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**Mesure des gaz des sols autour du système volcanique le plus récent de France métropolitaine (lac Pavin, Massif Central).**

**Soil gas measurements around the most recent volcanic system of metropolitan France (lake Pavin, Massif Central)**

GAL Frédéric<sup>1,\*</sup>, GADALIA Alain<sup>2</sup>

<sup>1</sup> BRGM, Metrology, Monitoring and Analysis Division, 3, avenue Claude-Guillemin, 45060 Orléans cedex 02, France

\* Corresponding author: [f.gal@brgm.fr](mailto:f.gal@brgm.fr)

<sup>2</sup> BRGM, Department of Geothermal Energy, 3, avenue Claude-Guillemin, 45060 Orléans cedex 02, France

**Résumé**

Les techniques de monitoring des teneurs en gaz dans les sols (CO<sub>2</sub>, O<sub>2</sub>, <sup>222</sup>Rn, <sup>4</sup>He) sont utilisées dans le cadre géographique du système volcanique récent du Pavin (Puy-de-Dôme), afin de réaliser un état des lieux des émanations gazeuses locales, et de déterminer si ce système peut présenter des indices de réactivation. Des teneurs jusqu'à 100% de CO<sub>2</sub> et 50 ppm d'hélium sont mesurées dans un étroit périmètre (mofette d'Escarot), soulignant une origine magmatique pour ces gaz. Les activités radon y sont assez importantes, sans toutefois présenter, par rapport aux zones environnantes, des enrichissements aussi importants que ceux mesurés pour le CO<sub>2</sub> ou l'hélium. Des enregistrements horaires sur plusieurs semaines de ces activités radon semblent indiquer l'existence, dans la zone de la mofette, de pulsations de longue période (40 jours), dont l'origine est mal cernée. En dehors de cette mofette, aucun indice de présence de gaz d'origine profonde n'est mis en évidence.

**Mots clefs**

Gaz des sols ; CO<sub>2</sub> ; Hélium ; Radon-222 ; Risques naturels ; Mofette

**Abstract**

Soil gas monitoring techniques ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $^{222}\text{Rn}$ ,  $^4\text{He}$ ) are used in the geographical context of the recent volcanic system of Lake Pavin (Puy-de-Dôme), to get a better knowledge of local gaseous emissions, in order to establish if this system can present evidences of reactivation or not. Concentrations up to 100%  $\text{CO}_2$  and 50 ppm of helium are measured in a narrow geographical area (Escarot mofette), together with a magmatic origin for these gases. Radon activities in the mofette area are quite high, but do not show, compared to surrounding areas, enrichments as high as those measured for  $\text{CO}_2$  or helium. Hourly records of these radon activities, performed during several weeks, suggest the existence of pulsed radon exhalation in the mofette area. The period of this pulsation is around 40 days but its origin remains poorly understood. Apart from this mofette, no evidence of gas originated from depth is highlighted.

**Keywords**

Soil gas ;  $\text{CO}_2$  ; Helium ; Radon-222 ; Natural risks ; Mofette

## Introduction

This article aims to present a preliminary evaluation of soil gas measurements carried out around Lake Pavin during three campaigns staggered from August 2008 to September 2009. Such measurements were initiated following new  $^{14}\text{C}$  dating that suggested the occurrence of phenomena related to volcanic activity around  $2130 \pm 40$  BP and  $340 \pm 40$  BP (Del Rosso and Bernardi, 2006; Lavina and Del Rosso, 2006). Previously, the phreato-plinian volcanic phase, which led to the emplacement of Pavin crater lake, was dated at  $6700 \pm 200$  years (Boivin *et al.*, 2003), constituting the most recent volcanic event in metropolitan France. Another phreatomagmatic phase, dated at 3450 years, has also been proposed by Brousse (1969), but has not been confirmed since then.

As a consequence, these possible recent events led to examine if some gaseous species, especially those known to be frequently affected by deep processes, such as  $\text{CO}_2$  or  $^4\text{He}$ , may be affected by effects linked to these last volcanic episodes. This study aims to analyze the characteristics of gas emanations, including  $\text{CO}_2$ , in order to determine if there are evidences of hydrothermal activity, experiencing reactivation or not. By the late '80s, this theme, related to natural hazards that can potentially represent Lake Pavin, has been explored through the determination of the origin of the  $\text{CO}_2$  gas phase and its quantification in the lake itself (Camus *et al.*, 1993; Michard *et al.*, 1994). Later on, solute fluxes were estimated (Viollier *et al.*, 1995), profiles characterising dissolved and rare gases were performed as well as isotope analyses in order to clarify the dynamics and the material balance of the lake (Olive and Boulègue, 2004). However, until now, no quantification of the distribution of the gas content in soils was performed. Only spot monitoring were made by Del Rosso and Bernardi (2006) on some piezometers at varying depths, concentrations rising up to 5% being measured at Escarot (Figure 1), 7% near a peat bog (Estivadoux) and up to 10% in a piezometer located under the outlet of the lake.

Soil gas monitoring techniques are used here to measure the levels of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{O}_2$ ,  $^4\text{He}$  and  $^{222}\text{Rn}$ , in that sense following the approach initiated in the 70s, particularly through researches in geothermal, mineral and hydromineral resources, as well as for volcanic and seismic monitoring (e.g. Aubert and Baubron, 1988; Israel et Bjornsson, 1967; Koga *et al.*, 1983; Sidle, 1984; Sugisaki, 1978; Sugisaki *et al.*, 1983). The soil gas method experienced further applications and developments in the last decade through studies of  $\text{CO}_2$  storage sites or natural analogues (e.g. in Europe : Annunziatellis *et al.*, 2008; Battani *et al.*, 2010; Beaubien *et al.*, 2008; Gal *et al.*, 2010; Krüger *et al.*, 2009; Pauwels *et al.*, 2007). Joint quantification of several gases can indeed help increase accuracy in detecting abnormalities associated with leakage of structural discontinuities in the crust (faults, magmatic fumaroles ...) and energy flows (Baubron and Sabroux, 1984; Baubron *et al.*, 2002; Ciotoli *et al.*, 1999; Guerra and

Lombardi, 2001; Klusman et Jaccks, 1987; Walia *et al.*, 2010). Indeed, soil gas monitoring combines the quantification of ubiquitous species in soil atmosphere ( $\text{CO}_2$  and  $\text{O}_2$ ) with that of radon-222 activities and helium-4 concentrations, both gases originated from the decay chain of uranium-238. These two gases have different origins and properties, which may allow better characterization of areas where important  $\text{CO}_2$  levels are encountered. Radon is a rare gas almost chemically inert, with poor intrinsic mobility. It is produced through the decay chain of uranium-238 and decays itself in a short period. Radon detected in soils has a near surface origin, but may indicate the presence of an area marked by advection processes of water or other gases. We therefore use radon to highlight areas where its own emanation is more important than the one only resulting from local geological background. The determination of helium concentrations is used to complete the set of analyzed gases, as this element may also reveal the presence of drains or structures with significant permeability. Helium contents may indeed deviate significantly from the average atmospheric concentration, indicating the existence of deep discharges or hydrothermal seepages (e.g. Toutain and Baubron, 1999). Due to its inert chemical nature, helium does not interact during migration from its source to the surface. At the opposite, helium is a very mobile element and therefore spreads very easily (its diffusion coefficient is almost 10 times that of  $\text{CO}_2$ ).

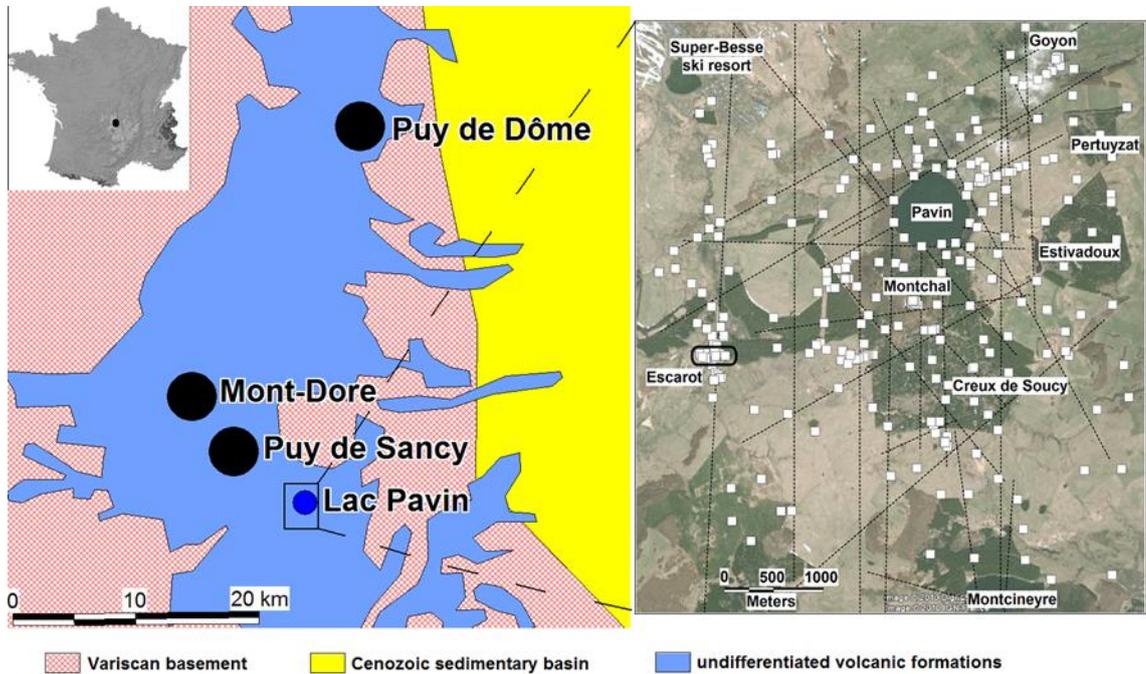


Figure 1 :

Localisation de la zone d'étude. Partie gauche : fond géologique simplifié, issu de la carte géologique 1/1000000<sup>ème</sup> du BRGM. Partie droite : les tirés représentent la fracturation supposée de la zone d'après Lavina et Del Rosso (2006), les carrés blancs les points d'échantillonnage et le rectangle la localisation d'Escarot ; le fond photographique est issu de Google Earth.

Location of the study area. Left side: simplified geological map, from the 1/1000000<sup>th</sup> French synthetic map (BRGM). The dashed lines represent the supposed fracturation of the area, after Lavina and Del Rosso (2006), white squares represent the sampling points and the rectangle indicates the location of Escarot; the background picture is taken from Google Earth.

### Geographical and geological settings

The study area lies between 1100 and 1400 m a.s.l.. The majority of the measurements were carried out between 1200 and 1300 m height, the outlet of Lake Pavin being located at 1197 m (Figure 1). This area of 30 km<sup>2</sup> covers the entire feeding area of the lake (approximately 2 km<sup>2</sup>, Del Rosso and Bernardi, 2006). Mean annual temperature recorded at Besse en Chandesse,

located 4 km North-East of the lake, is 6.3°C, with more than 100 days of frost per year (Préfecture de la région Auvergne, 2000), and rainfall amounts ranging between 1200 and 1600 mm per year (Devaux, 1980).

Geologically, the group formed by the Montchal, Montcineyre and Pavin volcanoes (Figure 1) is located along a N160° to N170°E vertical fault. In addition, the Pavin – Montchal group is located at the southern end of a N105° to N125°E dyke group, linked to the Sancy stratovolcano (Lavina, 1985). Finally, Lavina and Del Rosso (2006) identify a North-South graben, 2.5 kilometres wide, intensely fractured and now completely filled, emplaced at the base of the Pavin – Montchal system and extending 8 km southward. At greater geographic scale (Figure 1), this volcanic system is part of the large French Massif Central volcanic field with magmatic activity beginning in the late Mesozoic and continuing through to the Holocene, with much of the volcanic activity taking place at 4–6 Ma (Wittig *et al.*, 2007), and is emplaced close to the 45°30'N parallel that was evidenced to be a major chemical discontinuity in the sub-lithospheric mantle (Lenoir *et al.*, 2000). Alpine orogeny was also responsible of crustal faulting that led to the emplacement of Cenozoic grabens, the Limagne one (East from Pavin area) being the largest sedimentary basin of the French Massif Central. All those geological formations lie on Variscan terranes that result from a succession of 6 tectonometamorphic events that occurred between Silurian to Stephanian times (Faure *et al.*, 2009).

Various hydrothermal venues and carbogaseous springs, as well as spot emissions of CO<sub>2</sub>, are also reported in the study area. This regionally known CO<sub>2</sub> has carbon isotope ratios that bind it to a magmatic origin in the upper earth mantle, linked to attenuation and fracturing of the continental crust beneath the Massif Central (Olive and Boulègue, 2004).

## **Methods**

Investigations carried out around Lake Pavin are built around the procedures for measuring gases in the soil. The detailed methodology used by the authors can be found *e.g.* in Michel – Le Pierrès *et al.* (2010) and is greatly issued from the one used *e.g.* by Baubron and Sabroux (1984) or Baubron *et al.* (1992). We just recall here the basic principles of those methods.

The measurement of CO<sub>2</sub>, like that of CH<sub>4</sub> and O<sub>2</sub>, is done on site, the equipment used also allowing to collect samples for helium and radon analysis. Sampling and measurements are conducted at a constant depth of 1 m, first to allow comparison between measurements acquired at different times, and second to limit the influence of atmospheric gases (*e.g.* Hinkle, 1994). CO<sub>2</sub> and CH<sub>4</sub> concentrations are determined by non-dispersive infrared absorption and the concentrations of O<sub>2</sub> by electrochemistry (LFG20 gas analyzer, ADC Gas Analysis Limited, UK).

Determination of  $^{222}\text{Rn}$  activities is done by photomultiplication counting using samples taken in dedicated flasks ("Calen" counter, Algade, France), between 3 and 6 hours after on site collection. This time interval is needed to reach equilibrium in the flask and allow the disappearance of 219 and 220 radon isotopes, alpha emitters with very short period. Hourly measurements of radon activities at a specific location (Escarot) were also conducted using a Barasol probe (Algade, France), which measures activities by absorption spectrometry via a silicon detector.

Last, helium is quantified by mass spectrometry (leak detector Adixen ASM102S, France) with reference to the atmospheric content (5.24 ppm), using samples stored in Tedlar bags and analyzed on a semi-daily basis. The measured specie is the  $^4\text{He}$  isotope, the most abundant one, whose concentration approaches the one of total helium (*e.g.* Oliver *et al.*, 1984).

Occasionally, additional sampling was carried out in glass bulbs to determine  $\delta^{13}\text{C}_{\text{CO}_2}$  isotope ratios at laboratory by mass spectrometry (Delta S Thermo/Finnigan or Gas Bench system associated with a Delta + XP).  $\delta^{13}\text{C}_{\text{CO}_2}$  isotope ratios are expressed relative to the standard reference Vienna Pee Dee Belemnite (‰ VPDB). Other gaseous species present in these samples are also quantified by gas chromatography (Varian 3400), the following species being monitored:  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , Ar,  $\text{O}_2$ ,  $\text{N}_2$ , He,  $\text{H}_2$ ,  $\text{C}_n\text{H}_{2n+2}$  ( $n=0$  à 6).

Spot measurements were conducted in August and September 2008, February, April and September 2009, and acquisitions by the Barasol probe have been initiated in May 2009.

The interpretation of results should always be made in conjunction with weather conditions that prevailed before and during the measurement campaigns. Numerous of factors may affect the emission of gases (*e.g.* Finkelstein *et al.*, 1998 ; Toutain and Baubron, 1999): climatic ones (atmospheric pressure, temperature, soil moisture, wind effects and ventilation), but also intrinsic soil characteristics (composition, structure) and external forcing (diurnal variation linked to the sun, solar activity, earth tides). These factors primarily affect radon, but also  $\text{CO}_2$  (Heinicke *et al.*, 1993) and helium (Virk and Walia, 2001).

In this study, temperatures and pressures records were only collected since May 2009 by the Barasol probe. For the other campaigns, we refer to the weather history database of Météo-France (Table 1). The year 2008 was wetter than the 30 years average, but the sampling periods have not been greatly affected by this excess rainfall. At the opposite, 2009 is a dryer year, only the springtime being rainy. As the sampling strategy was focused on a complete scan of the area in 2008 and focus on specific areas in 2009, for which some data were then already available, it appears that weather conditions do not constitute the major factor explaining the variability on the measures. This is particularly due to the fact that large amounts of rainfall on

short time intervals are needed to significantly alter the concentrations of soil gas at depth. Hinkle (1994) reports a quantity of 50 mm to affect the CO<sub>2</sub> concentrations at 70 cm depth in Hawaiian soils, which are naturally quite moist. Moreover, we performed measurements at a greater depth, where the external forcing has a smaller influence (Wattananikorn *et al.*, 1998). This statement is corroborated by the Barasol data: between May the 16<sup>th</sup> and September the 7<sup>th</sup> 2009, soil temperatures varied only between 8.28 and 15.25°C (mean value: 12.77 ± 1.61°C), whereas, for example, air temperatures ranged from 13 to 26.2°C in August 2009 in Aurillac. Thermal attenuation in soils is well highlighted. Pressure measurements do not follow the same behaviour. As the Barasol probe is driven into the ground via PVC tubing, pressure changes replicate those of the atmosphere directly, and therefore are more variable over the same period. Barometric pressure, corrected to sea level, varied between 1002.7 and 1033.6 mbar (mean value: 1022.4 ± 4.5 mbar).

Table 1 :

Paramètres météorologiques au cours de campagnes de mesure ; d'après

<http://france.meteofrance.com>; la station météorologique de Clermont-Ferrand (331 m) est située à 30 km au NNE du Pavin ; la station d'Aurillac (639 m) à 70 km au SSW du Pavin.

Meteorological parameters during field surveys, from <http://france.meteofrance.com>; Clermont-Ferrand weather station (331 m a.s.l.) is located 30 km to the NNE of Lake Pavin; Aurillac weather station (639 m a.s.l.) is located 70 km to the SSW of Lake Pavin.

	<b>Clermont-Ferrand</b>		<b>Aurillac</b>	
	<b>T<sub>min</sub> / T<sub>max</sub> (°C)</b>	<b>Rainfall (mm)</b>	<b>T<sub>min</sub> / T<sub>max</sub> (°C)</b>	<b>Rainfall (mm)</b>
<b>Year 2007</b>	7.1 / 16.8	587	5.4 / 15.2	1131
<b>Year 2008</b>	6.5 / 16.6	734	5.1 / 15	1281
<b>Year 2009</b>	6.9 / 17.4	510	5.2 / 15.9	1073
<b>Mean 1971-2000</b>	6.1 / 16.3	592	4.9 / 14.6	1232
	<b>Pavin area</b>			
	<b>Climatological norms</b>	<b>Rainfall (mm)</b>		
<b>August 2008</b>	Slightly more humid than norms	# 60		
	Similar temperatures than norms			
<b>September 2008</b>	Rainfall deficit	# 100		
	Temperatures lesser than norms (by 1°C)			
<b>February 2009</b>	Rainfall deficit	# 50		
	Temperatures lesser than norms (by 1°C)			
<b>April 2009</b>	Rainfall excess (by a factor 2)	# 200		
	Temperature greater than norms			
<b>September 2009</b>	Rainfall deficit (50%)	# 60		
	Similar temperatures than norms			

## **Results and discussion**

### **Spot data**

Concentrations ranges for monitored gases are reported in Table 2. The CO<sub>2</sub> content varies between sub-atmospheric one to 100% (vol.). The oxygen content is inversely correlated and varies between 21.2 and 0% (vol.). Radon activities are comprised between 10 and 83,500 Bq/m<sup>3</sup>, helium concentrations between 5.1 and nearly 50 ppm. A majority of the measurements were made during periods of biological activity in soil: for CO<sub>2</sub>, 203 measurements were performed in August and September 2008, 6 in February 2009, 70 in April 2009 and 36 in September 2009.

Moreover, there is a very good correlation between measurements made on the field and laboratory measurements. The 8 samples analyzed show a very slight overestimation of CO<sub>2</sub> quantified by infrared detection on the field (+ 0.12%), and consequently a slight underestimation of the O<sub>2</sub> levels quantified by electrochemistry (- 2.3%). Other detected gases are atmospheric compounds, namely nitrogen and argon (Table 2), in quantities close to the atmospheric levels except for the sample at 99.5% CO<sub>2</sub>. Traces of methane have sometimes been reported, the maximum (120 ppm) was encountered in the periphery of a peat bog.

Table 2 :

Teneurs mesurées en gaz des sols autour du lac Pavin, par mesure directe (haut) et sur prélèvement au laboratoire (bas).

Soil gas concentrations around Lake Pavin: *in-situ* measurement (top) and laboratory analysis (bottom).

	CO <sub>2</sub> (%)	O <sub>2</sub> (%)	<sup>222</sup> Rn (Bq/m <sup>3</sup> )	<sup>4</sup> He (ppm)		
<b>Nb. of meas.</b>	315	307	240	88		
<b>Minimum</b>	0,03	0	10	5,14		
<b>Maximum</b>	100	21,2	83500	47,74		
<b>1<sup>st</sup> Quartile</b>	0,37	17,2	3180	5,23		
<b>Median value</b>	0,93	19,6	10800	5,25		
<b>3<sup>rd</sup> Quartile</b>	3,1	20,4	20800	7,52		
<b>Mean value</b>	9,03	17,6	15000	9,28		
<b>Std. dev.</b>	24,9	5	16000	8,27		
	CO <sub>2</sub> (GC)	O <sub>2</sub> (GC)	N <sub>2</sub> (GC)	Ar (GC)	CH <sub>4</sub> (GC)	δ <sup>13</sup> C <sub>CO2</sub> (‰ VPDB)
<b>Nb. Of meas.</b>	8	8	8	8	4	8
<b>Minimum</b>	0,63	0,2	1,3	0,02	0,001	-25,5 (CO <sub>2</sub> =
<b>Maximum</b>	99,5	20	79,5	1,04	0,012	-3 (CO <sub>2</sub> =
<b>1<sup>st</sup> Quartile</b>	1,6	13,6	77	0,89	0,001	-23,9
<b>Median value</b>	2,98	18	77,4	0,93	0,001	-23,1
<b>3<sup>rd</sup> Quartile</b>	6,68	19,8	78	0,97	0,004	-22,8
<b>Mean value</b>	15,92	14,9	68,3	0,83	0,004	-21
<b>Std. dev.</b>	31,8	6,7	25,3	0,31	0,005	6,9

The CO<sub>2</sub> concentrations mostly fall below 10% (vol.), except for specific areas that will be discussed later (Figure 2). This pivot point allows to define two different groups, and consequently two different behaviours, between CO<sub>2</sub> and O<sub>2</sub>. The first one, valid for CO<sub>2</sub> concentrations lesser than ten percent (line "a" in Figure 2), shows a very rapid decrease in oxygen concentrations as the carbon dioxide content increases, whereas the second one (line "b" in Figure 2) shows a less steeply decrease. The relative depletion of O<sub>2</sub> for the first group is done five times faster than for the second, respective relationships being, for a threshold value taken at 11% CO<sub>2</sub>: O<sub>2</sub> = -0.95 x CO<sub>2</sub> + 20.4 (n = 283 ; r<sup>2</sup> = 0.66) et O<sub>2</sub> = -0.2 x CO<sub>2</sub> + 20.8 (n = 32 ; r<sup>2</sup> = 0.94).

This observation therefore leads to distinguish the two following cases:

- the most frequent case, where oxygen levels decline rapidly as CO<sub>2</sub> levels increase (range 0.03 to 11% CO<sub>2</sub> approximately). Given maximum CO<sub>2</sub> concentrations encountered in natural environments where CO<sub>2</sub> emissions mainly result from biogenic processes (e.g. Gal *et al.*, 2010 ; Michel-Le Pierrès *et al.*, 2010), it is quite likely that the main mechanism of oxygen depletion is consumption of this gas by biological processes. This seems to be confirmed by the carbon isotope analyses (Table 2). Samples with CO<sub>2</sub> concentrations between 0.6 and 13.8% have isotope ratios of -22.3 to -25.5 ‰ VPDB (average -23.6 ‰), typically in the field of CO<sub>2</sub> produced from temperate climate vegetation ruled by Calvin photosynthesis cycle (-22 to -25 ‰ VDPB; Bakalowicz, 1979). In this perspective, the variability detected in the measurements may be based on the intensity of biological phenomena at the sampling point (inducing different CO<sub>2</sub> levels), the nature of the overlying vegetation or the result of reequilibrations between free CO<sub>2</sub> and CO<sub>2</sub> dissolved in soil pore water, as the moisture content of soils may vary (e.g. Amiotte-Suchet *et al.*, 1999).
- the second case, less frequent, suggests that oxygen depletion operates at a much slower rate. This lower oxygen consumption, that is not linked to the sampling period, indicates that the processes that need oxygen to occur are not preponderant. On the other hand, CO<sub>2</sub> levels for which this relationship is verified are high compared to average values commonly reported in soils (around 4%, Brooks *et al.*, 1983). An additional mechanism, provider of CO<sub>2</sub> but not of O<sub>2</sub>, should exist. In the context of the Massif Central, an endogenous process bringing additional CO<sub>2</sub> can be invoked. In this case, the isotopic ratio of the gas will be very different from that produced by biological activity, and close to -4 to -8 ‰ VPDB (e.g. Gerlach et Taylor, 1990). Moreover, the existence of a deep CO<sub>2</sub> flux is also known in this area, both at the Goyon mineral spring and in Lake Pavin itself (Olive and Boulègue, 2004 ; Assayag *et al.*, 2008). This other occurrence of a deep gas vent seems then to be verified in the present case, since the sample with 99.5% CO<sub>2</sub> provides a δ<sup>13</sup>C<sub>CO2</sub> at -3 ‰ VPDB.

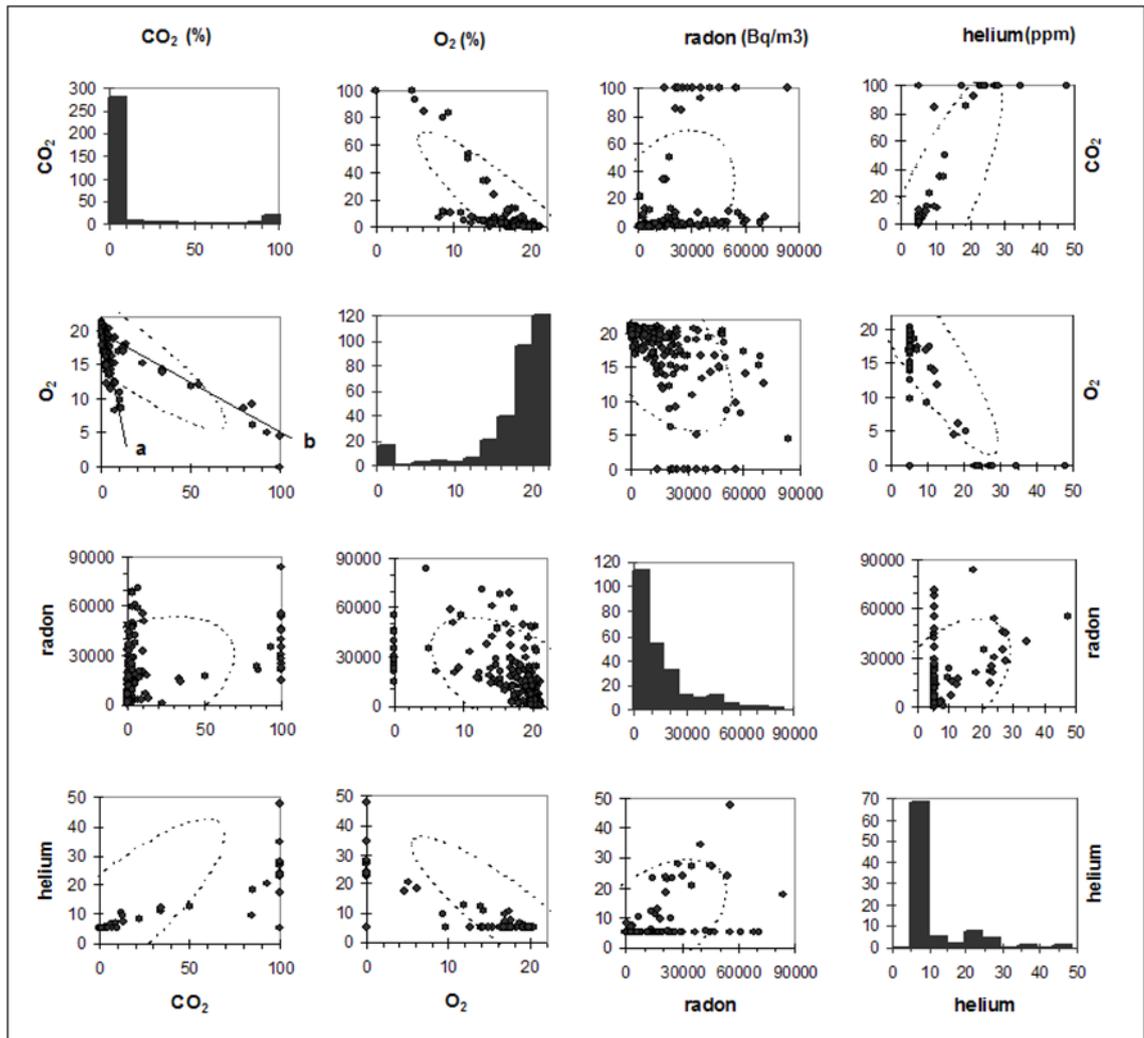


Figure 2

Relations entre les gaz mesurés dans les sols ; pour la signification des indices a et b, se référer au texte.

Relationships between gaseous species detected in soils; for significance of a and b labels, please refer to text.

In order to confirm this hypothesis, i.e. the existence of localized areas characterised by high CO<sub>2</sub> content originated from depth, let us examine <sup>4</sup>He and <sup>222</sup>Rn measurements.

Helium measurements have a median value almost identical to that of the atmosphere (Table 2), indicating that there is no widespread supply of helium in the area. Nevertheless, very important concentrations, exceeding 10 ppm, were measured for samples having 10% CO<sub>2</sub> or more (Table 2, Figure 2), but these helium rich samples do not correlate with radon amounts

(Pearson's correlation coefficient of the  $^4\text{He}/^{222}\text{Rn}$  ratio: 0.4). Accordingly, a common production mechanism for both radon and helium gases (i.e. production via the decay chain of uranium-238) does not seem to be a valuable explanation. A deeper origin of helium still seems the most likely, especially as the correlation between  $\text{CO}_2$  and helium is fairly good (Pearson's coefficient: 0.88). Yet, for nearly pure  $\text{CO}_2$  soil atmospheres, levels in helium are highly variable, covering the entire range of variation. Demixing phenomena in varying proportions, both quantitative and spatial, could cause these variations in the helium content of soils. Thus an area marked by a strong gas flux from depth is able to quickly carry the gas up to the surface without separation between species, while an area with a smaller and/or slower flux may allow the helium to degas preferentially, inducing the measurement of low helium levels. This led, as will be seen later, to the definition of anomalous areas with a smaller spatial extension for helium than for  $\text{CO}_2$  (Annunziatellis *et al.*, 2008). The occurrence, at Escarot, of both an important  $\text{CO}_2$  flux, clearly of magmatic origin, and high helium concentrations, emphasizes the specificity of this mofette, unlike other ones encountered in the Massif Central (e.g. Battani *et al.*, 2010).

Radon activities measured in soils around Lake Pavin do not exceed  $90,000 \text{ Bq/m}^3$  (Table 2), a rather low value compared to those encountered in the Limagne d'Allier (Gal *et al.*, 2010). As highlighted in the introduction, the combined use of radon and  $\text{CO}_2$  quite often highlights a good statistical relationship between these two gaseous species, the latter playing the role of carrier phase of the first (e.g. Etiope and Martinelli, 2002). In the present case, such an agreement is not established (Pearson's coefficient = 0.42), since high activities can be measured at low or high  $\text{CO}_2$  content (Figure 2). Frequently this relationship between  $\text{CO}_2$  and radon is attributed to the achievement of an optimum of the ratio "radioactive decay / radon transfer speed" without dilution by the  $\text{CO}_2$  phase. Consequently, measurements that are performed at the vertical of a more pronounced  $\text{CO}_2$  upflow zone should deliver a diluted radon signal and thus lower activities (Baubron *et al.*, 1992). Here, the highest activities are measured near the Escarot area that is also characterised by strong  $\text{CO}_2$  anomalies and uncommon helium enrichment.

Regarding the available data, we can not invoke a dilution effect to explain the  $\text{CO}_2$  – radon relationships at the Escarot mofette. On the other hand, it is possible that the heterogeneity of the volcanic formations lying at the surface masks this "plume" effect of the  $\text{CO}_2$ . Apart from this particular area, the poor correspondence between  $\text{CO}_2$  and radon may also be influenced by other carrier gas, e.g. such as  $\text{N}_2$  (Hong *et al.*, 2010; Walia *et al.*, 2010).

These contrasted behaviours between the different gases are used to produce a synthetic map of the study area (Figure 3). The interpolation technique used is the natural neighbour one. Krigging interpolation is not used, as semivariogram calculations suggest a too prominent

nugget effect, which makes this method poorly suited. From the natural neighbour mapping the following points emerged:

- the Escarot area is by far the most anomalous of the sector and has all the characteristics of a deep fed mofette: very high CO<sub>2</sub> and helium contents, slightly depleted carbon isotope ratios. The mofette can not be evidenced using radon activities, for the reasons mentioned above. The interpolated helium map can not help to define a preferred direction for degassing, this effect being induced by the calculating procedure. In contrast, high CO<sub>2</sub> levels are almost aligned along a North-South direction, which is the same as the one proposed by Lavina and Del Rosso (2006) for tectonic structures. This area is however limited to a relatively small extent, that we were able to visually estimate the extension in April 2009, thanks to the presence of a water saturated – upper soil layer due to snowmelt. Many gas exhausts, mainly of pure CO<sub>2</sub>, were identified in a 400 m long (North-South) and 100 m wide (East-West) corridor, centered on the so-called Escarot mofette;
- a second CO<sub>2</sub> anomalous zone can be identified in the immediate vicinity of the carbogaseous Goyon mineral spring, which is understandable through the occurrence of stripping and phase separation phenomena during the upwelling to the surface. In this area, no significant anomaly in helium contents is found, probably indicating a fluid circulation occurring under moderate to low fluxes;
- apart from the two above mentioned areas, some smaller scale anomalies are highlighted in Figure 3, but often linked to the existence of few measurements (mapping bias induced by the interpolation method). Two of these areas are located southward and south-eastward from Lake Pavin, but do not show apparent relationship with the geological structures. A third, perhaps more significant (larger number of measurements), is aligned along a North-East – South-West direction between the mofette and the lake, that may correspond to a direction also highlighted by Lavina and Del Rosso (2006);
- finally, the radon behaviour results from a combination of complex processes, namely emanation, diffusion and/or advection/convection, and finally exhalation ones (*e.g.* Ielsch *et al.*, 2010). As a whole, such an intricacy makes interpretations difficult to perform using the current dataset, except in the vicinity of the Escarot mofette, where this method can help to better define gas dynamics when a deep rising gas is present.

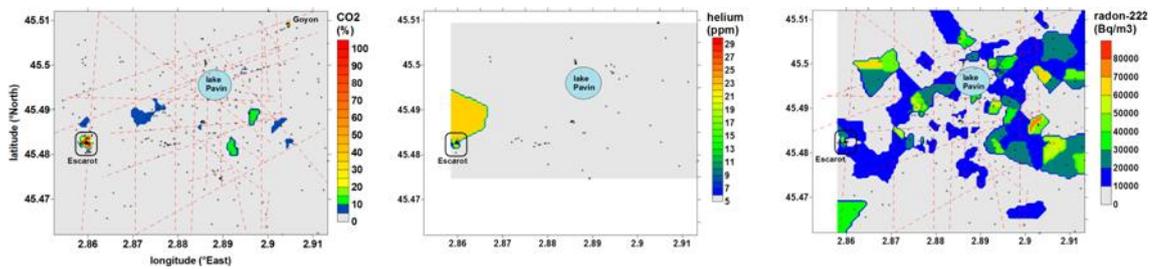


Figure 3 :

Cartographie synthétique de la zone d'étude : interpolations (méthode du voisin naturel) des teneurs en CO<sub>2</sub>, hélium et des activités en radon ; les tirets rouge représentent le schéma structural de la zone tel que proposé par Lavina et Del Rosso (2006).

Synthetic map of the study area: contours of the CO<sub>2</sub>, helium and radon activity concentrations are done using the natural neighbour interpolation method; red dashed lines figure the structural sketch as proposed by Lavina and Del Rosso (2006).

### Hourly radon measurements

Cartographie synthétique de la zone d'étude : interpolations (méthode du voisin naturel) des teneurs en CO<sub>2</sub>, hélium et des activités en radon ; les tirets rouge représentent le schéma structural de la zone tel que proposé par Lavina et Del Rosso (2006).

Synthetic map of the study area: contours of the CO<sub>2</sub>, helium and radon activity concentrations are done using the natural neighbour interpolation method; red dashed lines figure the structural sketch as proposed by Lavina and Del Rosso (2006).

In order to take into account the better knowledge of the mofette the radon may bring, long term radon monitoring has been done at Escarot. The Barasol probe was emplaced at 60 cm depth, in one of the most anomalous location, where the CO<sub>2</sub> content was measured at 100% (2 measurements) in April 2009 ( $\delta^{13}\text{C}_{\text{CO}_2} = -3 \text{ ‰ VPDB}$ ; 1 measurement), together with radon activities of 40,000 to 55,400 Bq/m<sup>3</sup> and helium concentrations of 34.5 to 47.7 ppm. <sup>222</sup>Rn activity, soil temperature and atmospheric pressure measurements extend from May 11 to September 7, 2009 (Table 3).

Table 3

	<sup>222</sup> Rn (Bq/m <sup>3</sup> )	soil temperature (°C)	Barometric pressure
			(mbar, normalised to sea level)
<b>Minimum</b>	54700	8,28	1002,7
<b>Maximum</b>	102900	15,25	1033,6
<b>1<sup>st</sup> Quartile</b>	66900	11,48	1020
<b>Median value</b>	72400	13,24	1023,2
<b>3<sup>rd</sup> Quartile</b>	79400	14	1025,6
<b>Mean value</b>	73800	12,77	1022,4
<b>Std. dev.</b>	9200	1,61	4,5

Statistiques calculées sur les enregistrements de la sonde Barasol (2764 mesures horaires).

Statistics calculated from the Barasol probe data (2764 hourly measurements).

Radon activities measured since May are on average higher than those measured punctually in April. This variability in radon activity over time is clearly visible in Figure 4, and is not related to pressure and/or temperature changes. Pressure variations are dictated by the alternation of anticyclones and depressions in the study area. Temperature variations reflect the gradual soil warming during summertime, the thermal optimum being reached at mid-August.

This meteorological derived information does not allow to identify a predominant mechanism leading to the occurrence of low or high radon activities. For example, the beginning of June is marked by a strong depression episode, with several tens of millimetres of rainfalls.

Nevertheless, the radon activities measured in June do not differ from those found a few days before rainfall occurrence. This is surprising, as a rainy episode is expected to cause either a decrease in activities by partial dilution of gas in water, or an increase by induced barrier effect, and, simultaneously, a decrease in atmospheric pressure will tend to increase the concentrations of gases by pumping effect (Charlet *et al.*, 1989 ; Finkelstein *et al.*, 1998 ; Garavaglia *et al.*, 1998 ; King, 1985 ; Kumar *et al.*, 2009 ; Richon *et al.*, 2003). At other times, a drop in activity is found contemporaneously with rainfalls (August 23), or, in other cases, an increase (July 22). The temporal evolution of radon activities thus relies upon other factors.

There is no more relationship with temperature, neither diurnal nor seasonal dependence (Figure 4). High activities (> 80,000 Bq/m<sup>3</sup>) are both measured in cool (11°C) or warmer (15°C) soil. At hourly time scale, this lack of relationship is reflected by a Pearson's correlation coefficient of only 0.147.

Other phenomena may contribute to the observation of variations of the radon activities, in particular the existence of cycles in the production of CO<sub>2</sub> in soil (*e.g.* Reardon *et al.*, 1979).

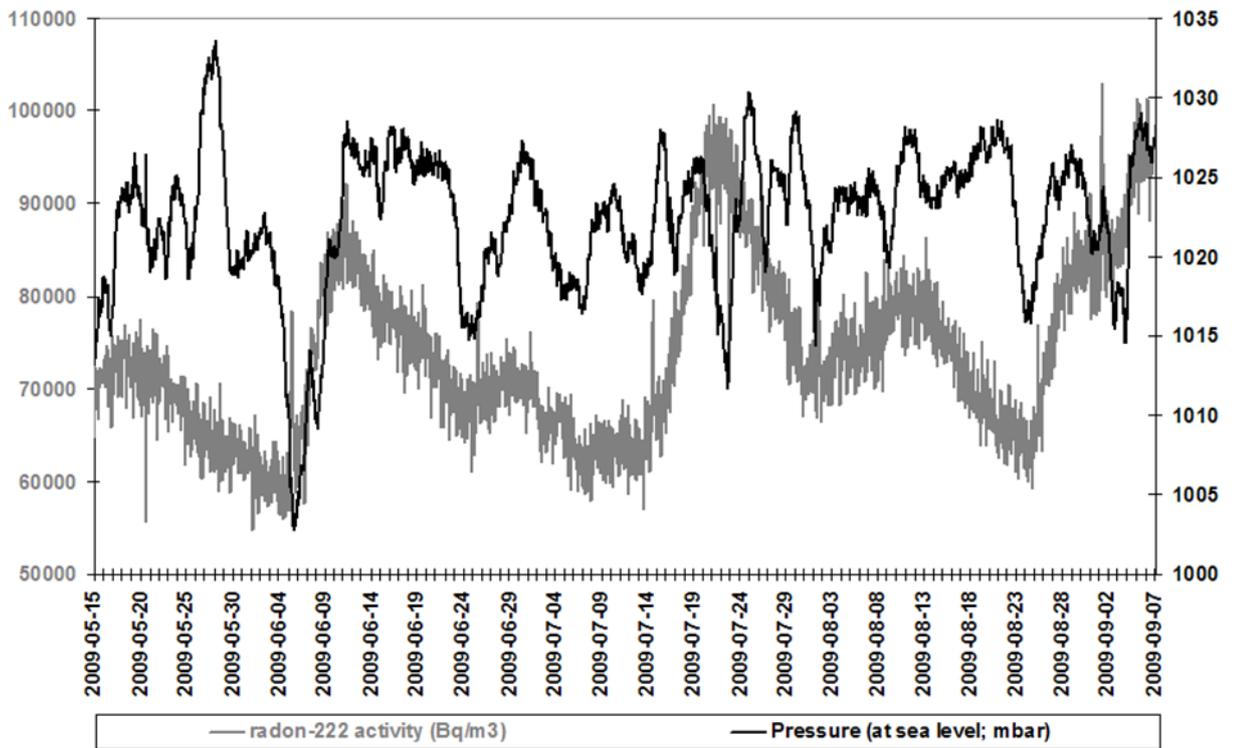
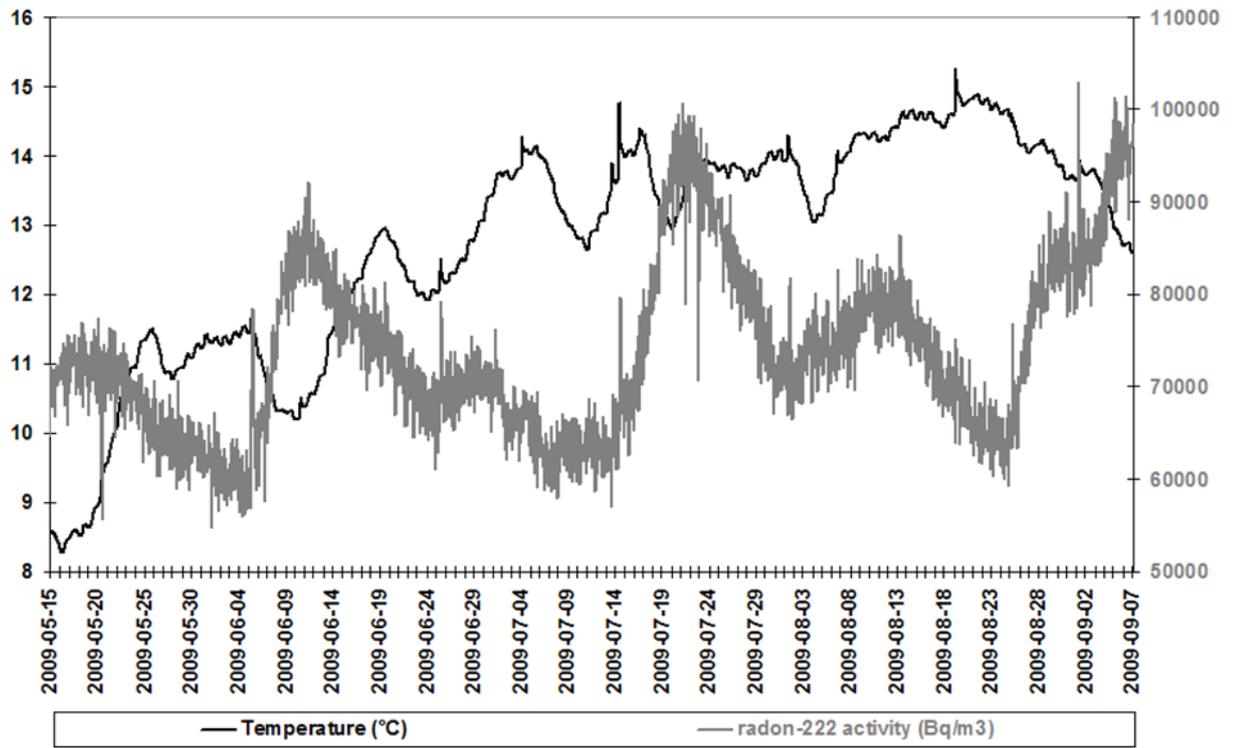
Nevertheless, this hypothesis is here unlikely, as the very high CO<sub>2</sub> levels encountered would

mask the possible influence of organic production, which could only contribute to some percents and not tens of percents. Moreover, the CO<sub>2</sub> gas phase has been identified to be of endogenous origin.

The most plausible explanation is a connection between radon activity trends and changes in CO<sub>2</sub> emissions related to deeper causes. Density spectra analysis suggests a long-term determinism of the radon activity pulses (Figure 5). Indeed, if temperatures preferentially evolve on a daily basis, and pressures on a semi-daily basis, two other trends seem to exist. The first one concerns pressure evolutions, suggesting the existence of a 460 hours-long period (c.a. 20 days); the second, concerning radon evolution, a 920 hours-long period (c.a. 40 days).

#### Figure 4

Variations horaires des activités en radon-222, de la température du sol et de la pression atmosphérique – zone de la mofette d'Escarot – période du 11 mai au 07 septembre 2009.  
Hourly variations of radon-222 activities, soil temperature and atmospheric pressure – Escarot mofette – period from the 11th of May to the 07th of September 2009.



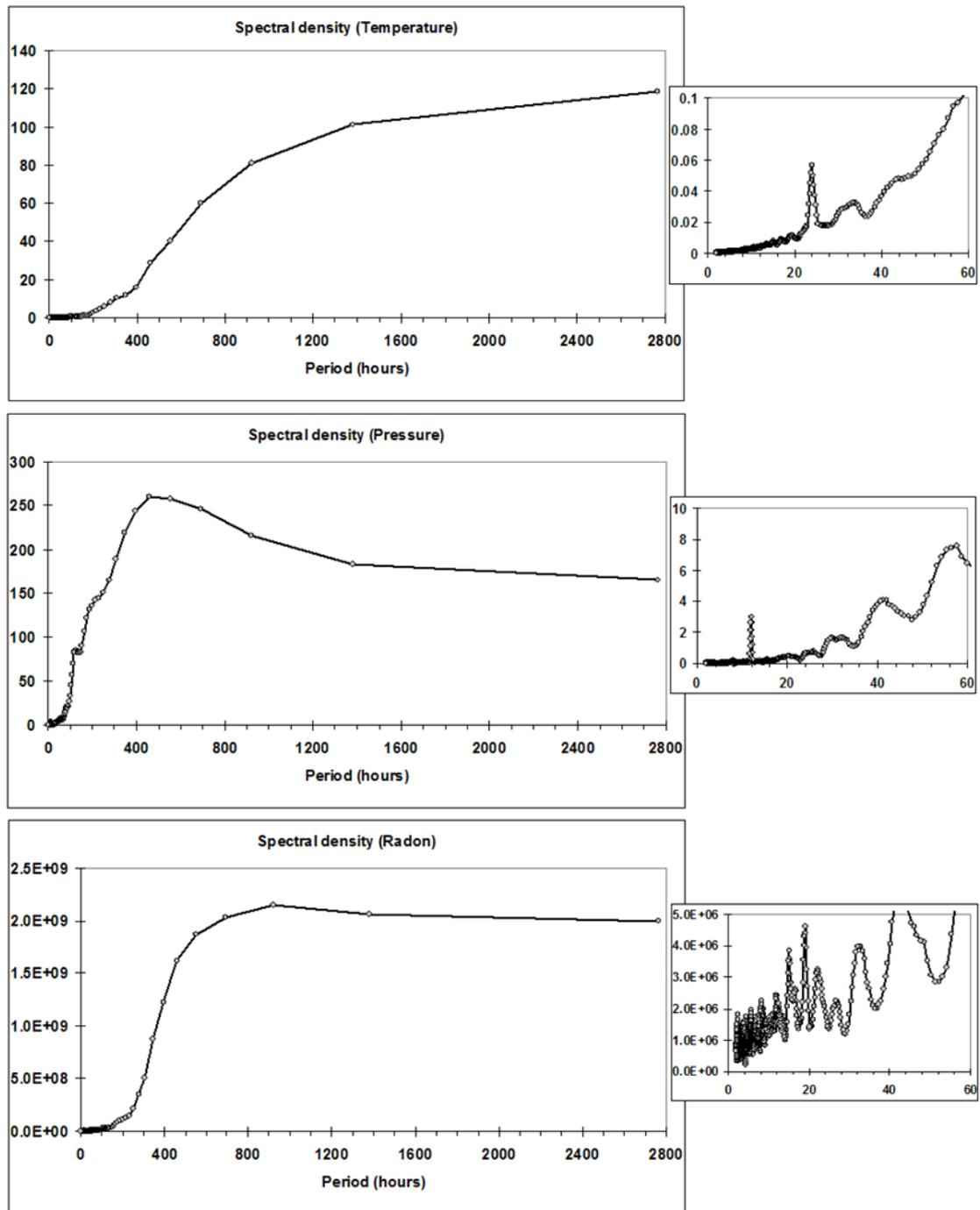


Figure 5

Analyse en densité spectrale des données acquises par la sonde Barasol.

Spectral density analysis of Barasol probe data.

Based on this observation, two full periods of 40 days are available through the records. To better compare these two time intervals, they have been brought together to a common temporal origin (Figure 6). Moreover, to enhance the readability of the figure, we chose to represent the 12 hours moving average rather than the hourly variations. The common origin is taken at a period of reduced activity, close to  $60,000 \text{ Bq/m}^3$ . A remarkable synchronicity appears when comparing these data. Around 8 days after the registration of the minimum radon activity, and following the appearance of a very short burst 24 to 36 hours after that minimum, a peak of the radon activity occurs, followed by a period of slow decline. Subsequently, a secondary peak of activity is visible, before activities decrease again to reach their lowest values.

This period of about 40 days does not seem to be directly dependent from lunar/solar and terrestrial tides, whose main periods are 12 and 24 hours with harmonics at 15 and 30 days (Cagniard, 1960). A possible link to cyclical  $\text{CO}_2$  fluxes at depth, and thus, to an activity underneath the study area (of geodynamic, of magmatic type?), may be the most likely phenomenon that could explain these temporal variations.

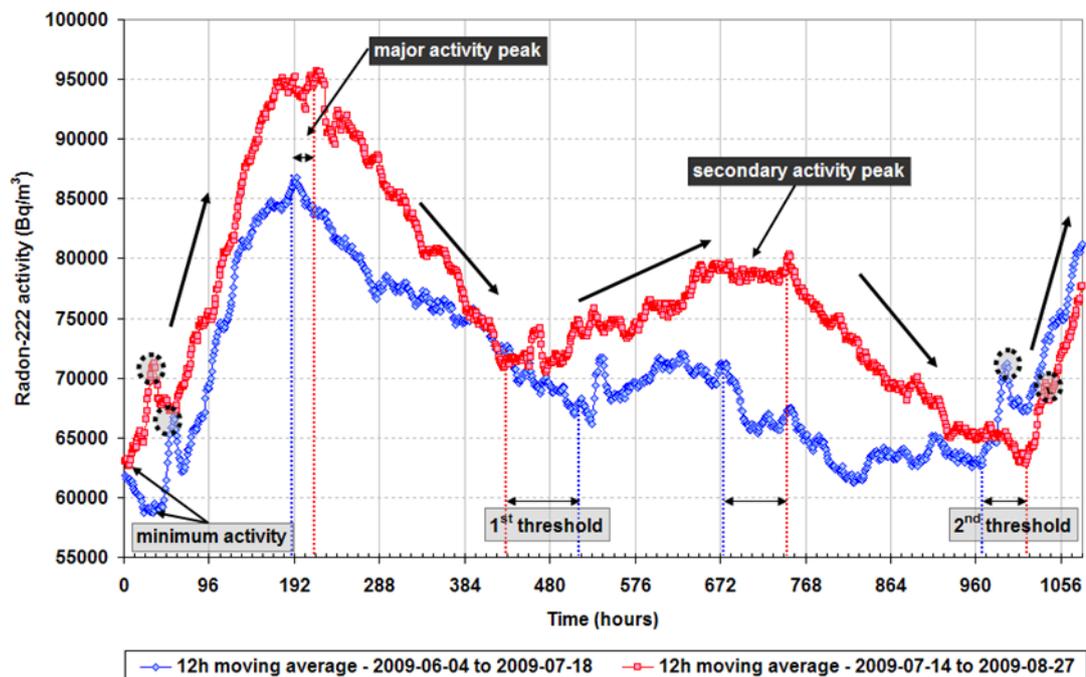


Figure 6 :  
 Comparaison de deux cycles de 40 jours sur les activités radon.  
 Comparison between two 40-days long radon activity cycles.

## **Conclusion**

In connection with natural hazards issues and gas hazard in Lake Pavin, quantifications of CO<sub>2</sub>, O<sub>2</sub>, helium and radon contents in soils have highlighted an area rich in gas, of mofette type. Such structures are not unique across the Massif Central (the Neyrac-les-Bains mofette in Ardèche; the “dog cave” in Chamalières and the Brissac geyser in Saint-Maurice-ès-Allier, Puy-de-Dôme), as well as the numerous carbogaseous occurrences reported *e.g.* by Matthews *et al.* (1987). As a consequence, the existence of a CO<sub>2</sub> degassing zone in such a geological context does not constitute, in itself, a sign of magmatic reactivation. However, the concomitance of high CO<sub>2</sub> and high helium concentrations confers to the Escarot mofette an original feature in the Massif Central. Examination of other parameters, including chemical and isotopic composition of groundwater, will be in the future associated with these soil gas measurements, to bring additional data that could help to constrain fluid dynamism near the mofette. The Escarot area seems to have its own dynamism, which appears at first sight dominated by a pulsation close to 40 days. Apart from this particular area, no area susceptible to experience significant CO<sub>2</sub> emissions is highlighted. Soil CO<sub>2</sub> concentrations are very frequently lesser than 5%, levels that occur naturally during periods of photosynthetic activity, even in areas completely devoid of recent Quaternary volcanic activity.

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## **Bibliography**

Amiotte-Suchet, P., Aubert, D., Probst, J.L., Gauthier-Lafaye, F., Probst, A., Andreux, F., Viville, D., 1999.  $\delta^{13}\text{C}$  pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study Vosges mountains, France. *Chem. Geol.* 159, 129–145.

Annunziatellis, A., Beaubien, S.E., Bigi, S., Ciotoli, G., Coltella, M., Lombardi, S., 2008. Gas migration along fault systems and through the vadose zone in the Latera caldera (central Italy): Implications for CO<sub>2</sub> geological storage. *Int. J. Green. Gas Con.* 2, 353-372.

Assayag, N., Jézéquel, D., Ader, M., Viollier, E., Michard, G., Prévot, F., Agrinier, P., 2008. Hydrological budget, carbon sources and biogeochemical processes in Lac Pavin (France): Constraints from  $\delta^{18}\text{O}$  of water and  $\delta^{13}\text{C}$  of dissolved inorganic carbon. *App. Geochem.* 23, 2800-2816.

Aubert, M., Baubron, J.C., 1988. Identification of a hidden thermal fissure in a volcanic terrain using a combination of hydrothermal convection indicators and soil atmosphere analysis. *J. Volcanol. Geoth. Res.* 35, 217-225.

Bakalowicz, M., 1979. Contribution de la géochimie des eaux à la connaissance de l'aquifère karstique et de la karstification. Th. Doct. Etat Sc. Nat., Univ. Paris VI, 269 p.

Battani, A., Deville, E., Faure, J.-L., Noirez, S., Tocqué, E., Jeandel, E., Benoît, Y., Schmitz, J., Parlouar, D., Gal, F., Le Pierrès, K., Brach, M., Braibant, G., Bény, C., Pokryszka, Z., Charmoille, A., Bentivegna, G., Pironon, J., de Donato, P., Garnier, C., Cailteau, C., Barrès, O., Radilla, G., Bauer, A., 2010. Geochemical study of the natural CO<sub>2</sub> emissions in the French Massif Central: How to predict origin, processes and evolution of CO<sub>2</sub> leakage. *Oil Gas Sci. Technol.*, vol. 65, No 4, 615-633.

Baubron, J.C., Sabroux, J.C., 1984. Analyses de gaz dans les sols sur les zones de Bouillante et de Moscou (Guadeloupe). BRGM report SGN 400 GTH, 94 p.

Baubron, J.C., Mercier, F., Rouzaire, D., 1992. Eaux minérales de Sainte Marguerite (Puy de Dôme) – Prospection géochimique in situ des gaz des sols. BRGM report R-36492-AUV-4S-92, 35 p.

Baubron, J.C., Rigo, A., Toutain, J.P., 2002. Soil gas profiles as a tool to characterise active tectonic areas: the Jaut Pass example (Pyrenees, France). *Earth Planet. Sc. Lett.* 196, 69–81.

Beaubien, S.E., Ciotoli, G., Coombs, P., Dictor, M.C., Krüger, M., Lombardi, S., Pearce, J.M., West, J.M., 2008. The impact of a naturally occurring CO<sub>2</sub> gas vent on the shallow ecosystem

and soil chemistry of a Mediterranean pasture (Latera, Italy). *Int. J. Green. Gas Con.* 2, 373-387.

Boivin, P., Besson, J.-C., Briot, D., Gourgaud, A., Labazuy, P., de Larouzière, F.D., Livet, M., Mergoil, J., Miallier, D., Morel, J.-M., Vernet, G., Vincent, P., 2003. *Volcanologie de la chaîne des Puys, Parc Naturel Régional de la chaîne des Puys (Ed.), Carte et fascicule, 4<sup>th</sup> ed.*

Brooks, G.A., Folkoff, M.E., Box, E.O., 1983. A global model of soil carbon dioxide. *Earth Surf. Proc. Land.* 8, 79–88.

Brousse, R., 1969. L'âge des lacs du sud du Mont-Dore. *Ann. Stat. Biol. Besse-en-Chandesse* 4, 201-208.

Cagniard, L., 1960. *Introduction à la physique du globe, Technip (Ed.).*

Camus, G., Michard, G., Olive, P., Boivin, P., Desgranges, P., Jézéquel, D., Meybeck, M., Peyrus, J.C., Vinson, J.M., Viollier, E., Kornprobst, J., 1993. Risque d'éruption gazeuse carbonique en Auvergne. *Bull. Soc. Géol. France*, t.164, n°6, 767-781.

Charlet, J.M., Doremus, P., Quinif, Y., Losfeld, A., Garcia, F., 1989. Réalisation et exploitation d'une campagne de mesures des émanations radon dans le bassin de Mons, essai d'application à la prévision des risques sismiques. *Annales de la Société Géologique de Belgique*, tome 112, fascicule 2, 381-392.

Ciotoli, G., Etiope, G., Guerra, M., Lombardi, S., 1999. The detection of concealed faults in the Ofanto Basin using the correlation between soil-gas fracture surveys. *Tectonophysics* 301, 321-332.

Del Rosso d'Hers, T., Bernardi, M., 2006. *L'hydrologie, l'hydrogéologie et l'hydrogéochimie du système volcanique holocène Montchal – Pavin. Réunion Annuelle des Sciences de la Terre, Dijon, 2006.*

Devaux, J., 1980. Contribution à l'étude limnologique du lac Pavin (France) – I : Facteurs abiotiques et phytoplancton. *Hydrobiologia*, vol.68, No 2, 167-189.

Etioppe, G., Martinelli, G., 2002. Migration of carrier and trace gases in the geosphere: an overview. *Phys. Earth Planet. In.* 129, 185-204.

Faure, M., Lardeaux, J.M., Ledru, P., 2009. A review of the pre-Permian geology of the Variscan French Massif Central. *C. R. Geoscience* 341, 202-213.

Finkelstein, M., Brenner, S., Eppelbaum, L., Ne'eman, E., 1998. Identification of anomalous radon concentrations due to geodynamic processes by elimination of Rn variations caused by other factors. *Geophys. J. Int.* 133, 407-412.

Gal, F., Le Pierrès, K., Brach, M., Braibant, G., Bény, C., Battani, A., Tocqué, E., Benoît, Y., Jeandel, E., Pokryszka, Z., Charmoille, A., Bentivegna, G., Pironon, J., de Donato, P., Garnier, C., Cailteau, C., Barrès, O., Radilla, G., Bauer, A., 2010. Surface gas geochemistry above the natural CO<sub>2</sub> reservoir of Montmiral (Drôme-France), source tracking and gas exchange between soil, biosphere and atmosphere. *Oil Gas Sci. Technol.*, vol. 65, No 4, 635-652.

Garavaglia, M., Braitenberg, C., Zadro M., 1998. Radon monitoring in a cave of North-Eastern Italy, *Phys. Chem. Earth* 23, vol. 9-10, 949-952.

Gerlach, T. M., Taylor, B. E., 1990. Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano, *Geochim. Cosmochim. Ac.* 54, 2051-2058.

Guerra, M., Lombardi, S., 2001. Soil gas method for tracing neotectonic faults in clay basins: the Pisticci field (Southern Italy). *Tectonophysics* 339, 511-522.

Heinicke, J., Koch, U., Martinelli, G., 1993. Simultaneous measurements of radon and CO<sub>2</sub> in spring water for earthquake prediction research. *Proceedings of the Scientific meeting on the seismic protection, Venice 12-13 July 1993*, 152-155.

Hinkle, M.E., 1994, Environmental conditions affecting concentrations of He, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in soft gases, *App. Geochem.* 9, 53-63.

Hong, W.L., Yang, T.F., Walia, V., Lin, S.J., Fu, C.C., Chen, Y.G., Sano, Y., Chen, C.H., Wen, K.L., 2010. Nitrogen as the carrier gas for helium emission along an active fault in NW Taiwan. *App. Geochem.* 25, Issue 4, 593-601.

Ielsch, G., Cushing, M.E., Combes, Ph., Cuney, M., 2010. Mapping of the geogenic radon potential in France to improve radon risk management: methodology and first application to region Bourgogne. *J. Environ. Radioact.*, doi:10.1016/j.jenvrad.2010.04.006, in press

Israel, H., Bjornsson, S., 1967. Radon ( $Rn^{222}$ ) and thoron ( $Rn^{220}$ ) in soil air over faults. *Z. Geophys.*, 33 (1), 48-64.

King, C.Y., 1985. Impulsive Radon Emanation on a Creeping Segment of the San Andreas Fault, California. *Pure Appl. Geophys.* 122, 340-352.

Klusman, R.W., Jaacks, J.A., 1987. Environmental influences upon mercury, radon and helium concentrations in soils gases at a site near Denver, Colorado. *J. Geochemi. Explor.* 27, 259-280.

Koga, A., Taguchi, S., Mahon, W.A.J., 1983. Geochemistry of near surface gases in Ngawha geothermal area, N.Z.. *Proceedings of the 5<sup>th</sup> New Zealand Geothermal Workshop.*

Krüger, M., West, J., Frerichs, J., Oppermann, B., Dictor, M.C., Joulain, C., Jones, D., Coombs, P., Green, K., Pearce, J., May, F., Möller, I., 2009. Ecosystem effects of elevated  $CO_2$  concentrations on microbial populations at a terrestrial  $CO_2$  vent at Laacher See, Germany. *GHGT-9, Energy Procedia* 1, 1933-1939.

Kumar, A., Singh, S., Mahajan, S., Singh Bajwa, B., Kalia, R., Dhar, S., 2009. Earthquake precursory studies in Kangra valley of North West Himalayas, India, with special emphasis on radon emission. *Appl. Radiat. Isotopes* 67, 1904–1911.

Lavina, P., 1985. Le volcan du Sancy et le « Massif Adventif » (Massif des Monts Dore - Massif Central Français). *Etudes Volcanologiques et structurales. Thèse 3<sup>ème</sup> cycle, Clermont-Ferrand.*

Lavina, P., Del Rosso d'Hers, T., 2006. Le système volcanique holocène Montcineyre – Montchal – Pavin. *Les nouvelles découvertes. Présentation à la Réunion Annuelle des Sciences de la Terre, Dijon, 2006.*

Lenoir, X., Garrido, C.J., Bodinier, J.-L., Dautria, J.M., 2000. Contrasting lithospheric mantle domains beneath the Massif Central (France) revealed by geochemistry of peridotite xenoliths. *Earth Planet. Sci. Lett.* 181, 359–375.

Matthews, A., Fouillac, C., Hill, R., O'Nions, R.K., Oxburgh, E.R., 1987. Mantle-derived volatiles in continental crust: The Massif Central of France. *Earth Planet. Sc. Lett.* 85, 117-128.

Michard, G., Viollier, E., Jézéquel, D., Sarazin, G., 1994. Geochemical study of a crater lake: Pavin lake, France – Identification, location and quantification of the chemical reactions in the lake. *Chem. Geol.* 115, 103-115.

Michel – Le Pierrès, K., Gal, F., Brach, M., Guignat, S., 2010. Radon, Helium and CO<sub>2</sub> measurements in soils overlying a former exploited oilfield, Pechelbronn district, Bas-Rhin, France. *J. Environ. Radioactiv.* 101, 835-846.

Olive, P., Boulègue, J., 2004. Etude biogéochimique d'un lac méromictique: le lac Pavin, France. *Géomorphologie: relief, processus, environnement* 4, 305-316.

Oliver, B.M., Bradley, J.G., Farrar, H., 1984. Helium concentration in the Earth's lower atmosphere. *Geochim. Cosmochim. Ac.* 48, 1759-1767.

Pauwels, H., Gaus, I., Le Nindre, Y.-M., Pearce, J., Czernichowski-Lauriol, I., 2007. Chemistry of fluids from a natural analogue for a geological CO<sub>2</sub> storage site (Montmiral, France): Lessons for CO<sub>2</sub>-water-rock interaction assessment and monitoring. *App. Geochem.* 22, 2817-2833.

Pelletier, J.P., 1968. Un lac méromictique, le Pavin (Auvergne). *Annales de la Station Biologique de Besse-en-Chandesse* 3, 147-170.

Préfecture de la région Auvergne, 2000. Arrêté N°2000/SGAR/CB/N°121 portant approbation du Plan régional pour la qualité de l'Air,

<http://www.drire.gouv.fr/auvergne/telechargement/saveQualit%E9DeLairVol1.pdf>

Reardon, E.J., Allison, G.B., Fritz, P., 1979. Seasonal chemical and isotopic variations of soil CO<sub>2</sub> at Trout Creek, Ontario. *J. Hydrol.* 43, 355-371.

Richon, P., Sabroux, J.-C., Halbwachs, M., Vandemeulebrouck, J., Poussielgue, N., Tabbagh, J., Punongbayan, R., 2003. Radon anomaly in the soil of Taal volcano, the Philippines: A likely precursor of the M 7.1 Mindoro earthquake (1994). *Geophys. Res. Lett.* 30, No 9, 1481.

Side, W.C., 1984. Carbon monoxide as a geothermal indicator. Geothermal Resources Council Bulletin, June 1984, 13-18.

Sugisaki, R., 1978. Changing He/Ar and N<sub>2</sub>/Ar ratios of fault air may be earthquake precursors. Nature 275, 209-211.

Sugisaki, R., Ido, M., Takeda, H., Isobe, Y., Hayashi, Y., Nakamura, N., Satake, H., Mizutani, Y., 1983. Origin of hydrogen and carbon dioxide in fault gases and its relation to fault activity. J. Geol. 91, 239-258.

Toutain, J.-P., Baubron, J.-C., 1999. Gas geochemistry and seismotectonics: a review. Tectonophysics, 304, 1–27.

Viollier, E., Jézéquel, D., Michard, G., Pèpe, M., Sarazin, G., Albéric, P., 1995. Geochemical study of a crater lake (Pavin Lake, France): Trace-element behaviour in the monimolimnion. Chem. Geol. 125, 61-72.

Virk, H.S., Walia, V., 2001. Helium/radon precursory signals of Chamoli Earthquake, India. Radiat. Meas. 34, 379–384.

Walia, V., Lin, S.J., Fu, C.C., Yang, T.F., Hong, W-L., Wen, K-L., Chen, C-H., 2010. Soil-Gas Monitoring: A Tool for Fault Delineation Studies along Hsinhua Fault (Tainan), Southern Taiwan. App. Geochem. 25, 602-607.

Wattananikorn, K., Kanaree, M., Wiboolsake, S., 1998. Soil gas radon as an earthquake precursor: some considerations on data improvement. Radiat. Meas., Vol. 29, No. 6, 593-598.

Wittig, N., Baker, J.A., Downes, H., 2007. U–Th–Pb and Lu–Hf isotopic constraints on the evolution of sub-continental lithospheric mantle, French Massif Central. Geochim. Cosmochim. Ac. 71, 1290-1311.