
27	Pannonian System	Hungary	w	86.4	2.870	10.40	-	-	-	-	-	-	-2.7	-43.4	-201	[22]
28	Velenje Basin	Slovenia	w	87.1	-	12.90	-	-	-	-	-	-	1.0	-41.1	0.0	[23]
29	Colliery	Australia	w	86.4	-	13.93	19.80	0.040	-	-	-	-	-5.8	-62.6	-226	[24, 25]
30	Darkes Forest	Australia	w	59.3	-	40.00	--	-	-	-	-	-	-6.2	-64.0	-235	[24, 25]
31	Collinsville	Australia	w	94.7	-	5.30	-	0.050	-	-	-	-	-8.0	-60.3	-210	[24, 25]
32	Taranaki	New Zealand	w	67.6	3.950	25.70	35.00	1.350	-	-	-	-	-0.3	-42.0	-166	[25-27]
33	Walbrzych coal basin	Poland	w	69.8	18.560	9.66	15.50	1.426	-	-	-	-	-8.3	-38.7	-199	[25, 28]
34	Chiayi-Yunshui	Taiwan	w	61.8	11.613	25.97	44.28	0.363	-	-	-	-	-6.7	-35.7	-174.7	[25, 29]
35	Platong	Thailand	w	71.9	0.880	24.00	-	3.561	0.009	-	0.002	-	-6.1	-39.2	-218.0	[25, 30]
36	Wildcat	West Virginia	w	83.5	2.230	13.00	-	0.124	0.005	-	0.106	-	-3.5	-35.0	-164.0	[30]
37	Indian creek	Wyoming	w	61.3	2.730	33.40	-	0.260	-	-	0.114	-	-2.9	-34.5	-150.0	[30]
38	Labarge platform	Wyoming	w	60.5	7.710	21.50	-	0.015	4.005	-	0.592	-	-5.1	-42.7	-140.0	[25, 30]

Tab.2: Molecular and isotopic composition of the gas related to SHGS suggested in this work. Gas composition is in vol.%. Isotopic data:  $\delta^{13}\text{C}$ : ‰ VPDB;  $\delta^2\text{H}$ : ‰ VSMOW;  $R/R_a = ({}^3\text{He}/{}^4\text{He})_{\text{sample}}/({}^3\text{He}/{}^4\text{He})_{\text{atmosphere}}$ ;  $R_a = 1.39 \times 10^{-6}$ . Sediment thickness in km. Heat Flux in  $\text{mW}/\text{m}^2$ . Hyphen: no data. Type: v= vent; bp= bubbling pool; w: well. For the molecular composition mean values are reported for the sites: 5, 6, 7, 13, 14, 15, 16, 29, 32, 33, 34, 38. Asterisk is for SHGSs recognized in previous works and discussed in chapter 3. [1] Welhan & Lupton, 1987; [2] Welhan, 1988; [3] Lowenstern et al., 2015; [4] Merrill et al., 2014; [5] Mazzini et al., 2011; [6] Mazzini et al., 2012; [7] Mazzini & Lusi Lab Team, 2017; [8] Sun et al., 2010; [9] Grassa et al., 2004; [10] Tassi et al., 2012 ; [11] Caracausi et al., 2003; [12] Ciotoli et al., 2013 ; [13] Sella et al., 2014; [14] Carapezza et al., 2015 ; [15] Botz et al., 2002; [16] Lowenstern et al., 1999; [17] Bergfeld et al., 2001; [18] Giggenbach et al., 1997; [19] Shuai et al., 2018; [20] Dai et al., 2009; [21] Jenden et al., 1993; [22] Palcsu et al., 2014; [23] Lazar et al., 2014; [24] Smith et al., 1982; [25] Sherwood et al., 2017; [26] Giggenbach et al., 1997; [27] Hulston et al., 2001; [28] Kotarba & Rice, 2001; 29] Lu & Lin, 1986; [30] Jenden et al., 1988.

ID	LOCATION	COUNTRY	TYPE	Heat Flux (a)	Sediment thickness (b)	Distance from volcanoes (c)	Distance from hydrocarbon fields (d)
1*	Guaymas Basin	California	v	453	0.7	77	652
2	Heart Lake	Wyoming	v	487	1.4	22	42
3	Johnson Spring	Wyoming	bp	487	1.4	38	39
4*	Salton Sea	California	bp	118	1	4	193
5*	Lusi Crater	Indonesia	bp	73	2.3	11	0
6	Chukou Fault	Taiwan	bp	67	0.6	117	0
7	Salinelle Paternò	Italy	bp	103	5.5	18	0
8	Torrite di Siena	Italy	bp	103	1.3	29	40
9*	Fiumicino	Italy	bp	216	2	28	49
10	Laghi del Vescovo	Italy	bp	148	3.4	22	1
11	Calypso North	New Zealand	v	78	0.3	71	241
12	Calypso North	New Zealand	v	78	0.3	68	240
13	The Geysers	Northern California	v	100	1.7	17	54
14	Clear Lake	Northern California	v	100	1.7	13	41
15	Sulphur Bank	Northern California	v	78	1.1	10	44
16	Wilbur Spring	Northern California	v	78	1.1	32	23
17	Gulf of Thailand	Thailand	w	68	4.5	215	326
18	Gulf of Thailand	Thailand	w	68	5.9	200	325
19	Gulf of Thailand	Thailand	w	68	4.7	182	320
20*	Songliao Basin	China	w	65	5	316	154
21	Yingqiong Basin	China	w	73	4.3	160	156
22	Changling Basin	China	w	62	1.9	122	7
23	Dongfang	China	w	74	0.7	98	87
24	Sheep Mountain	Colorado	w	71	0.6	53	7
25	Sheep Mountain	Colorado	w	71	0.6	53	7
26	Pannonian System	Hungary	w	71	1.4	26	0
27	Pannonian System	Hungary	w	71	1.4	32	0
28	Velenje Basin	Slovenia	w	62	0.6	203	45
29	Colliery	Australia	w	72	0.7	241	268
30	Darkes Forest	Australia	w	65	1.2	786	1
31	Collinsville	Australia	w	65	1.2	788	15
32	Taranaki	New Zealand	w	68	1.3	36	0
33	Walbrzych coal basin	Poland	w	66	0.4	134	47
34	Chiayi-Yunshui	Taiwan	w	69	0.9	21	0
35	Platong	Thailand	w	63	0.6	305	256
36	Wildcat	West Virginia	w	51	2.4	1979	0
37	Indian creek	Wyoming	w	99	0.3	529	898
38	Labarge platform	Wyoming	w	139	3.7	125	0

Tab.3: Values of heat flux ( $mW/m^2$ ), sediment thickness (km), distance from nearest volcano (km) and distance from nearest hydrocarbon field (km) for the recognized SHGS.



<b>Geological factor</b>	<b>Samples</b>	<b>Mean</b>	<b>Conf. limit</b>	<b>Conf. limit</b>	<b>Median</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Std.Dev.</b>
<b>a</b>	38	114.4	<b>77.5</b>	<b>156.1</b>	72.5	51.0	453.0	111.5
<b>b</b>	38	1.8	<b>1.3</b>	<b>2.4</b>	1.3	0.1	5.9	1.6
<b>c</b>	38	188.1	<b>73.3</b>	<b>302.9</b>	69.4	3.5	1949.2	349.23
<b>d</b>	38	120.5	<b>57.5</b>	<b>183.5</b>	41.6	0.0	897.9	191.7

*Tab.4: Confidence limit values relative to the selected geological factors: a) heat flux ( $mW/m^2$ ); b) sediment thickness (km); c) distance from nearest volcano (km); d) distance from nearest hydrocarbon fields (km).*

# Sediment-Hosted Geothermal Systems: review and first global mapping

Procesi M.<sup>1</sup>, Ciotoli G.<sup>2,1</sup>, Mazzini A.<sup>3</sup>, Etiope G.<sup>1,4</sup>

<sup>1</sup> Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata 605, 00143 Roma, Italy

<sup>2</sup> Istituto di Geologia Ambientale e Geoingegneria—CNR-IGAG, Roma, Italy Centre for Earth

<sup>3</sup> Centre for Earth Evolution and Dynamics (CEED), University of Oslo, Norway

<sup>4</sup> Faculty of Environm. Science and Engineering, Babes Bolyai University, Cluj-Napoca, Romania

## SUPPLEMENTARY MATERIAL

ID	SITE	COUNTRY	TYPE	CO <sub>2</sub> %	N <sub>2</sub> %	O <sub>2</sub> %	CH <sub>4</sub> %	H <sub>2</sub> %	H <sub>2</sub> S %	He %	Ar %	δ <sup>13</sup> C CO <sub>2</sub>	δ <sup>13</sup> C CH <sub>4</sub>	δ <sup>2</sup> H CH <sub>4</sub>	R/Ra	Ref
1	Deception Island 1	Antarctica	G	98.4	0.820	0.145	0.002	0.068	0.513		0.018					[1]
2	Deception Island 2	Antarctica	G	98.3	0.837	0.203	0.003	0.012	0.591		0.018					[1]
3	Deception Island 3	Antarctica	G	98.6	0.571	0.050	0.005	0.150	0.604		0.012					[1]
4	Copahue volcano 7	Argentina	V	98.5	0.030	0.001	0.019	0.017	1.411		0.000					[1]
5	Copahue volcano 8	Argentina	V	96.0	0.380	0.023	0.068	1.647	1.774		0.002					[1]
6	Copahue volcano 5	Argentina	V	98.9	0.270	0.003	0.366	0.246	0.248		0.001					[1]
7	Copahue volcano 3	Argentina	V	98.0	0.694	0.007	0.369	0.429	0.539		0.002					[1]
8	Copahue volcano 6	Argentina	V	97.3	0.871	0.009	0.397	0.616	0.779		0.003					[1]
9	Copahue volcano 4	Argentina	V	97.0	0.668	0.019	0.576	0.555	1.139		0.003					[1]
10	Copahue volcano 1	Argentina	V	96.1	1.452	0.019	0.644	0.712	1.043		0.006					[1]
11	Copahue volcano 2	Argentina	V	95.8	1.456	0.012	0.648	1.042	0.990		0.005					[1]
12	Copahue volcano 9	Argentina	V	93.8	2.591	0.349	1.027	1.076	1.017		0.050					[1]
13	Copahue volcano 10	Argentina	V	93.5	1.277	0.023	2.696	0.503	2.005		0.006					[1]
14	LSTG-14	Chile	G	92.6	2.2	0.004	0.002	1.4	0.03	0.0003	0.002					[2]
15	LSTG-15	Chile	G	92.7	2.7	0.006	0.002	0.89	0.05	0.0002	0.003					[2]
16	LSTG-17	Chile	G	92.5	3.1	0.002	0.002	1.3	0.05	0.0002	0.002					[2]
17	Lascar volcano 9	Chile	V	85.6	6.716	0.065	0.002	1.215	0.151		0.008					[2]
18	LSTG-16	Chile	G	94.6	2.2	0.011	0.002	0.92	0.07	0.0004	0.004					[2]
19	LSTG-18	Chile	G	91.6	2.9	0.002	0.002	1.4	0.05	0.0002	0.002					[2]
20	LSTG-27	Chile	G	92.3	2.1	0.008	0.002	1.2	0.03	0.0002	0.003					[2]
21	Tacora volcano 4	Chile	V	95.1	1.346	0.004	0.002	0.009	2.760		0.001					[1]
22	Tacora volcano 6	Chile	V	94.2	1.454	0.001	0.002	0.012	3.619		0.002					[1, 2]
23	LSTG-26	Chile	G	93.7	1.7	0.003	0.003	0.98	0.06	0.0002	0.002					[2]
24	Tacora volcano 5	Chile	V	95.9	1.364	0.006	0.003	0.012	2.233		0.002					[1]
25	Lascar volcano 8	Chile	V	91.1	3.663	0.053	0.003	0.666	0.154		0.006					[1]
26	Tacora volcano 7	Chile	V	95.2	1.238	0.003	0.003	0.011	2.915		0.002					[1]
27	Tacora volcano 9	Chile	V	94.3	1.419	0.003	0.003	0.011	3.595		0.002					[1]
28	Tacora volcano 10	Chile	V	94.8	1.322	0.002	0.004	0.010	3.322		0.001					[1]
29	LSTG-23	Chile	G	96.6	0.32	0.000	0.004	0.02	1.1	0.0003	0.001					[2]
30	LSTG-13	Chile	G	95.1	2.0	0.002	0.004	0.93	0.39	0.0001	0.003					[2]
31	LSTG-25	Chile	G	95.5	0.34	0.001	0.004	0.03	1.7	0.0004	0.001					[2]
32	LSTG-4	Chile	G	95.2	0.65	0.002	0.004	0.02	2.5	0.0002	0.001					[2]
33	LSTG-22	Chile	G	95.9	0.36	0.000	0.004	0.02	1.1	0.0004	0.000					[2]
34	LSTG-28	Chile	G	94.9	2.1	0.004	0.004	0.80	0.11	0.0001	0.002					[2]
35	Tacora volcano 8	Chile	V	94.8	1.355	0.003	0.004	0.013	3.107		0.002					[1]
36	Lascar volcano 12	Chile	V	85.4	7.467	0.049	0.004	0.859	0.184		0.013					[1]
37	Lascar volcano 10	Chile	V	84.1	9.258	0.068	0.005	0.629	0.182		0.009					[1]
38	LSTG-20	Chile	G	94.2	0.38	0.001	0.005	0.03	3.2	0.0005	0.001					[2]
39	LSTG-6	Chile	G	94.9	0.53	0.002	0.005	0.03	2.7	0.0001	0.001					[2]
40	LSTG-21	Chile	G	95.2	0.39	0.001	0.005	0.03	1.8	0.0007	0.001					[2]
41	LSTG-24	Chile	G	95.7	0.39	0.000	0.005	0.03	1.5	0.0006	0.001					[2]

ID	SITE	COUNTRY	TYPE	CO <sub>2</sub> %	N <sub>2</sub> %	O <sub>2</sub> %	CH <sub>4</sub> %	H <sub>2</sub> %	H <sub>2</sub> S %	He %	Ar %	δ <sup>13</sup> C CO <sub>2</sub>	δ <sup>13</sup> C CH <sub>4</sub>	δ <sup>2</sup> H CH <sub>4</sub>	R/Ra	Ref
42	LSTG-2	Chile	G	94.0	2.8	0.041	0.005	0.70	0.03	0.0002	0.002					[2]
43	Lascar volcano 11	Chile	V	84.0	8.413	0.051	0.005	0.892	0.199		0.013					[1]
44	LSTG-3	Chile	G	93.9	2.7	0.036	0.005	0.71	0.03	0.0002	0.002					[2]
45	LSTG-5	Chile	G	95.2	0.81	0.005	0.005	0.00	2.2	0.0002	0.001					[2]
46	Lascar volcano 7	Chile	V	83.5	8.111	0.062	0.005	1.612	0.198		0.009					[1]
47	LSTG-11	Chile	G	93.1	2.8	0.009	0.006	1.1	0.05	0.0002	0.002					[2]
48	LSTG-1	Chile	G	92.9	3.0	0.050	0.006	0.91	0.04	0.0002	0.003					[2]
49	LSTG-12	Chile	G	94.7	1.9	0.016	0.006	1.1	0.39	0.0002	0.003					[2]
50	LSTG-10	Chile	G	92.0	3.5	0.009	0.006	1.1	0.11	0.0002	0.002					[2]
51	LSTG-9	Chile	G	99.0	0.45	0.000	0.007	0.01	0.42	0.0005	0.001					[2]
52	LSTG-8	Chile	G	98.9	0.47	0.000	0.007	0.01	0.43	0.0006	0.001					[2]
53	LSTG-29	Chile	G	98.5	0.74	0.001	0.007	0.05	0.49	0.0007	0.002					[2]
54	El Tatio 2	Chile	G	99.0	0.628	0.003	0.008	0.020	0.367		0.005					[1]
55	LSTG-7	Chile	G	98.9	0.51	0.000	0.008	0.01	0.45	0.0010	0.001					[2]
56	LSTG-19	Chile	G	98.7	0.67	0.001	0.009	0.04	3.46	0.0008	0.002					[2]
57	LSTG-30	Chile	G	98.6	0.60	0.001	0.009	0.04	0.44	0.0009	0.003					[2]
58	El Tatio 1	Chile	G	99.0	0.655	0.003	0.012	0.011	0.329		0.004					[1]
59	El Tatio 3	Chile	G	99.3	0.448	0.006	0.020	0.014	0.202		0.004					[1]
60	El Tatio 4	Chile	G	99.3	0.580	0.006	0.022	0.016	0.118		0.006					[1]
61	Tacora volcano 1	Chile	V	85.3	11.184	0.001	0.022	0.087	2.680		0.012					[1]
62	Lascar volcano 6	Chile	V	76.6	16.744	0.077	0.023	2.055	0.818		0.026					[1]
63	Lascar volcano 5	Chile	V	76.8	14.400	0.029	0.027	2.068	0.860		0.033					[1]
64	Tacora volcano 2	Chile	V	87.4	9.496	0.014	0.027	0.086	2.518		0.008					[1]
65	Tacora volcano 3	Chile	V	80.6	15.648	0.081	0.029	0.154	2.886		0.016					[1]
66	El Tatio 5	Chile	G	99.3	0.547	0.005	0.042	0.009	0.073		0.005					[1]
67	Lascar volcano 4	Chile	V	74.4	18.630	0.060	0.043	2.024	1.030		0.098					[1]
68	Lascar volcano 1	Chile	V	75.4	20.721	0.046	0.049	1.927	0.444		0.129					[1]
69	Lascar volcano 3	Chile	V	75.5	20.099	0.056	0.069	1.823	0.526		0.142					[1]
70	Lascar volcano 2	Chile	V	78.5	17.906	0.046	0.073	1.592	0.480		0.123					[1]
71	PGM21	Costa Rica	G	99.1	0.770		0.029	0.080				-29.9		6.81		[3]
72	PGM11	Costa Rica	G	99.6	0.380		0.016	0.040				-27.4		6.86		[3]
73	PGM05	Costa Rica	G	99.0	0.890		0.025	0.030				-24.1		6.23		[3]
74	PGM29	Costa Rica	G	99.8	0.007		0.180	0.000				-22.8		6.68		[3]
75	PGM45	Costa Rica	G	95.1	0.107		4.370	0.170				-16.6		6.66		[3]
76	Rincon de la Vieja	Costa Rica	V	97.8	0.300	0.038	0.000	0.021	1.400	0.000	0.002					[4]
77	Turrialba volcano 1	Costa Rica	V	91.5	0.942	0.000	0.000	0.030	6.904		0.001					[1]
78	Turrialba volcano 3	Costa Rica	V	96.6	0.054	0.000	0.000	0.116	1.725		0.000					[1]
79	Turrialba volcano 4	Costa Rica	V	96.4	0.551	0.001	0.000	0.363	2.007		0.001					[1]
80	Turrialba volcano 2	Costa Rica	V	90.8	1.423	0.006	0.000	0.005	7.364		0.002					[1]
81	CAS02	Costa Rica	G	99.4	0.550		0.002	0.010							4.34	[3]
82	PGM01	Costa Rica	G	98.2	1.370		0.025	0.320							6.52	[3]
83	PGM10	Costa Rica	G	98.7	1.070		0.028	0.120							6.64	[3]
84	PGM03	Costa Rica	G	97.8	1.930		0.035	0.090								[3]
85	PGM12	Costa Rica	G	98.4	1.190		0.040	0.310							6.49	[3]
86	PGM03	Costa Rica	G	96.2	3.450		0.042	0.200								[3]
87	PGM20	Costa Rica	G	93.3	6.290		0.144	0.070							6.67	[3]
88	PGM02	Costa Rica	G	96.4	3.100		0.150	0.260							7.15	[3]
89	PGM31	Costa Rica	G	98.8	0.019		1.010	0.080							6.24	[3]
90	VPOCL	Costa Rica	G	97.4	0.027		1.830	0.050							7.15	[3]
91	PGM46	Costa Rica	G	97.1	0.052		2.530	0.060							6.55	[3]
92	AH23	El Salvador	G	98.4	1.470		0.013	0.090							7.07	[3]
93	AH17	El Salvador	G	97.9	1.740		0.015	0.210							7	[3]
94	SV01	El Salvador	G	95.7	3.450		0.019	0.540							6.34	[3]
95	TR09	El Salvador	G	72.1	23.190		0.020	0.200							5.71	[3]
96	LV01	El Salvador	G	51.8	31.690		0.020	0.370							3.47	[3]
97	IF01	El Salvador	G	83.6	11.040		0.020	0.270							5.95	[3]
98	TR4B	El Salvador	G	96.1	3.480		0.027	0.310							5.8	[3]
99	TR02	El Salvador	G	95.3	4.200		0.030	0.230							5.59	[3]
100	AH22	El Salvador	G	96.7	3.000		0.036	0.200							6.86	[3]
101	AH20	El Salvador	G	96.8	2.580		0.038	0.380							6.93	[3]
102	AH06	El Salvador	G	93.4	5.980		0.049	0.340							7.01	[3]

ID	SITE	COUNTRY	TYPE	CO <sub>2</sub> %	N <sub>2</sub> %	O <sub>2</sub> %	CH <sub>4</sub> %	H <sub>2</sub> %	H <sub>2</sub> S %	He %	Ar %	δ <sup>13</sup> C CO <sub>2</sub>	δ <sup>13</sup> C CH <sub>4</sub>	δ <sup>2</sup> H CH <sub>4</sub>	R/Ra	Ref
103	AH4B	El Salvador	G	97.2	2.510		0.056	0.220							6.9	[3]
104	SV02	El Salvador	G	95.9	3.300		0.068	0.520							6.48	[3]
105	AH21	El Salvador	G	96.8	2.550		0.070	0.350							7.08	[3]
106	TR4C	El Salvador	G	93.1	6.470		0.093	0.210							5.54	[3]
107	AH16A	El Salvador	G	87.9	10.970		0.244	0.200							6.77	[3]
108	EPR	EPR	V									-7	-15	-102		[5]
109	Afar 6	Ethiopia	V	96.5	1.574	0.520	0.060	0.003	1.254		0.038					[1]
110	Afar 7	Ethiopia	V	97.5	0.904	0.288	0.090	0.001	1.171		0.022					[1]
111	Afar 2	Ethiopia	V	97.4	0.809	0.348	0.115	0.242	1.082		0.019					[1]
112	Afar 4	Ethiopia	V	96.0	2.049	0.572	0.116	0.001	1.248		0.051					[1]
113	Afar 1	Ethiopia	V	97.2	1.823	0.393	0.121	0.001	0.362		0.044					[1]
114	Afar 3	Ethiopia	V	97.4	0.753	0.230	0.141	0.239	1.228		0.018					[1]
115	Afar 5	Ethiopia	V	97.1	0.722	0.248	0.203	0.268	1.437		0.016					[1]
116	Milos	Greece	G	61.6			1.300					0.4	-17.8	-149		[6]
117	Milos	Greece	G	56.3			0.514					0.7	-14.7	-146		[6]
118	Milos	Greece	G	70.1			0.929					1.1	-13.7	-189		[6]
119	Milos	Greece	G	67.8			0.300					-0.2	-11.6	-166		[6]
120	Milos	Greece	G	61.4			0.488					0	-10.1	-126		[6]
121	Milos	Greece	G	74.3			0.463					0.3	-9.4	-132		[6]
122	Nysiros Island 14	Greece	G	82.7	0.023	0.000	0.012	0.225	17.032		0.000					[1]
123	Nysiros Island 9	Greece	G	82.2	0.072	0.001	0.020	0.112	17.613		0.000					[1]
124	Nysiros Island 2	Greece	G	86.7	0.017	0.000	0.038	0.099	13.103		0.000					[1]
125	Nysiros Island 6	Greece	G	82.5	0.406	0.004	0.055	1.896	15.118		0.002					[1]
126	Nysiros Island 10	Greece	G	77.9	0.058	0.000	0.185	0.802	21.084		0.000					[1]
127	Nysiros Island 4	Greece	G	82.1	0.078	0.001	0.217	0.320	17.320		0.000					[1]
128	Nysiros Island 5	Greece	G	82.8	0.058	0.000	0.230	0.360	16.594		0.000					[1]
129	Nysiros Island 13	Greece	G	82.3	1.034	0.000	0.275	0.341	16.068		0.004					[1]
130	Nysiros Island 3	Greece	G	84.7	0.193	0.001	0.756	0.677	13.645		0.001					[1]
131	Nysiros Island 11	Greece	G	82.1	1.016	0.029	1.051	1.402	14.385		0.003					[1]
132	Nysiros Island 1	Greece	G	77.3	0.258	0.001	1.190	1.065	20.137		0.001					[1]
133	Nysiros Island 12	Greece	G	89.5	1.131	0.020	2.295	0.971	6.077		0.003					[1]
134	Nysiros Island 8	Greece	G	78.2	0.279	0.002	2.568	2.745	16.234		0.001					[1]
135	Nysiros Island 7	Greece	G	73.3	1.304	0.009	3.119	5.334	16.955		0.004					[1]
136	G0703	Iceland	G	97.4	2.30		0.015		0.06							[7]
137	G0713	Iceland	G	96.8	0.69		0.015		2.16							[7]
138	G0715	Iceland	G	94.0	0.75		0.017		3.65							[7]
139	Reykjanes	Iceland	G	93.3	1.790		0.018	1.104	3.799		0.026					[7]
140	G0701	Iceland	G	91.6	1.63		0.019		4.96							[7]
141	G0704	Iceland	G	92.0	2.04		0.019		4.69							[7]
142	G0711	Iceland	G	91.4	1.50		0.019		5.78							[7]
143	G0712	Iceland	G	91.3	1.63		0.019		5.58							[7]
144	G0716	Iceland	G	96.6	0.66		0.019		1.93							[7]
145	G0709	Iceland	G	90.0	5.09		0.020		3.82							[7]
146	G0707	Iceland	G	91.6	1.64		0.021		5.36							[7]
147	The Hole	Italy	G	79.9	19.300	0.130	0.590	0.001			0.100	3.7		-176		[8]
148	Bagni di Tivoli	Italy	G	98.1	1.700	0.001	0.033	0.000	0.130		0.026	-5.2	-36.4	-161		[8]
149	Vesuvio	Italy	V	99.5	0.390	0.018	0.059	0.000	0.010		0.009	-6.7	-36.1	-138		[8]
150	Fosso S.Antonino	Italy	G	96.1	3.300	0.062	0.190	0.002	0.210	0.000	0.075	1.02	-33.4	-166	1.04	[9]
151	Bullicame	Italy	G	98.0	1.000	0.005	0.014	0.000	1.000		0.004	-1.3	-31.3	-158		[8]
152	acqua forte ponzano	Italy	G	96.6	3.200	0.039	0.085	0.000	0.029	0.000	0.076	-0.47	-31.2	-165	0.88	[9]
153	monte caio	Italy	G	96.8	2.900	0.240	0.016	0.001	0.033	0.000	0.055	-4.73	-30.6	-154	0.74	[9]
154	Bagni di Tivoli	Italy	G	96.8	2.800	0.220	0.033	0.000	0.140		0.035	0.9	-30.1	-135		[8]
155	Bagni di S.Filippo	Italy	G	98.7	1.100	0.170	0.016	0.000	0.010		0.019	-1.1	-29.4	-135		[8]
156	Solfatara Pomezia	Italy	G	99.2	0.680	0.022	0.004	0.000	0.068		0.013	-2.1	-29.3	-139		[8]
157	Trevignano	Italy	G	96.6	3.100	0.091	0.037	0.002	0.110	0.000	0.062	0.26	-29.2	-155	0.61	[9]
158	Lago Vico	Italy	G	99.0	0.700	0.006	0.270	0.002		0.000		-3.1	-28.9	-176	0.77	[10]
159	Acqua Forte	Italy	G	99.2	0.790	0.010	0.006	0.001	0.008	0.000	0.013	-1.9	-28.4	-168	0.69	[10]
160	Le Zitelle	Italy	G	99.4	0.570	0.017	0.024	0.006	0.009	0.001	0.010	-2.3	-28.1	-156	1.19	[10]
161	Lagoni Rossi	Italy	G	92.6	5.200	0.001	2.100	0.000	0.002		0.007	-1.1	-28.1	-164		[8]
162	Latera1	Italy	G	97.7	1.600	0.080	0.255	0.000	0.400		0.010	0.2	-27.9	-139		[8]
163	San Filippo	Italy	G	95.3	2.003	0.002	1.713		0.142	0.001	0.001	-3.33	-27.8	-143		[11]

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164	Torre Alfina	Italy	G	99.0	0.840	0.000	0.120	0.000	0.042		0.003	0.4	-27.3	-131		[8]
165	Bagnaccio	Italy	G	99.3	0.660	0.011	0.037	0.006	0.014	0.000	0.010	-2	-26.9	-150	0.65	[10]
166	S. Cristoforo	Italy	G	99.1	0.810	0.017	0.061	0.004	0.010	0.000	0.014	-2.4	-26.7	-153	0.9	[10]
167	Le Zitelle	Italy	G	99.1	0.790	0.007	0.062	0.003	0.023	0.000	0.013	1.1	-26.6	-148	0.67	[10]
168	Masse S.Sisto	Italy	G	99.2	0.760	0.016	0.035	0.005	0.011	0.000	0.012	-2.6	-26.4	-155	0.69	[10]
169	Sasso Pisano	Italy	G	92.3	0.580	0.000	2.400	2.800	1.800		0.009	-3.2	-26.4	-136		[8]
170	Solfatara di Nepi	Italy	G	99.4	0.540	0.006	0.007	0.002	0.043	0.000	0.005	-1.2	-26.3	-149	0.55	[10]
171	Foralupo	Italy	G	99.3	0.610	0.012	0.068	0.006	0.014	0.000	0.008	0.23	-26.3	-153	0.56	[10]
172	Muralto (o Montecchie)	Italy	G	99.1	0.750	0.017	0.070	0.002	0.016	0.000	0.009	-0.73	-26.1	-166	0.57	[10]
173	Lo Spuntone	Italy	G	89.0	4.500	0.720	1.000	3.700	1.000		0.045	-3.7	-25.9	-161		[8]
174	Caldara Manziana	Italy	G	99.1	0.664	0.001	0.217	0.000	0.054	0.000	0.001	-2.79	-25.7	-101	0.59	[12]
175	Zancona	Italy	G	95.5	0.320	0.010	4.100				0.008	-1.8	-25.6	-144		[8]
176	Grotte S.Stefano	Italy	G	99.4	0.500	0.005	0.023	0.007	0.021	0.000	0.007	0.28	-25.5	-145	0.5	[10]
177	Bullicame	Italy	G	99.3	0.600	0.010	0.016	0.005	0.022	0.000	0.012	-1.2	-25.3	-144	0.69	[10]
178	castel campanile	Italy	G	96.0	3.600	0.021	0.270	0.002		0.000	0.071	-1.69	-25.2	-160	0.07	[9]
179	Mola di Bassano	Italy	G	99.3	0.600	0.010	0.035	0.004	0.002	0.000	0.006	-1.1	-25.1	-147		[10]
180	Tor Caldara	Italy	G	99.7	0.320	0.006	0.022	0.000			0.008	-0.9	-24.8	-143		[8]
181	Foralupo	Italy	G	98.8	0.690	0.004	0.390	0.002	0.099	0.000	0.008	0.49	-24.8	-151	0.46	[10]
182	Poggio dell'Ulivo	Italy	G	98.7	0.700	0.011	0.460	0.003	0.084	0.000	0.006	0.35	-24.8	-156	0.5	[10]
183	Sasso Pisano	Italy	G	90.7	0.717	0.033	2.152	2.238	3.226	0.001	0.003	-3.83	-23.7	-134		[13]
184	Monte Solferata	Italy	G	98.5	0.679	0.033	0.520	0.000	0.218	0.000	0.001	-1.14	-23.3	-132	0.37	[10]
185	Tuscania	Italy	G	99.1	0.840	0.022	0.008	0.002	0.033	0.000	0.013	-0.76	-22.6	-138	0.36	[10]
186	Favara Grande	Italy	G	91.4	0.700	0.005	2.500	3.000	2.400		0.006	-2.5	-22.3	-134		[8]
187	Parco di Diosilla	Italy	G	99.1	0.544	0.001	0.304	0.000	0.051	0.000	0.000	-1.83	-22.1	-152	0.57	[12]
188	Piana di Stigliano	Italy	G	99.2	0.382	0.003	0.402	0.000	0.057	0.000	0.001	-1.66	-21.2	-116	0.48	[12]
189	Pan1	Italy	G	99.1	0.160	0.022	0.001	0.030	0.660		0.003	-0.9	-20.6	-103		[8]
190	Parco della Mola	Italy	G	98.5	0.566	0.039	0.842	0.000	0.057	0.000	0.001	0	-20.4	-137	0.62	[12]
191	S.Pompeo	Italy	G	96.9	0.900	0.061	0.890	0.230	1.000		0.015	-1.1	-20.1	-106		[8]
192	Pan2	Italy	G	98.3	0.610	0.089	0.001	0.016	1.000		0.012	-1.5	-19.7	-111		[8]
193	Vejano	Italy	G	99.2	0.361	0.002	0.373	0.000	0.054	0.000	0.000	0.46	-19.5	-137	0.59	[12]
194	Pan3	Italy	G	98.5	0.400	0.031	0.001	0.031	1.000		0.008	-1.3	-19.3	-104		[8]
195	Solfatara (BG)	Italy	G	98.5	0.290	0.000	0.010	0.240	0.650		0.001	-0.9	-17.8			[8]
196	Favara Grande	Italy	G	97.7	0.194	0.006	0.736	0.835	0.481		0.003	-3.7	-17.6	-121		[14]
197	Ermeta	Italy	G	86.9	4.100	0.900	2.900	5.000	0.070		0.001	-3.7	-17.6	-121		[8]
198	Vulcano Island crater 17	Italy	V	96.9	1.934	0.012	0.000	0.015	0.863		0.002					[1]
199	Vulcano Island crater 7	Italy	V	95.3	1.684	0.075	0.000	0.231	0.540		0.006					[1]
200	Vulcano Island crater 11	Italy	V	95.0	1.131	0.003	0.000	0.095	1.679		0.001					[1]
201	Vulcano Island crater 16	Italy	V	98.2	0.906	0.003	0.000	0.108	0.640		0.001					[1]
202	Vulcano Island crater 5	Italy	V	96.8	1.111	0.000	0.000	0.064	0.458		0.001					[1]
203	Vulcano Island crater 2	Italy	V	93.3	1.626	0.104	0.000	0.190	0.853		0.002					[1]
204	Vulcano Island crater 6	Italy	V	99.3	0.308	0.000	0.000	0.009	0.358		0.000					[1]
205	Vulcano Island crater 4	Italy	V	95.1	0.853	0.001	0.000	0.887	2.512		0.002					[1]
206	Vulcano Island crater 13	Italy	V	92.0	1.290	0.001	0.000	0.156	3.116		0.002					[1]
207	Vulcano Island crater 3	Italy	V	88.1	2.687	0.151	0.000	0.095	1.529		0.004					[1]
208	Vulcano Island crater 9	Italy	V	96.8	1.090	0.000	0.000	0.055	1.056		0.001					[1]
209	Vulcano Island crater 18	Italy	V	95.2	0.741	0.003	0.000	1.819	2.064		0.002					[1]
210	Vulcano Island crater 10	Italy	V	91.6	4.004	0.014	0.000	1.130	2.098		0.004					[1]
211	Vulcano Island crater 1	Italy	V	93.0	2.735	0.168	0.000	0.034	0.831		0.004					[1]
212	Vulcano Island crater 14	Italy	V	95.1	1.705	0.138	0.000	0.730	0.448		0.002					[1]
213	Vulcano Island crater 8	Italy	V	93.3	4.460	0.023	0.000	0.041	2.092		0.014					[1]
214	VO2	Italy	V	48.5	48.900	0.878	0.000	0.385	0.062	0.001	0.560					[8]
215	SE2	Italy	V	52.2	43.200	3.660	0.000	0.134	0.026	0.001	0.440					[8]
216	VO1	Italy	V	50.7	46.700	0.665	0.000	0.417	0.056	0.001	0.520					[8]
217	BN1	Italy	V	69.7	26.600	2.860	0.000	0.156	0.029	0.001	0.250					[8]
218	Vulcano Island crater 12	Italy	V	92.7	1.732	0.000	0.000	0.446	1.380		0.001					[1]
219	BN2	Italy	V	68.0	28.400	2.660	0.000	0.274	0.025	0.000	0.240					[8]
220	Vulcano Island crater 19	Italy	V	84.8	2.594	0.256	0.000	3.259	3.615		0.003					[1]
221	Pantelleria Island 2	Italy	G	97.8	1.427	0.395	0.001	0.000	0.305		0.037					[1]
222	Vulcano Island crater 15	Italy	V	92.1	2.021	0.010	0.001	0.848	2.303		0.004					[1]
223	SE1	Italy	V	53.4	41.100	4.750	0.001	0.081	0.015	0.000	0.450					[8]
224	VOF7	Italy	V	95.5	2.000	0.056	0.001	0.001	0.845	0.002	0.018					[8]

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225	SE3	Italy	V	54.3	38.700	6.290	0.001	0.111	0.032	0.000	0.410					[8]
226	Ischia Island 5	Italy	V	91.9	5.829	1.832	0.002	0.021	0.396		0.025					[1]
227	Ischia Island 1	Italy	V	91.3	6.675	1.707	0.002	0.017	0.226		0.026					[1]
228	Ischia Island 2	Italy	V	96.0	2.603	1.076	0.002	0.020	0.243		0.010					[1]
229	Phlegrean Fields 10	Italy	V	99.0	0.141	0.001	0.003	0.086	0.803		0.000					[1]
230	Phlegrean Fields 6	Italy	V	98.6	0.200	0.002	0.003	0.130	1.097		0.000					[1]
231	Phlegrean Fields 1	Italy	V	99.5	0.116	0.003	0.003	0.067	0.273		0.001					[1]
232	Phlegrean Fields 7	Italy	V	98.7	0.184	0.001	0.004	0.134	0.986		0.000					[1]
233	Phlegrean Fields 4	Italy	V	98.7	0.180	0.007	0.004	0.134	0.891		0.001					[1]
234	Phlegrean Fields 3	Italy	V	98.9	0.182	0.001	0.005	0.106	0.824		0.001					[1]
235	Ischia Island 4	Italy	V	98.1	0.556	0.027	0.005	0.746	0.517		0.003					[1]
236	Phlegrean Fields 8	Italy	V	98.4	0.240	0.003	0.005	0.210	1.087		0.000					[1]
237	Phlegrean Fields 9	Italy	V	97.7	0.269	0.001	0.005	0.219	1.742		0.000					[1]
238	Phlegrean Fields 2	Italy	V	99.4	0.172	0.001	0.006	0.100	0.309		0.001					[1]
239	Ischia Island 3	Italy	V	98.7	0.915	0.068	0.012	0.055	0.272		0.003					[1]
240	Phlegrean Fields 5	Italy	V	97.3	0.793	0.002	0.015	0.778	1.109		0.003					[1]
241	Pantelleria Island 1	Italy	G	99.5	0.143	0.004	0.019	0.000	0.314		0.004					[1]
242	Phlegrean Fields 11	Italy	V	98.2	0.221	0.002	0.020	0.146	1.381		0.000					[1]
243	TF	Italy	V	39.4	52.500	7.520	0.029	<0.0001	<0.001	0.001	0.580					[8]
244	Vesuvio volcano 2	Italy	V	97.5	0.196	0.002	0.041	0.753	1.455		0.001					[1]
245	Vesuvio volcano 1	Italy	V	97.3	0.400	0.003	0.042	0.762	1.422		0.001					[1]
246	Larderello 4	Italy	G	83.4	10.238	2.764	0.406	2.116	0.898		0.147					[1]
247	Larderello 2	Italy	G	73.6	19.500	4.615	0.425	0.907	0.676		0.273					[1]
248	Pantelleria Island 3	Italy	G	97.7	0.194	0.006	0.736	0.835	0.481		0.003					[1]
249	Larderello 3	Italy	G	93.6	1.389	0.028	0.902	2.769	1.303		0.006					[1]
250	BT	Italy	V	61.7	35.600	1.190	1.200	0.021	<0.001	0.001	0.310					[8]
251	Larderello 1	Italy	G	92.5	1.505	0.028	1.446	2.036	2.513		0.005					[1]
252	Larderello 5	Italy	G	91.4	1.574	0.015	2.442	2.788	1.827		0.009					[1]
253	Issaikyo	Japan	V	86.6	5.780		0.006	0.061	7.330		0.023					[15]
254	Galion	L. Antilles	G	72.1	8.000	0.000	0.000	0.856	18.600	0.003	0.044					[16]
255	Penville	L. Antilles	G	74.6	6.000	0.625	0.000	0.000	17.700	0.020	0.717					[16]
256	Sulphur springs	L. Antilles	G	77.7	8.600	2.389	0.000	0.004	10.900	0.000	0.000					[16]
257	Sulphur Springs	L. Antilles	G	98.6	0.600	0.000	0.001	0.235	0.900	0.001	0.007					[16]
258	Galion	L. Antilles	G	67.2	12.100	0.857	0.002	1.152	17.400	0.011	0.741					[16]
259	Galion	L. Antilles	G	93.7	5.500	0.370	0.002	0.467	0.700	0.003	0.003					[16]
260	Sulphur springs	L. Antilles	G	76.9	5.800	0.000	0.005	0.563	16.100	0.002	0.000					[16]
261	Valley of Desolation	L. Antilles	G	80.0	2.200	0.108	0.008	0.333	16.500	0.000	595.000					[16]
262	Valley of Desolation	L. Antilles	G	71.9	11.600	1.058	0.012	0.441	14.100	0.000	0.000					[16]
263	Sulphur Springs	L. Antilles	G	97.7	0.800	0.000	0.013	1.475	0.700	0.000	0.003					[16]
264	Valley of Desolation	L. Antilles	G	96.5	1.100	0.001	0.014	0.000	2.400	0.474	0.004					[16]
265	Watten Waven	L. Antilles	G	99.3	0.500	0.001	0.014	0.152	1.300	0.002	0.006					[16]
266	Valley of Desolation	L. Antilles	G	96.5	0.400	0.002	0.015	0.750	10.800	0.000	0.004					[16]
267	Valley of Desolation	L. Antilles	G	50.2	9.000	0.000	0.030	5.494	32.900	0.000	0.158					[16]
268	Watten Waven	L. Antilles	G	98.3	1.300	0.001	0.034	0.305	0.500	0.000	0.009					[16]
269	Valley of Desolation	L. Antilles	G	97.6	2.200	0.000	0.066	0.000	1.500	0.913	0.012					[16]
270	Watten Waven	L. Antilles	G	78.4	2.000	0.000	0.070	0.618	18.600	0.005	0.018					[16]
271	Valley of Desolation	L. Antilles	G	67.0	6.330	0.380	0.078	2.980	22.000		0.031					[16]
272	Watten Waven	L. Antilles	G	68.9	10.500	2.035	0.088	0.791	15.700	0.007	1.690					[16]
273	Valley of Desolation	L. Antilles	G	71.4	2.500	0.000	0.116	4.541	19.900	0.000	0.012					[16]
274	Champagne	L. Antilles	G	93.4	5.900	0.024	0.161	0.001	0.200	0.029	0.165					[16]
275	Champagne	L. Antilles	G	76.2	4.700	0.381	0.178	0.000	2.800	0.008	0.289					[16]
276	Valley of Desolation	L. Antilles	G	49.2	5.200	0.000	0.216	8.163	35.400	0.000	0.032					[16]
277	Penville	L. Antilles	G	73.1	3.500	0.000	0.661	0.001	18.100	0.007	0.005					[16]
278	El Chichon volcano 6	Mexico	V	92.5	2.051	0.021	0.003	1.945	3.442		0.010					[1]
279	El Chichon volcano 3	Mexico	V	95.3	1.398	0.050	0.004	1.046	2.235		0.007					[1]
280	El Chichon volcano 1	Mexico	V	93.5	1.264	0.039	0.005	3.447	1.787		0.008					[1]
281	El Chichon volcano 2	Mexico	V	97.4	0.339	0.000	0.008	0.788	1.509		0.001					[1]
282	El Chichon volcano 5	Mexico	V	82.6	10.124	0.259	0.010	5.443	1.492		0.035					[1]
283	El Chichon volcano 4	Mexico	V	91.3	1.510	0.017	0.023	1.295	5.873		0.004					[1]
284	Women Bath	New Mexico	G	98.5	0.690	0.004	0.016	0.100				-3.6			6.16	[17]
285	Men Bath	New Mexico	G	98.3	0.890	0.033	0.021	0.170				-4.63				[17]

ID	SITE	COUNTRY	TYPE	CO <sub>2</sub> %	N <sub>2</sub> %	O <sub>2</sub> %	CH <sub>4</sub> %	H <sub>2</sub> %	H <sub>2</sub> S %	He %	Ar %	δ <sup>13</sup> C CO <sub>2</sub>	δ <sup>13</sup> C CH <sub>4</sub>	δ <sup>2</sup> H CH <sub>4</sub>	R/Ra	Ref
286	Tony	New Mexico	G	98.8	0.420	0.007	0.022	0.290								[17]
287	Main Fumarole	New Mexico	G	99.0	0.250	0.002	0.033	0.044								[17]
288	Footbath Spring	New Mexico	G	97.9	0.620	0.030	0.064	0.480				-2.47			5.16	[17]
289	Waikite	New Zealand	G	87.0	12.000		1.000									[18]
290	Ngatamariki	New Zealand	G	93.0	1.500		2.400			0.001						[18]
291	Ngawha	New Zealand	G	93.1	0.600		4.200									[18]
292	MT40	Nicaragua	G	93.2	6.080		0.325	0.110					-24.6		6.99	[3]
293	MT27	Nicaragua	G	95.1	4.030		0.288	0.240					-24.2		6.75	[3]
294	MT36-43	Nicaragua	G	94.2	4.170		1.182	0.460					-23.9		6.96	[3]
295	MT43	Nicaragua	G	93.9	3.980		1.343	0.780					-23.5		6.72	[3]
296	4	Nicaragua	G	98.6	0.720		0.007	0.680							7.37	[3]
297	1026	Nicaragua	G	92.9	6.960		0.010	0.000							7.69	[3]
298	1025	Nicaragua	G	91.1	5.900		0.091	0.510							7.04	[3]
299	1023	Nicaragua	G	92.7	5.760		0.148	0.380							6.79	[3]
300	1024	Nicaragua	G	93.0	4.960		0.183	0.460							6.79	[3]
301	3	Nicaragua	G	80.1	0.370		0.183	19.310							7.72	[3]
302	MT38	Nicaragua	G	94.8	4.690		0.242	0.140							6.74	[3]
303	MT35	Nicaragua	G	95.5	4.080		0.260	0.110							6.76	[3]
304	2	Nicaragua	G	85.3	14.180		0.267	0.050							7.5	[3]
305	MT20	Nicaragua	G	95.4	4.110		0.305	0.150							6.71	[3]
306	MT38A	Nicaragua	G	90.0	8.570		0.421	0.090							7.05	[3]
307	MT35	Nicaragua	G	95.1	4.280		0.424	0.100							6.75	[3]
308	MT42	Nicaragua	G	95.4	3.900		0.436	0.200							6.79	[3]
309	MT40B	Nicaragua	G	93.9	5.540		0.442	0.070							7.04	[3]
310	MT42	Nicaragua	G	94.3	4.950		0.458	0.180							6.78	[3]
311	MT27	Nicaragua	G	91.3	7.930		0.484	0.110							6.8	[3]
312	Cagua	Philippines	G	93.0	1.350	<0.004	0.000	1.250								[19]
313	MAMt Apo	Philippines	G	95.7	2.300	0.004	0.003	0.391								[19]
314	DA	Philippines	G	84.6	0.580		0.056	2.070	12.400							[20]
315	DC	Philippines	G	84.0	0.340		0.078	2.810	12.800							[20]
316	DB	Philippines	G	87.6	0.610		0.085	2.760	8.900							[20]
317	DJ	Philippines	G	89.4	0.760	0.181	0.218	1.200	8.200							[20]
318	BD	Philippines	G	98.4	0.110	0.113	0.251	0.000	0.100		0.013					[20]
319	DE	Philippines	G	92.7	0.190		0.340	4.310	2.400							[20]
320	BA	Philippines	G	97.1	0.290		0.367	0.020	1.800							[20]
321	DF	Philippines	G	92.2	0.250		0.428	5.080	2.200							[20]
322	BB	Philippines	G	97.7	0.800		0.451	0.001	1.000							[20]
323	DW	Philippines	G	94.6	0.480	<0.004	0.530	2.390	2.100	0.000	0.003					[20]
324	DG	Philippines	G	94.4	0.430	0.015	0.586	2.110	2.500		0.005					[20]
325	DH	Philippines	G	94.3	0.260	0.003	0.621	2.070	2.700		0.003					[20]
326	BC	Philippines	G	93.9	0.123		0.701	0.004	1.100							[20]
327	DD	Philippines	G	92.4	0.640	0.210	0.908	4.200	1.700							[20]
328	DI	Philippines	G	87.7	0.940	0.158	1.225	2.300	7.700							[20]
329	Mambucal	Philippines	G	95.5	2.970	<0.004	1.290	0.042								[19]
330	Mambucal	Philippines	G	95.5	2.970		1.290	0.039		0.002	0.004					[19]
331	Teide volcano 1	Spain	V	96.0	1.544	0.069	0.002	0.419	1.781		0.022					[1]
332	Teide volcano 2	Spain	V	96.9	0.770	0.042	0.002	0.504	1.684		0.008					[1]
333	Tatun 6	Taiwan	G	95.0	4.845	0.030	0.047	0.001	0.083		0.011					[1]
334	Tatun 4	Taiwan	G	97.6	2.074	0.015	0.053	0.001	0.261		0.012					[1]
335	Tatun 5	Taiwan	G	93.1	0.509	0.000	0.118	0.000	6.280		0.001					[1]
336	Tatun 3	Taiwan	G	91.6	1.657	0.006	0.668	0.030	6.043		0.003					[1]
337	Tatun 2	Taiwan	G	78.1	2.361	0.001	1.079	0.001	18.483		0.003					[1]
338	Tatun 7	Taiwan	G	86.1	0.927	0.000	1.155	0.175	11.657		0.001					[1]
339	Tatun 1	Taiwan	G	72.0	8.152	0.786	6.410	0.096	12.498		0.069					[1]
340	Beryl Spring	USA	V	95.2	0.313	0.097	0.019	0.111		0.001	0.008	-2.51			12	[21]
341	Sulphur Caldron2	USA	V	99.2	0.168	0.001	0.026	0.113		0.002	0.002	-1.91			15.4	[21]
342	Yellowstone 12	USA	V	97.7	0.262	0.002	0.027	0.195	1.803		0.006					[1]
343	Yellowstone 1	USA	V	98.8	0.197	0.001	0.028	0.142	0.740		0.003					[1]
344	Mud Geyser	USA	V	100.0	0.168	0.002	0.033	0.057		0.002	0.002	-1.96			16.2	[21]
345	Roaring Mountain2	USA	V	96.0	0.444	0.105	0.036	0.184		0.017	0.010	-3.36			2	[21]
346	Yellowstone 3	USA	V	99.0	0.193	0.000	0.037	0.074	0.643		0.003					[1]

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347	Mud Geyser	USA	V	99.8	0.200	0.001	0.039	0.066		0.002	0.003	-2.09			16.5	[21]
348	Yellowstone 11	USA	V	98.5	0.213	0.001	0.041	0.079	1.154		0.003					[1]
349	Yellowstone 5	USA	V	96.5	0.535	0.002	0.044	0.148	2.759		0.014					[1]
350	Crater Hills	USA	V	97.5	0.203	0.001	0.051	0.011		0.003	0.004	-2.01			10.7	[21]
351	Yellowstone 6	USA	V	97.4	0.245	0.001	0.056	0.016	2.272		0.005					[1]
352	Guardian	USA	V	90.3	2.068	0.124	0.091	0.265		0.002	0.027	-2.21			8.76	[21]
353	Yellowstone 2	USA	V	96.0	1.633	0.001	0.196	0.545	1.600		0.041					[1]
354	Yellowstone 10	USA	V	96.5	0.450	0.003	0.205	0.703	2.018		0.011					[1]
355	Pocket Basin	USA	V	94.5	8.400	0.880	0.257	0.217		0.004	0.118				2.98	[21]
356	Yellowstone 7	USA	V	77.1	17.601	2.606	0.287	0.011	2.112		0.213					[1]
357	Yellowstone 8	USA	V	95.4	0.332	0.001	0.296	0.151	3.821		0.008					[1]
358	Norris Canyon Rd	USA	V	95.8	0.388	0.001	0.305	0.017		0.005	0.009	-2.05			5.28	[21]
359	Yellowstone 13	USA	V	96.6	0.555	0.001	0.353	0.025	2.399		0.014					[1]
360	Yellowstone 9	USA	V	95.7	1.598	0.008	0.355	0.341	1.989		0.043					[1]
361	Bison Flat	USA	V	96.2	0.381	0.002	0.378	0.163		0.006	0.009	-2.87			4.26	[21]
362	Fountain Paint Pot	USA	V	87.3	2.557	0.039	0.833	0.006		0.006	0.064	-1.68			6.38	[21]
363	Yellowstone 14	USA	V	93.6	3.012	0.005	0.928	0.008	2.360		0.079					[1]
364	Yellowstone 4	USA	V	90.4	0.202	0.005	2.997	1.932	3.334		0.001					[1]
365	Behind Inkpot	USA	V	89.0	0.279	0.008	4.857	2.724		0.002	0.001	-2.65			4.65	[21]

*Tab.1: Molecular and isotopic composition of the gas related to volcanoes and hydrothermal geothermal systems. Gas composition is in vol.%. Isotopic data: δ<sup>13</sup>C: ‰ VPDB; δ<sup>2</sup>H: ‰ VSMOW; R/Ra© = (<sup>3</sup>He/<sup>4</sup>He)<sub>sample</sub> / (<sup>3</sup>He/<sup>4</sup>He)<sub>atmosphere</sub>; Ra = 1.39 x 10<sup>-6</sup>. Type: V= volcano; G= hydrothermal geothermal system. Empty cells mean “not measured”. [1] Tassi et al., 2010; [2] Aguilera et al., 2011; [3] Snyder et al., 2003; [4] Tassi et al., 2005; [5] Welhan & Lupton, 1987; [6] Botz et al., 1996; [7] Fridriksson et al., 2016; [8] Tassi et al., 2012; [9] Cinti et al., 2017; [10] Cinti et al., 2014; [11] Minissale et al., 1997 (a); [12] Cinti et al., 2011; [13] Minissale et al., 1997; [14] Minissale, 2004; [15] Kiyosu, 1983; [16] Joseph et al., 2011; [17] Goff, Janik, 2002; [18] Giggenbach et al., 1993 (a); [19] Giggenbach et al., 1993 (b); [20] Reyes et al., 1993; [21] Chiodini et al., 2012.*

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