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Origin and flux of a gas seep in the Northern Alps (Giswil, Switzerland)

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ABSTRACT

Natural gas seeps in the Alpine region are poorly investigated. However, they can provide useful information regarding the hydrocarbon potential of sedimentary Alpine units and related geofluid migration, typically controlled by pressurized gas accumulations and tectonics. A gas seep located near Giswil, in the Swiss Northern Alps, was investigated, for the first time, for molecular and isotopic gas composition, methane flux to the atmosphere, and gas flux variations over time. The analyses indicated that the gas was thermogenic ($CH_4 > 96\%$; $\delta^{13}C_1$: $-35.5‰$ to $-40.2‰$) and showed evidence of subsurface petroleum biodegradation (^{13}C-enriched CO_2, and very low C_{3+} concentrations). The source rock in the region is marine Type II kerogen, which is likely the same as that providing thermogenic gas in the nearby Wilen shallow well, close to Lake Sarnen. However, the lack of $\delta^{13}C_{CO2}$ and $\delta^{13}C_3$ data for that well prevented us from determining whether the Wilen and Giswil seeps are fed by the same reservoir and seepage system. Gas fluxes from the Giswil seep, measured using a closed-chamber system, were significant and mainly from two major vents. However, a substantial gas exhalation from the soil occurs diffusely in an area of at least 115 m^2, leading to a total CH_4 output conservatively estimated to be at least 16 tonnes per year. Gas flux variations, monitored over a 1-month period by a special tent and flowmeter, showed not only daily meteorological oscillations, but also an intrinsic 'pulsation' with periods of enhanced flux that lasted 2–6 h each, occurring every few days. The pulses are likely related to episodes of gas pressure build-up and discharge along the seepage system. However, to date, no relationship to seismicity in the active Sarnen strike-slip fault system has been established.

Key words: Alps, isotopes, methane, organic geochemistry, seeps, Switzerland

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INTRODUCTION

Natural hydrocarbon seepage has for many years served petroleum exploration as a direct indicator of subsurface gas and/or oil accumulation. The occurrence of surface macro-seeps (visible gas vents from soil or rocky outcrops) is also, in general, an indication of a fault in an active petroleum seepage system (Abrams 2005) belonging to a total petroleum system (Magoon & Schmoker 2000; Etiope *et al.* 2009a). Therefore, an assessment to determine the origin and flux of seeping gas is a key task for understanding (without drilling) the subsurface hydrocarbon potential, the genesis, and the quality of gas, e.g. the presence of shallow microbial gas, deeper thermogenic accumulations, and/or oil and non-hydrocarbon, undesirable gases (CO_2, N_2, H_2S).

A global analysis of more than 200 onshore seeps worldwide (including 143 mud volcanoes) has revealed that methane is thermogenic in approximately 80% of cases, that microbial gas is found in only 4% of seeps, and that mixed gas characterizes the remaining cases (Etiope *et al.* 2009a,b). In Europe (excluding Azerbaijan), there are more than 150 active gas seeps (Etiope 2009a,b), at least 10 are found in Switzerland. Most of the seeps in Switzerland are located in the southern Swiss Alps hydrocarbon province, in the Canton Ticino (Greber *et al.* 1997). These seeps mainly release microbial gas (around Lago Maggiore) and subordinately thermogenic gas (Stabio and Ponte Falloppia). To date, Greber *et al.* (1997) have provided the only study related to the nature of Alpine seeps as potential indicators of hydrocarbon resources. The seepage of gas from deeper sections and its thermogenic origin has been reported for the Molasse Basin, in western Switzerland (e.g. Cuarny burning seep) and in central Switzerland where the only productive well, in the Entlebuch Valley, operative from 1985 to 1994, represents the petroleum resource (limited) of Switzerland (Granicher 1997; Eng 2005). Additionally, the presence of non-conventional reserves of very deep gas (>5000 m) in the Swiss Molasse Basin has been suggested, analogous to productive deep wells in the eastward extension of the basin in Southern Germany and Austria (Granicher 1997). Such deep reservoirs could be a target for future explorations in Switzerland as seeps can provide a first insight regarding their occurrence and nature.

In this paper, we present compositional, isotopic, and flux data for a large gas seep located in the Central Swiss Alps near Giswil (Canton of Obwalden). With respect to Alpine geologic units, the seep is located in the penninic Schlierenflysch, close to the underlying ultrahelvetic and helvetic units near a major alpine transverse fault (Sarnen strike-slip fault system). In order to determine the characteristics of gas origin, flux to the atmosphere, and flux variations over time, the seep has been the object of an extensive study. Gas molecular composition and isotopic data were acquired during 11 sample campaigns performed over a 3-month period. The properties studied included stable carbon isotopic ratios of methane, ethane, and carbon dioxide ($\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_{CO2}$), hydrogen isotopic ratio of methane (δD_1), and isotopic ratio of helium ($^3He/^4He$); these parameters were compared with published data from a nearby shallow well in Wilen, where a 125-m deep drill hole for a geothermal probe triggered an unintended gas outburst that could not be stopped after 1 month of controlled release (Wyss 2001). Methane flux to the atmosphere from the Giswil seep was determined throughout the seepage area, and long-term monitoring of the total gas flux was performed for 1 month in order to evaluate the relationship between potential external and internal forcing mechanisms such as atmospheric fluctuations and seismic events. Therefore, the work described here represents one of the most detailed and complete studies for parameters such as temporal variations of gas composition, isotopes, and flux data available for a gas seep, and provides a useful reference for future research regarding hydrocarbon seeps, as well as for studies in petroleum geology and geofluid circulation in the Alpine region.

SEEP DESCRIPTION AND GEOLOGIC SETTING

The Giswil seep is located on the southern bank of the Mülibach stream in Kleinteil, approximately 2 km west of the village of Giswil in the Canton of Obwalden (Central Switzerland; Fig. 1). The seep comprised a main horseshoe-shaped pothole of approximately 2 m^2 and smaller satellite potholes that are approximately 4 m apart (hereafter referred to as vent A and B, respectively; Fig. 2). The seep releases gas (no water) that can be easily ignited, producing a flame up to 20 cm in height (Fig. 2c), and was discovered around 1930 by farmers burning leaves (Kopp 1955). Since that time, a part from a pilot study on noble gas concentrations in 1989, the origin of the seep has not been studied. Other occurrences of gas in

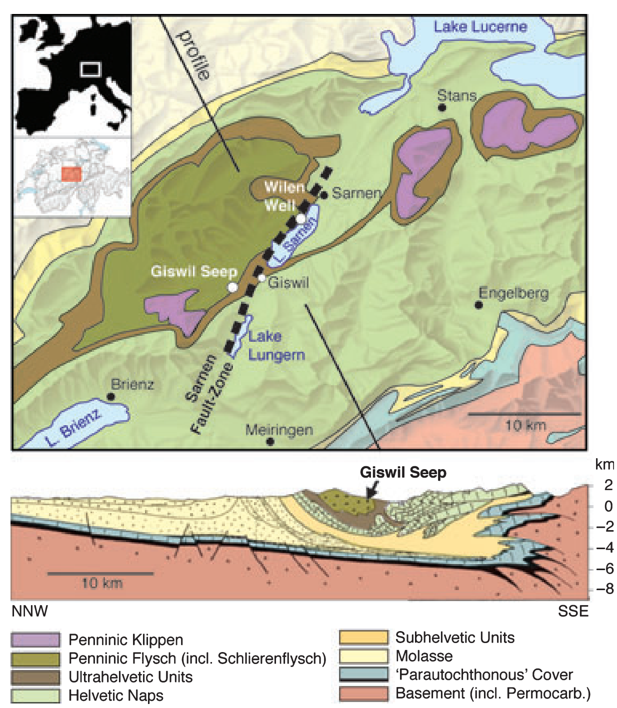

Fig. 1. Top: Map with tectono-stratigraphic units of Central Switzerland (modified after 'Tectonic Map of Switzerland' 1:500 000 by swisstopo) with the locations of the Giswil seep and the Wilen well. Two inserts show the location of the study area within Europe and Switzerland, respectively. The location of the geologic cross-section is indicated by a black line. The approximate track of the Sarnen strike-slip zone is denoted with a black dashed line. Bottom: Geologic cross-section (no vertical exaggeration) striking NNW–SSE perpendicularly across the general tectonic units (i.e. parallel to the transport direction of the alpine naps, profile taken from Trümpy 1980). The location of the Giswil seep is projected onto the profile at the appropriate position near the base of the Schlieren Flysch Unit.

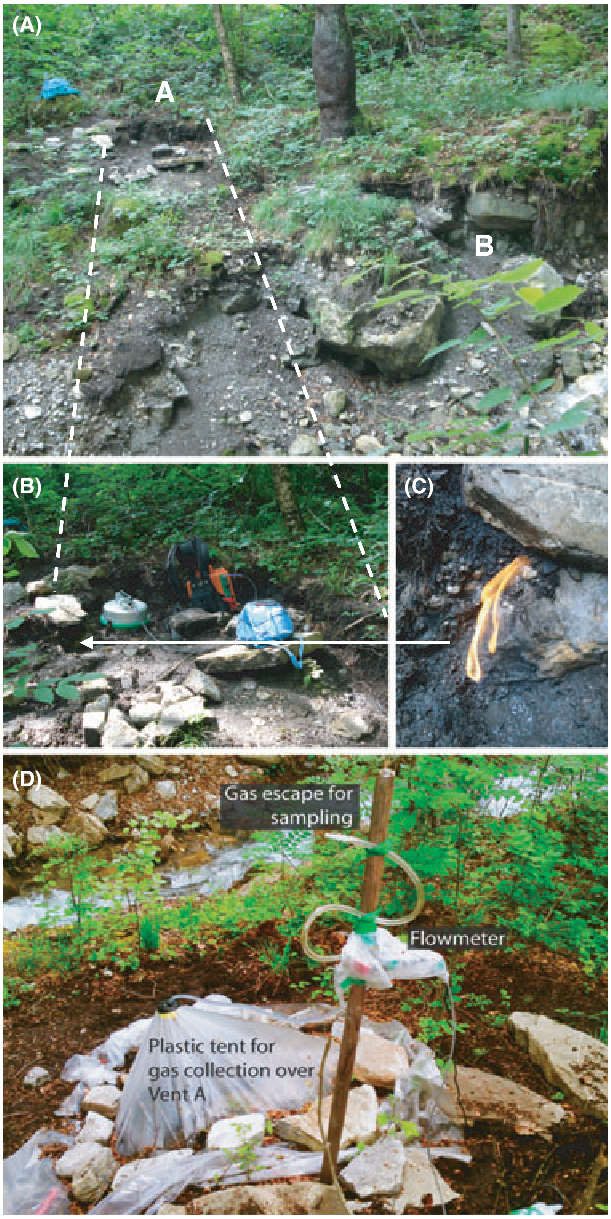

Fig. 2. The Giswil seep, composed of two main vent zones, A and B (A); the closed chamber for CH_4 flux measurements (B); the flame produced at Vent A (C); and the tent for long-term flux monitoring (D).

the Obwalden Valley have been reported for the western shores of Lake Sarnen (Wilen; Wyss 2001), as well as for Lake Lungern where mud volcanoes on the lake floor have been suggested (Bossard & Gächter 1981; Pfaffen 2006).

The Giswil seep area lies approximately 10 km SSE of the northern Alpine front in a valley that cuts through a stack of tectonostratigraphic units (Fig. 1). These units generally strike WSW–ENE and belong to the alpine nap succession that has a general transport direction to the NNW. The seep is located adjacent to a river bed containing coarse and loose Quaternary deposits that reach a thickness of approximately 30 m (Bodmer *et al.* 1996). Below these deposits, the substrate comprised (from top to bottom) penninic Schlierenflysch, ultrahelvetic Wengen beds, and helvetic Wildhorn nap (Fig. 1) (Schindler 1980). The succession is underlain by subhelvetic units, Molasse, and eventually, at approximately 5 km depth, a crystalline basement with a Mesozoic sediment cover (Fig. 1). The Valley of Obwalden is parallel to a major Alpine transverse fault, the left-lateral Sarnen strike-slip system, that runs NNE–SSW and cuts obliquely through the alpine structures. The main track in the area follows the western shore of Lake Sarnen that is approximately 1 km to the east of the seep where it can be mapped to the Wengen beds (Schindler 1980). The morphology of the Mülibach River is found in the seep site as the Sarnen fault direction, and may be related to this main tectonic structure. Even if a link of the seep to the fault zone is likely, no direct fault-evidence can be recognized, as the valley flanks of the creek comprised unconsolidated Quaternary deposits.

Gas escape is often related to seismically active fault zones (Johnson & McEvilly 1995; Miller 1996), and understanding the neotectonic setting of a seep area is highly significant for understanding the mechanisms and controls of gas migration and release. The Sarnen fault system is seismically active and represents one of the more active areas in Switzerland (Monecke *et al.* 2004). On 18 September, 1601 AD, an earthquake occurred south of Vierwaldstättersee with a magnitude of Mw = 6.2, and had an epicentral intensity of Io = VII–VIII (Fäh *et al.* 2003; Schwarz-Zanetti *et al.* 2003). The earthquake was the second largest known to occur in the historic epoch north of the Alps, and its epicenter must have been located somewhere between the Valley of Engelberg to the East and the Sarnen Valley. Therefore, it may have been caused by movement of the Sarnen fault system. On 14 March 1964, after a series of numerous seismic events that occurred over several months, an earthquake with a magnitude of Mw = 5.7 and Io = VII occurred approximately 5 km east of Lake Sarnen with a hypocenter at a depth of 5–7 km (Fäh *et al.* 2003). A focal mechanism proposed by Ahorner *et al.* (1972) suggested an NNE–SSW trending, steeply dipping, strike–slip fault. However, a review of the data revealed no clear solution for the focal mechanism (Deichmann *et al.* 2000). The active historic earthquake record for the Sarnen Valley is not reflected in the instrumental record, which shows no enhanced seismicity in the area since 1975. The area is characterized by the occurrence of earthquake clusters, such as those that occurred in 1964, 1777, and 1917 (Fäh *et al.* 2003; Schwarz-Zanetti *et al.* 2003). The few events recorded by instruments point to a rather shallow hypocentral depth (1–15 km), but with ambiguous fault plane solutions (Deichmann *et al.* 2000).

METHODOLOGY

Gas analysis

In 2009, gas from the Giswil seep was sampled and analyzed 11 times during different time periods. Samples in April and May (G1–G9) were taken using a gun connected to a tube that originated in a tent made by flexible and transparent plastic covering the main seep (Fig. 2d, Vent A). Samples (2 ml) were preserved in helium- or nitrogen-filled 120-ml glass bottles. Additionally, a few samples with a volume of 30 ml were taken in NaCl-solution filled bottles in order to measure the propane content. The samples were analyzed at the Eawag laboratory for C_1–C_3 and for CO_2 using a gas chromatograph (Agilent 6890) equipped with a Carboxen 1010 column (30 m; Supelco), a flame ionization detector (FID), and an autosampler. Oven temperature was kept constant at 100°C. Concentrations were determined using integrated areas and two different methane standards (Scott; Supelco) with lower- and higher-end concentrations when compared with measured samples. Accuracy was ±3% for CH_4 and CO_2; detection limit: CO_2: 35 ppmv; HC: 5–10 ppmv. The methane isotopic composition was determined using a gas preconcentrator (Trace gas; GV Instruments) connected to a mass spectrometer (GV Instruments; accuracy ± 0.3‰). Hydrogen isotopes of CH_4 were measured at the Helmholtz-Centre for Environmental Research in Germany (Thermo mass spectrometer; accuracy ± 4‰). Samples for the helium isotope analyses were collected in copper tubes and measured using the method of Beyerle *et al.* (2000). In June 2009, two samples from the main gas vent A (Fig. 2) were collected using an inverted funnel connected to a syringe and a T-valve equipped silicon tube, and stored in a 150-ml glass tube equipped with two vacuum stop-cocks. One sample (G10) was analyzed at Isotech Labs Inc. (IL, USA) for C_1–C_6 hydrocarbons, He, H_2, H_2S, Ar, O_2, CO_2, and N_2 (Carle AGC 100-400 TCD-FID GC). The detection limits were as follows: CO_2, N_2, Ar, O_2: 40 ppmv; He, H_2 and HC: 10 ppmv; H_2S: 150 ppmv; accuracy 2%; 10% at the detection limit; and isotopic compositions $\delta^{13}C_1$, $\delta^{13}C_2$, δD_1, $\delta^{13}C_{CO2}$ (Finnigan Delta Plus XL mass spectrometer, accuracy ± 0.1‰ for $\delta^{13}C$ and ± 2‰ for δD). The second sample (G11) was analyzed for CH_4, CO_2, N_2, O_2, He, and the $^3He/^4He$ isotopic ratio at INGV, Sezione di Palermo. Chemical analyses were carried out with a Perkin Elmer 8500 gas chromatograph equipped with a 4-m Carbosieve 5A column and a double detector (FID and a hot wire detector; the detection limits were 5 ppmv for O_2 and N_2, and 1 ppmv for CH_4 and CO_2; the analytical errors were ±3%). The isotopic analyses of helium were performed by a static vacuum mass spectrometer (GVI5400TFT) that allows for the simultaneous detection of ^3He and ^4He-ion beams, thereby keeping the $^3He/^4He$ measurement error to very low values. Typical uncertainties in low-^3He (radiogenic) samples are within ±5%.

Gas flux

Methane flux was measured using the closed-chamber method in both macro-seep zones (vents A and B), in other smaller potholes, and throughout an area of 115 m^2 at 43 separate points. We used a static 10-l accumulation chamber connected to a portable methane detector with wireless data communication via a palm-top computer (West Systems srl, Italy). Methane flux was calculated using the linear regression of increased gas concentration values over time (Thielemann *et al.* 2000; Baciu *et al.* 2008). The methane sensor included semiconductor (range: 0–2000 ppmv; lower detection limit: 1 ppmv; resolution: 1 ppmv), catalytic (range: 2000 ppmv to 3% v/v), and thermal conductivity (3–100% v/v) detectors. The flux was corrected for air temperature and atmospheric pressure directly using the palm-top pc. The system is capable of measuring flux levels of 10^2–10^3 mg m^{-2} day^{-1} in approximately 2–3 min, down to 30 mg m^{-2} d^{-1} in approximately 10 min.

Long-term gas flux monitoring

Long-term flux measurements were recorded with a mass flowmeter (red-y smart meter GSM) from 6 to 26 May 2009. The flowmeter was installed at the end of a plastic tube in order to read the flow escaping from the plastic tent. Data were stored every 10 s on a local computer. The measurement error was approximately 0.5%. The volumetric flow was significantly influenced by daily temperature variations, measured by a datalogger at the flow meter, within the tent. To compensate for in-tent temperature variations, that reduce or increase the measured escaping volume, raw flow values were corrected for temperature using a linear best-fit correlation using MATLAB. Residual variations in gas flow were compared with weather data from the weather station in Interlaken (30 km to the SW), which provided air pressure and relative humidity, and with the seismic activity as recorded by the Swiss Seismologic Survey during the monitoring period.

RESULTS AND DISCUSSIONS

Gas composition and origin

Compositional and isotopic data indicate that the gas released from the Giswil seep is thermogenic (Table 1; Fig. 3). CH_4 was dominant (>96%; $\delta^{13}C_1$: from −35.5‰ to −40.2‰) with ethane (C_2H_6) concentrations >1% ($\delta^{13}C_2$: −24.8‰). The concentrations of propane (C_3H_8)

Table 1 Giswil seep gas composition and isotopic data.

Sample (day.month)	N_2	CO_2	He	CH_4	C_2H_6	C_3H_8	$\delta^{13}C_1$	δD_1	$\delta^{13}C_2$	$\delta^{13}C_{CO2}$	R/Ra
G1 (8.4)		0.52		81.52	1.10	0.0019	−38.8	−172.4			
G2 (12.4)		0.66		88.63	1.18	0.0017	−39.2	−166.5			
G3 (14.4)		0.66		90.63	1.22	0.0017	−39.0	−172.2			0.198
G4 (16.4)		0.61		83.72	1.14		−40.2	−166.5			
G5 (20.4)		0.75		90.58	1.24						0.218
G6 (28.4)		0.61		95.03	1.33						
G7 (7.5)		0.44		80.26	1.11						
G8 (11.5)		0.48		87.54	1.21						0.154
G9 (26.5)		0.61		90.38	1.26			−178.1			0.157
G10 (19.6)	0.27	0.71	0.0040	97.56	1.45	< 0.001	−35.5	−159.3	−24.8	+15.1	
G11 (19.6)	0.30	0.64	0.0043	96.44							0.10
Wilen well	0.02	0.10	0.0060	96.68	3.18	1.09	−37.2	−148.0	−26.3		

Gas composition is in %vol. Isotopic data: $\delta^{13}C$: ‰, VPDB; δD: ‰, VSMOW).
R/Ra = $(^3He/^4He)_{sample}/(^3He/^4He)_{atmosphere}$; Ra = 1.39×10^{-6}); H_2, C_4–C_6 hydrocarbons and H_2S are below the detection limit (see text). Only G10, G11, and Wilen well (Wyss 2001) data are corrected for air contamination. The composition and the δD_1 values in April and May are averages from one to three samples.

and other heavier alkanes were unexpectedly extremely low, with a maximum of 20 ppmv. They were often found below the detection limit (10 ppmv). The helium concentration and the isotopic ratio in the Giswil seep are typical of hydrocarbon-rich gases in sedimentary basins with dominant crustal signatures and minor mantle components (R/Ra: 0.1–0.2), and are consistent with He isotope data from the Alpine region (Marty *et al.* 1992). The Bernard's plot (Fig. 3a) would suggest a source rock kerogen closer to Type II.

The lack of significant concentrations of C_{3+} alkanes is typical of dry, over-mature thermogenic gases. In a dry gas, ethane should also be scarce, but instead reaches 1.4% in Giswil gas. The specific lack of C_{3+} may be indicative of gas altered by hydrocarbon biodegradation at depth (Pallasser 2000; Etiope *et al.* 2009b) as oil or gas biodegradation leads to a preferential C_{3+} consumption increasing C_2/C_3 and $C_1/(C_2 + C_3)$ ratios. Very low C_{3+} concentrations are also frequently observed in thermogenic mud volcano gases, which are generally influenced by molecular fractionation during advective migration (Etiope *et al.* 2009a). Due to molecular adsorption on solid grains of mud and differential solubility, seeping gas becomes dryer (more methane, less ethane and propane) than reservoir gas. Independently of mud volcanism, molecular fractionation has been observed in seeps with very low gas fluxes (possibly due to higher residence times and gas–water interaction processes; Etiope *et al.* 2009a), but not in high-flux seeps like Giswil. The positive $\delta^{13}C_{CO2}$ value, +15‰, is, however, indicative of secondary methanogenesis following biodegradation (Pallasser 2000; Etiope *et al.* 2009b). In fact, the positive $\delta^{13}C_{CO2}$ value could indicate a residual CO_2 from reduction to CH_4 (secondary microbial CH_4) after CO_2 was produced by petroleum degradation. Accordingly, a lack of C_{3+} alkanes is likely due to biodegradation in subsurface hydrocarbon pools, which implies that CH_4 should have a microbial (secondary) component. Such a mixing between primary thermogenic and secondary microbial CH_4 is often difficult to recognize

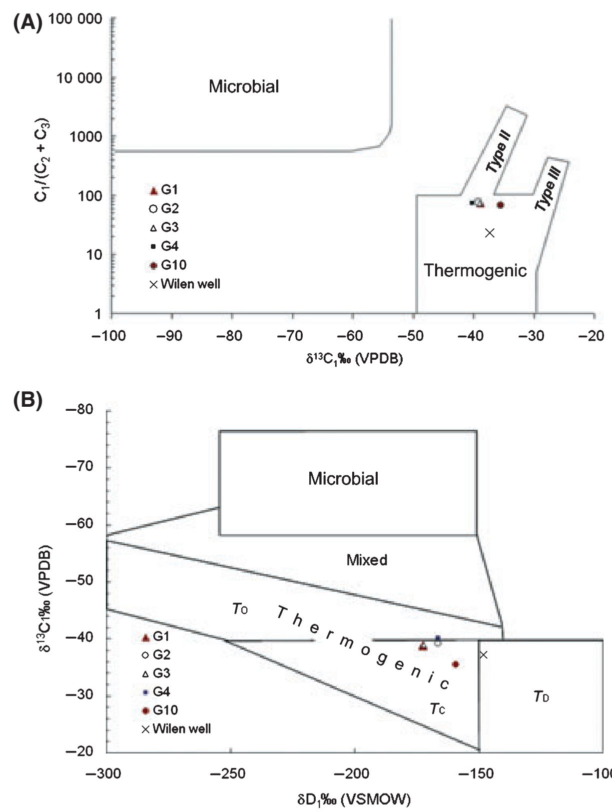

Fig. 3. Genetic zonation of the Giswil gas seep: (A) The methane carbon isotope versus HC molecular composition diagram (Bernard *et al.* 1978; Whiticar 1999); (B) The methane carbon and hydrogen isotope diagram (Schoell 1983). T_O, thermogenic with oil; T_C, thermogenic with condensate; T_D, dry thermogenic. Wilen well gas data (Wyss 2001) are shown for comparison.

on the basis of $\delta^{13}C_1$ alone. The carbon isotopic ratio of secondary methane may be within the typical thermogenic range, and anyway the relative amount of secondary methane is often too low to induce a significant shift in isotopic values (Etiope *et al.* 2009b). However, we observed a variability over time for $\delta^{13}C_1$ (from −40‰ in April to −35‰ in June) that can be explained by dynamic variations in mixing for the two gas components that are likely controlled by gas pressure and flux variations, typical in a seepage system.

Gas composition and carbon and hydrogen isotopic composition of CH_4 for the Giswil seep are very similar to those of the thermogenic gas sampled in the Wilen well (Wyss 2001), located approximately 7 km NE of Giswil, above Lake Sarnen. Both gas occurrences are located roughly at the base of the Schlieren Flysch Unit (Fig. 1). The well is only 125 m deep, therefore, the thermogenic gas pool results from the migration of gas from deeper accumulations and source rocks, which should be marine source rocks, of Type II (Wyss 2001). Unfortunately, there are no $\delta^{13}C_{CO2}$ or $\delta^{13}C_3$ data available for Wilen, so it was not possible to establish whether the reservoir and/or the petroleum seepage system (as defined by Abrams 2005) are the same as those of Giswil. However, the Wilen gas shows a high concentration of propane and is, therefore, unlikely to be significantly biodegraded; this could suggest that Giswil gas and the shallow Wilen pool are fed by different seepage systems and reservoirs.

The source rock for Giswil gas seems to be of marine origin and the same as that for Wilen gas (kerogen Type II). Using the calibration data available for Type II source rocks from Berner & Faber (1996), as interpreted by Wyss (2001) (Fig. 4), the Giswil gas can be characterized by a maturity (vitrinite reflectance) of R_o: 1.6–1.7% and is therefore similar to values for Wilen gas (R_o: 1.4–1.6%). Comparing this maturity data to values measured in similar geologic formations along the northern alpine margin, using the marine Type II origin, Wyss (2001) postulated two possible potential source rocks: (i) the shallow Schlierenflysch or underlying Habkern Mélange, or (ii) the deeper Mesozoic authochthnous sediments (reservoir rock in the Finsterwald well in Entlebuch) or the overlying Flysch units (Fig. 1).

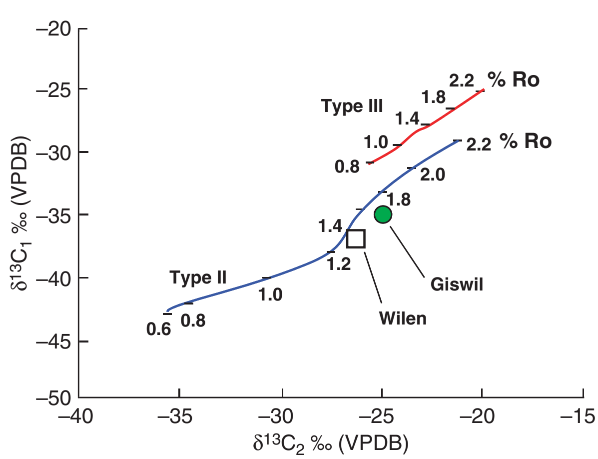

Fig. 4. The relationship between the methane and ethane carbon isotopic compositions for Giswil and Wilen gas. The vitrinite reflectance/isotope composition line (maturation line) was obtained using the calibration data for Type II source rocks from Berner & Faber (1996), as interpreted by Wyss (2001).

Gas flux

Seepage flux distributions and data are shown in the contour map and the 3D plot of Fig. 5. Thanks to rapid measurements for gas flux obtained from the closed-chamber system using an online detector, it soon became evident that gas emission was substantial throughout a large area, and not confined to the main pothole A. At pothole A, we found a maximum emission of approximately 10 kg m^{-2} day^{-1}, with gas easily burning and producing a flame up to 20 cm in height (Fig 2c). A rough estimate for the CH_4 flux from the point issuing the flame of approximately 0.9 t $year^{-1}$ (tonnes per year) was derived from correlation plots between flame height, flame diameter, and gas flux. The correlation was established on the basis of experimental calibrations and theoretical models developed from fire engineering problems (Delichatsios 1990; Hosgormez *et al.* 2008). Very high flux values (approximately 6 kg m^{-2} day^{-1}) were detected in pothole B (Fig. 2a), which is actually a second gas vent occurring within the general zone of diffuse gas escape. The gas exhalation was, however, pervasive and exceeded 1 g m^{-2} day^{-1} throughout most of the investigated area (significant diffuse exhalations, up to 180 g m^{-2} day^{-1}, were also found close to the river). Flux values decreased down to hundreds of mg m^{-2} day^{-1} outside the seep zone and in the grassland outside the forest area. No significant seepage (values below the detection limit of 50 mg m^{-2} day^{-1}, imposed by a short-time chamber exposure) was found beyond 30 m from the seep zone on the other side of the river. Simply summing up the flux values recorded at the 43 points, and by assuming that each value was valid for 1 m^2, without considering the flux from the soil between the measurement points, would provide a total output of 12.4 t $year^{-1}$. A more quantitative estimate for the total output of methane from the measured seepage area could, however, be derived from spatial interpolation between the individual gas measurements. An application of 'linear kriging' interpolation for soil degassing (flux values with lower variance) and 'natural neighbor' for the higher and focused seep flux values yielded a total flux of 16 t $year^{-1}$. Approximately 8 t $year^{-1}$ are estimated to escape from vent A only, and 2.2 t $year^{-1}$ are estimated from vent B. The remaining 5 t $year^{-1}$ (i.e. 30%

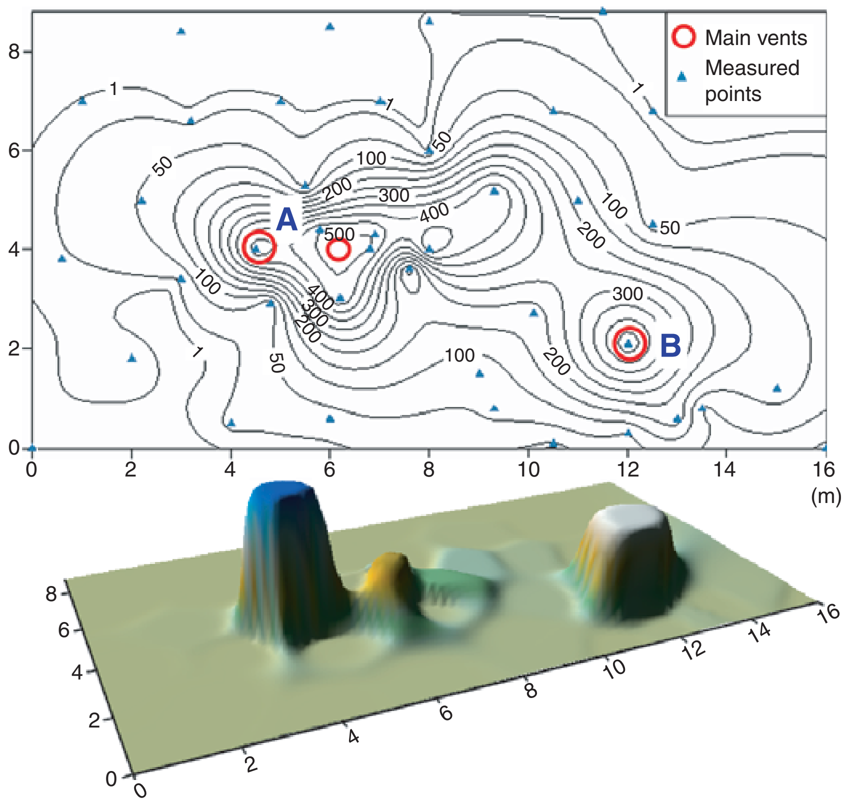

Fig. 5. The contour map and the 3D representation of the seepage CH_4 flux distributions (isolines of flux in g m^{-2} d^{-1}). The contour map shows the distribution of the flux values from the soil around the vents, whereas the 3D surface highlights the relative magnitude of gas venting.

of total output) are released from diffuse degassing from the soil.

The single flux values, their distribution, and total output are typical of large and very active gas macro-seeps, such as those investigated in Romania, Italy, or Greece (Etiope *et al.* 2006, 2007; Etiope 2009a), which are linked to active seepage systems and reservoirs. Thousands of similar seeps exist worldwide (Etiope 2009b). However, gas flux has been measured in only a few cases. Likewise, the relevant gas flux of Giswil can only be explained by the existence of a pressurized gas pool able to continuously provide tens of tonnes of gas per year, flowing along a channel of enhanced permeability in a conduit like a fault system.

Long-term flux variations

The flux measured in the tent on vent A shows a mean flow of approximately 50–60 ml min^{-1}, which fluctuates in amplitude and frequencies (Fig. 6). Such a flow, which is 2 orders of magnitude lower than the flow observed when using a closed-chamber system (or that estimated by flame height) is clearly not representative of the actual seep but refers to the flux constrained by the tent system (i.e. is caused by small overpressurizations –smaller pressure gradients – driving the gas exhalation) that become inhibited due to the resistance of flow-meter installation. The bulk gas most likely used alternative pathways for exhalation, such as other potholes or the surrounding soil outside the tent. However, as installation and resistance remained constant for the duration of long-term flow measurements, the relative changes in flux were significant and required a physical explanation from interior or external boundary conditions.

The flux data displayed strong daily fluctuations most likely controlled by temperature (and therefore pressure) in the sealed tent (Fig. 6). A best-fit correction for the temperature-dependence removed most of this daily rhythm. However, the frequency spectra of the residual signal still contained a dominant 24-h period that became weaker after the correction. Next to this daily signal, the frequency analysis showed a less pronounced half-day (12 h) and an approximately 3-day (65–75 h) cyclicity in the power spectra (Fig. 7). The average flux values showed, over the entire 20 day period, a decreasing trend from approximately 60 to 50 ml min^{-1}. Several short-term periods showed elevated flux values with numerous spikes. Most of these spikes marked increasing flux values with maximum values up to 110 ml min^{-1} (Fig. 8). These high-flux periods usually lasted between 2 and 6 h. During the 20-day measurement period, seven such high-flux pulses could be identified suggesting an average recurrence rate of 3 days.

Neither the air pressure nor the relative humidity correlated with the temperature-corrected residual flux. Prominent 2–6 h periods were found to occur independent of atmospheric factors and showed no match to the

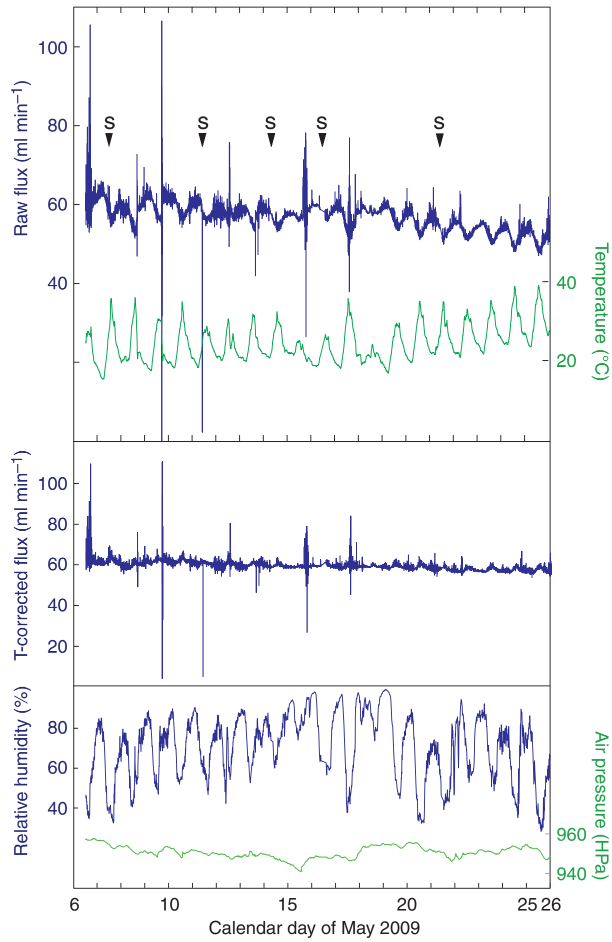

Fig. 6. Flux data from the Giswil seep measured between 6 and 26 May 2009 as correlated to atmospheric data. Top: Uncorrected gas flux data (blue) and temperature data (green) during the measurement period. The black arrows labeled with 's' indicate sampling periods when artefacts may have altered the flow values. Note the strong daily pattern. Middle: Gas flux data applied after a best-fit temperature correction removed most of the daily pattern. Bottom: A correlation of the flow data with relative humidity (blue) and air pressure, both measured at station Interlaken. Note the lack of an obvious correlation to temperature-corrected flux data.

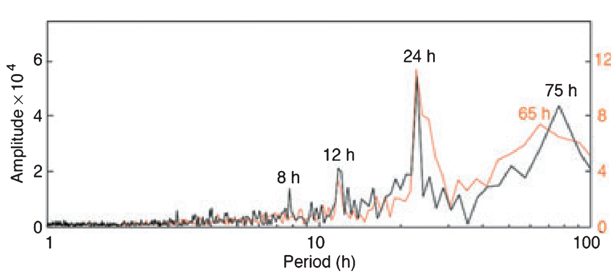

Fig. 7. Spectral analysis of raw long-term flux data (orange) and temperature-corrected long-term flow data (black). Note the dominant period of 24 h (also in the temperature-corrected data) as well as the less significant periods of 8, 12, and approximately 72 h (approximately 3 days).

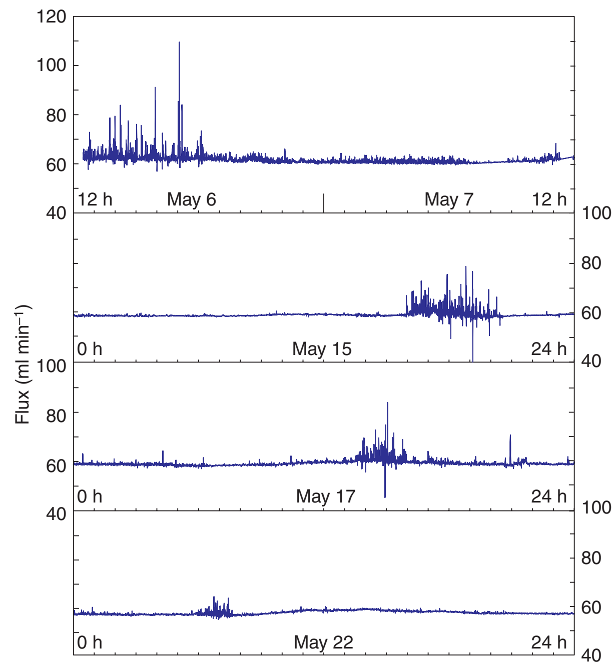

Fig. 8. Four examples of flux data on a daily scale. All examples show periods of enhanced flux values lasting 2–6 h and sometimes reaching twice the background values. The pulsation for the Giswil seep did not correlate to the seismic event record or to registered atmospheric data.

earthquake (magnitude Mw = 1.5) that was recorded at a distance of 30 km from the seep on 22 May 2009 at 14:25. However, as the closest seismic stations in the seismic network are 15–20 km from the seep, the instrumental seismic record is not sensitive enough to record smaller events. Therefore, we cannot rule out the possibility that periods of increased gas release may be related to enhanced microseismicity in the Sarnen fault system. In any event, we interpret the flux peaks as a repetitive pulsation of the seep, typical of the seepage behavior observed in other areas (e.g. Marinaro *et al.* 2006). Such pulsations are generally attributed to processes in gas pressure build-up and discharges along the migration channel in the subsoil.

CONCLUSIONS

For the first time, an Alpine natural gas seep has been thoroughly investigated for fluxes and complete isotopic and molecular composition. The main conclusions of the study can be summarized as follows:

(1) Thus far, the Giswil seep is the largest natural emission of thermogenic gas in the Alpine region that has been measured. Methane-rich (>96% v/v) gas leaks from two main vents, but a diffuse exhalation, with fluxes of tens to hundreds of g m^{-2} day^{-1}, occur throughout a surface of 115 m^2. In total, at least 16 t of CH_4 are released annually into the atmosphere.

(2) The gas shows signals of petroleum biodegradation, frequently occurring in subsurface hydrocarbon reservoirs, associated with secondary methanogenesis.

Giswil gas is similar to that discovered in the nearby Wilen well (close to Lake Sarnen). Giswil and Wilen gases likely derive from the same source rocks (marine kerogen, Type II, maturity equivalent to R_o values of 1.4–1.7%). However, for this study, it was not possible to establish if the gases were migrating from the same reservoir or seepage system. A more complete gas analysis (including $\delta^{13}C_{CO2}$) in the Wilen gas could clarify this possibility.

(3) Continuous flux monitoring over a period of 20 days showed seepage oscillations related not only to external, meteorological factors, but also to intrinsic 'pulsations' with repetitive periods of 2–6 h in duration; these pulsations were characterized by spikes with elevated flux values that can be considered as a sort of 'breathing' of the seep, as typically observed for other areas.

The results can provide a useful reference for:

(1) studies and assessments of the emission of methane from geologic sources, today recognized as an important natural source of greenhouse gases (e.g. Etiope *et al.* 2008) and endorsed by the European guidebook and pollutant emission inventory (EMEP-EEA, 2009). The data here provide values for methane flux that can be added to the European and worldwide databases (Etiope 2009a,b) and that are useful for assessments of the 'emission factors' for the category 'Geological seepage' (Snap Code 110900) in the EMEP-EEA Guidebook (EMEP-EEA, 2009).

(2) Studies designed to determine the seepage of hydrocarbons in petroleum (oil and gas) exploration.

The high flux and the thermogenic nature of the gas released in the seep are indicative of an active system that is likely fed by deep and pressurized gas reservoirs. Future investigations should focus on a more detailed isotopic evaluation for other gas occurrences in the area (such as for the Wilen well), especially for CO_2 and propane, and on the search for other possible seepage sites in the area that are detectable only by instrumentation. Such an investigation could provide insights regarding the potential and extent of the seepage system (Abrams 2005), and information regarding the occurrence of one or different reservoirs feeding the Giswil seep and the Wilen shallow pool.

In addition, extended noble gas analysis (e.g. including elemental abundance of Ne and Xe and $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios) are expected to yield valuable information of the sources and mixing conditions of the fluids in the area of Giswil. Further efforts will investigate the factors responsible for pulsations in the Giswil seep. In particular, a refined seismic network with sensitive stations nearby the seep would be able to determine whether or not periods characterized by methane spikes coincide with microseismic activities in the Sarnen strike-slip fault system.

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