Isotopically light carbon dioxide in nitrogen rich gases: the gas distribution pattern in the French Massif Central, the Eifel and the western Eger Rift

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Abstract

Based on characteristics of the distribution pattern of the western Eger Rift spring gases, a distribution pattern is presented for the gases of the French Massif Central. The central parts of these areas with ascending magmatic CO_2 are characterised by high gas fluxes, high CO_2 contents of up to 99.99 vol% and isotopially heavy CO_2. In the peripheries, the decrease of $\delta^{13}C$ values of CO_2 and CO_2 contents in the gas phase is compensated by a rise in N_2 contents. It can be demonstrated that gas fractionation in contrary to mixtures with isotopically light biogenic or crustal CO_2 controls the distribution pattern of gas composition and isotopic composition of CO_2 in these spring gases. Dissolution of CO_2 results in formation of HCO_3 causing isotope fractionation of CO_2 and an enrichment of N_2 in the gas phase. With multiple equilibrations, values of about –17 ‰ or lower are obtained. The scale of gas alteration depends on the gas flux and the gas-water ratios respectively and can result in N_2-rich gases. Essential for the interpretation are gas flux measurements with mass balances derived for most of the springs. Without such mass balances it is not possible to discriminate between mixture and fractionation. The processes of isotopic and chemical solubility fractionations evidently control the gas distribution pattern in other regions as well.

Key words *Eger Rift – French Massif Central – Eifel – carbon dioxide – gas fractionation – isotope composition*

1. Introduction

In areas with both low CO_2 abundance and contents in the gas phase as for example in complexes of crystalline basement or in areas with younger volcanic activity, one frequently encounters CO_2 with isotopic compositions of $\delta^{13}C$ values lesser than –10 ‰. In many cases, such values are interpreted as biogenic/organic CO_2 or mixtures between magmatic and biogenic CO_2 or respectively mantle and crustal end members (*e.g.*, Griesshaber *et al.*, 1992). It appears that CO_2 gases with low $\delta^{13}C$ values occurring in the margin areas of regions with ascending magmatic CO_2 as for example in mineral springs of the western Eger Rift, the Eifel or the French Massif Central (Batard *et al.*, 1982) confirm this interpretation.

However, due to the high solubility of CO_2 in water and the HCO_3 formation, fractionations of the CO_2-rich gases take place (*e.g.*, Batard *et al.*, 1982; Capasso *et al.*, 1997; D'Alesandro *et al.*, 1997; Chiodini *et al.*, 1999; Weinlich *et al.*, 1999). Commonly, the isotopic data are compared and calculated with a single equilibration. However, in the peripheral areas of regions with magmatic CO_2 marked by longer migration

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pathways, it can be assumed that gases migrate in different water systems, for example along various faults where dissolution of CO_2 and fractionation with concomitantly formed HCO_3^- can take place several times. This results in a comprehensive gas fractionation concerning both gas composition and isotopic composition of CO_2 and can yield N_2-rich gases.

2. Gas distribution pattern in European areas with magmatic CO_2

2.1. *Western Eger Rift (Czech Republic)*

In the western Eger Rift the main release of magmatic CO_2-rich gases is bound to gas release-centres in the Cheb Basin and Karlovy Vary north and Mariánské Lázně south of the main structures of Eger Rift (Weinlich *et al.*, 1998). These structures of the Krušné hory (Erzgebirge) main fault together with the central fault both dipping to south and the Litoměřice deep fault dipping to north form a Y-structure. This Y-structure splits the gas flux and forms a shielded gas free zone within the Eger Rift.

The gases of the mofettes and springs in these areas with the highest gas fluxes are characterised by high CO_2 contents of up to 99.99 vol% and $\delta^{13}C$ values of –3.9 up to –1.9 ‰ (fig. 1). In some mofettes and springs the gas flux reach values up to 28 m^3/h in Bublák and 35 m^3/h in Soos (Cheb Basin) or about 100 m^3/h in the Mariiny mofette in Mariánské Lázně. The magmatic nature of these gases is indicated, besides these $\delta^{13}C$ values, by high proportions of mantle-derived helium with R/R_a values up to 6 (Weinlich *et al.*, 1999).

With increasing distances from these gas release-centres the gas flux falls and related to it the CO_2 becomes isotopically lighter whereas the CO_2 contents decrease and are compensated by a rise of the N_2 and He contents. To the east and south of Konstantinovy Lázně the CO_2 contents drop linked with gas fluxes of lower than a half l/h up to values of 87 and 67 vol%, respectively. To the north of the Eger Rift nitrogen contents of 98 vol% are attained apart from 0.7 vol% CO_2 as in the Schönbrunn fluorite mine or in other spring gases in the Erzgebirge (Weinlich, 1989). Linked with the decrease of the CO_2 contents in the gas phase

is a decrease of the $\delta^{13}C$ values of CO_2. South of the Eger Rift, the $\delta^{13}C$ values fall to –7.4 ‰ in the Konstantinovy Lázně area and to –8.8 ‰ in Bavaria, respectively. In the same way, the $\delta^{13}C$ values of CO_2 decrease north of the Eger Rift down to – 6.0 ‰ in Bad Elster and in the N_2-rich gases of Schönbrunn down to a value of –17.4 ‰.

The gases in the mofettes and mineral springs in the western Eger Rift migrate upwards along faults in the area with exposed metamorphic rocks of Variscian in the north and of Moldanubian consolidated basement in the south or with exposed Variscan granite intrusions. The metamorphic rocks in this area have very low potential if any for a CO_2 release because all organic carbon is fixed thermodynamically as very stable graphite. In the course of the Variscan, metamorphism mobilised and displaced organic carbon with $\delta^{13}C$ values of – 14 ‰ is present in the form of CO_2 gases among others in the fluid inclusions of granitic quartz in Schönbrunn. With a decrepitation temperature of 800°C (Weise *et al.*, 2001), the release of CO_2 gases by mineral waters is today hardly possible.

2.2. *Eifel (Lower Rhine Graben, Germany)*

CO_2-rich gases linked with Quaternary volcanic activities occur also in the Eifel. Griesshaber *et al.* (1992) report isotopic compositions of CO_2 ranging from –7.8 ‰ up to –3 ‰. The lighter isotopic values are explained with the aid of lower R/R_a values due to mixing of magmatic and biogenic CO_2.

May (2002) describes the occurrence of CO_2-rich gases linked with higher gas fluxes within the central West Eifel and the decrease of CO_2 contents in its margin areas (fig. 2). So gases with up to 98.3 vol% CO_2 predominate for *e.g.*, in Wallenborn in the central part of the West Eifel and with up to 99 vol% in Laach lake in the East Eifel. The $\delta^{13}C$ values of CO_2 in the West Eifel range from –5.7 up to –2.0 ‰ (Hubberten, 2004, pers. comm.) and in the central parts of the East Eifel from –5.1 up to –3 ‰ (Griesshaber *et al.*, 1992).

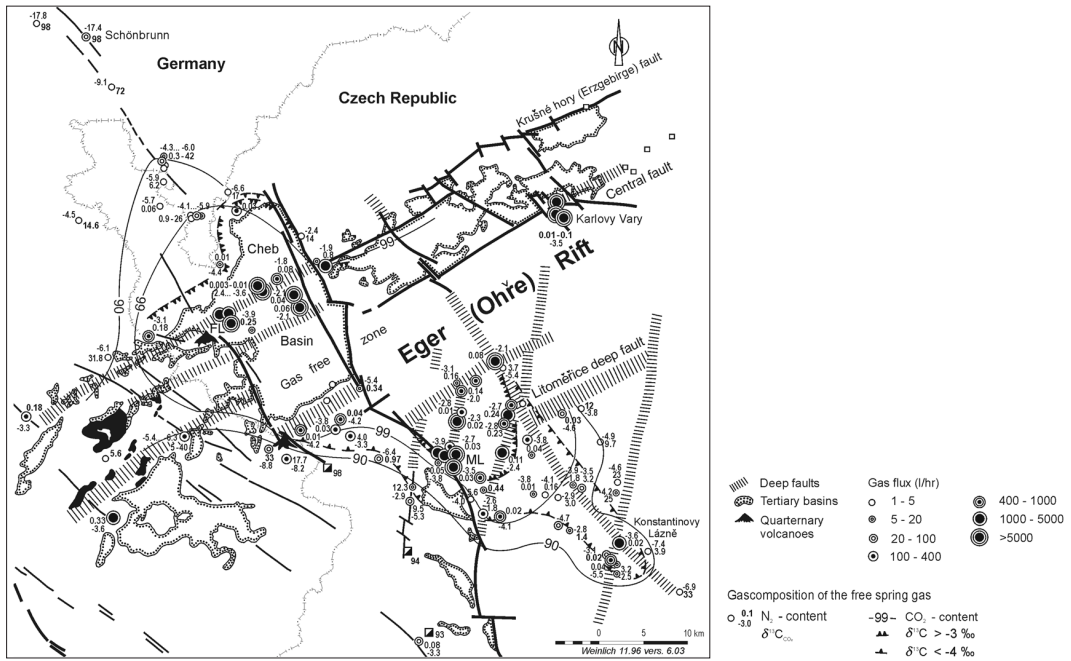In contrast, away from these areas with high gas fluxes, gases with higher N_2 contents occur

Fig. 1. Distribution pattern of gas flux (free gas), gas composition (air-free) and $\delta^{13}C_{CO_2}$ values of gases in mineral springs and mofettes in the western Eger Rift, Czech Republic (data taken from Weinlich *et al*., 1998, 1999, 2003). Legend: ML – Mariánské Lázně; FL – Františkovy Lázně; half-filled squares – uranium mines with gas blowouts.
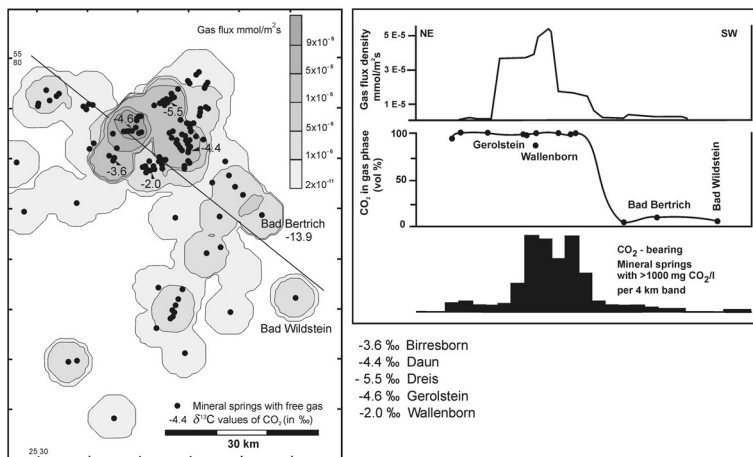

Fig. 2. Gas flux distribution (moving average for circles with 8.6 km diameter), isotope composition of CO_2 and schematic profile of CO_2 flux, spring density and gas composition across the West Eifel, after May (2002). Carbon isotope data from Griesshaber *et al*. (1992) and Hubberten (2004, pers. comm.). The Brubble spring of Wallenborn (wallen – seethe, born – spring) is a geyser-like spring with gas release of 11.3 m³ per eruption period (May, 2002) the spring with the highest gas flux and the highest $\delta^{13}C_{CO_2}$ value (–2.0 ‰) in the West Eifel.

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in the spring gases of Aachen (27 vol% N_2, 72 vol% CO_2) located to the northwest of Eifel or in the southeast at Bad Bertrich (90 vol% N_2, 6.2 vol% CO_2) and Bad Wildstein (98.5 vol% N_2, 0.13 vol% CO_2) (May, 2002). Congruent with the alteration of gas composition Beyer (1995) reports $\delta^{13}C$ values of CO_2 ranging from –10.2 up to – 6.3 ‰ for the thermal springs of Aachen.

In the N_2-rich gas of Bad Bertrich, $\delta^{13}C$ value of CO_2 amounts to –13.9 ‰ (own analysis). The $\delta^{13}C$ values of CO_2 in these marginal springs are significantly lower than in the central parts.

The gases ascent along faults in an area with exposed Devonian sediments and are occur mainly in the areas of the Maar-type Quaternary volcanism in the East and West Eifel.
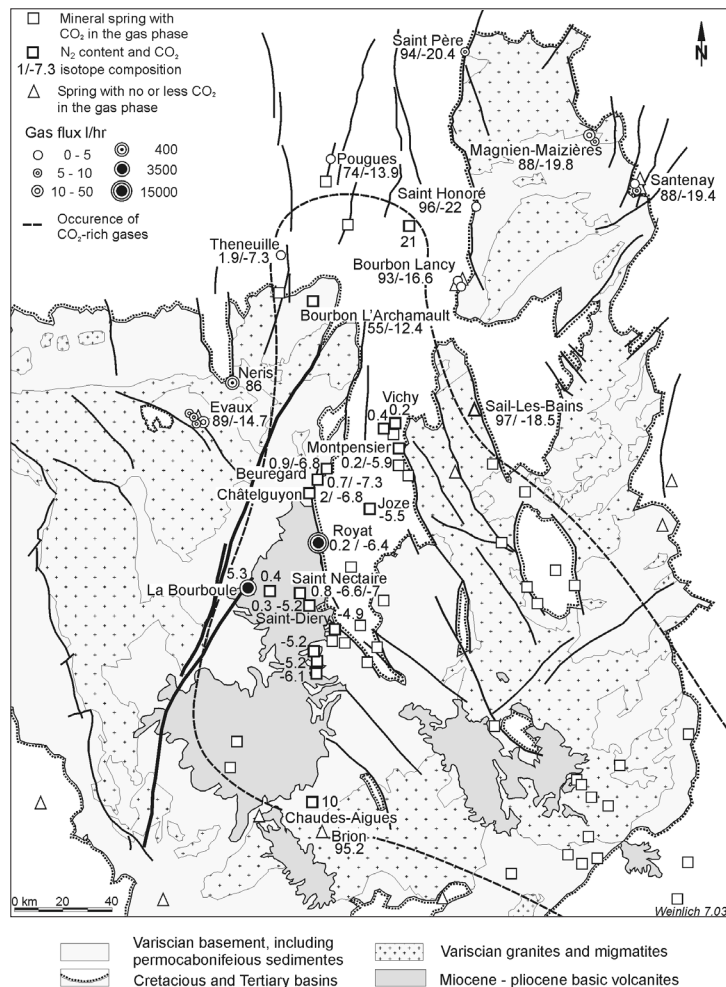

Fig. 3. Distribution of gas flux (free gas), gas composition and $\delta^{13}C_{CO_2}$ values of the gases of the mineral springs of the French Massif Central. Compiled after data from Moureu and Lepape (1912), Moureu (1923), Baubron *et al.* (1979), Schoeller and Schoeller (1979), Batard *et al.* (1982) and Matthews *et al.* (1987). Based on the hydrologic map (Risler *et al.*, 1973) and tectonic map (Autran *et al.*, 1980).

2.3. *French Massif Central*

In the French Massif Central CO_2 occurs with $\delta^{13}C$ values ranging from –23 ‰ up to –4 ‰.

The CO_2-rich gases of Vichy, Royat or Mont Dore and Cezallier (>99 vol% CO_2) are bound to the area of Limagne depression or its direct vicinity. Matthews *et al*. (1987) proved the mantle-derived nature of these gases with R/R_a of up to 5.5. Gas flux measurements (Moureu and Lepape, 1912; Batard *et al*., 1982) carried out on these spring gases in the above region also show that the CO_2-rich gases are linked with high gas fluxes.

According to the gas composition and isotope data by Moureu (1923), Schoeller and Schoeller (1979), Baubron *et al*. (1979), Batard *et al*. (1982) and Matthews *et al*. (1987) a similar distribution pattern also prevails there. In the central part of the Massif Central isotopically heavy CO_2 with $\delta^{13}C$ values of –7 up to –5 ‰ occurs linked exclusively with CO_2-rich gases whereas isotopically lighter CO_2 with $\delta^{13}C$ values ranging from –23 up to –12 ‰ is linked with N_2-rich gases of Evaux (89-93 vol%), Sail-Les-Bains (97.2 vol%) Maizières (88.2 vol%) or Santenay (86-88 vol% N_2) in the margin areas (fig. 3). The latter values are in the range of «typical» biogenic CO_2.

Apart from the Limagne depression filled with Oligocene – Quaternary sediments where the spring gases migrate upward along marginal faults and the volcanic complex of Mont Dore these spring gases migrate upward along faults in areas with exposed Variscian metamorphic rocks or granites.

3. CO_2 fractionation

3.1. *The gases in the western Eger Rift*

In contrast to other gases, CO_2 is very vulnerable to fractionation processes. Firstly, due to its good solubility in water compared to N_2, HC's and rare gases, the gas composition can be altered solely by solubility fractionations. This results in enrichment of the inert gases as observed by an aureole of N_2-richer gases in the surroundings of all regions with CO_2-rich magmatic gases in Europe. Figure 4 demonstrates that with an ongoing solution of CO_2 resulting
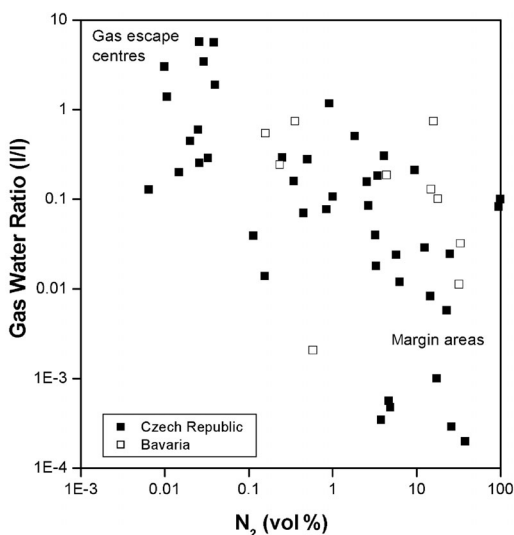

Fig. 4. Rise of N_2 (air-free) in gases with decreasing free gas-water ratio due to increased gas fractionation, *i.e.* selective CO_2 solution in water. The unavoidable scattering in the data is due to varying air proportions in the gases by different partial pressures influencing the bubble point pressure of the gas-water systems (data from Weinlich *et al*., 1998, 2003).

in a decrease of the gas/water ratios the gases in the western Eger Rift are enriched in N_2 in the gas phase (Weinlich *et al*., 1998).

Secondly, linked with the solution of CO_2 are decreasing pH values of these waters. This results in leaching of cations from the adjacent rocks and formation of HCO_3^- ions. Between the newly formed HCO_3^- and CO_2 in the gas phase exists an isotope fractionation of about 10 ‰ (at 10°C) (Wendt, 1968).

With ongoing HCO_3^- formation, the remaining CO_2 in the gas phase becomes isotopically lighter. Consequently, the decreasing gas flux correlates with decreasing $\delta^{13}C$ value of CO_2 in the gas phase as demonstrated in the distribution pattern for the Eger Rift gases.

However, isotopically lighter CO_2 can be also a result of mixing of biogenic and magmatic CO_2. The key for discrimination between mixing or fractionation is the compilation of complete mass balances of CO_2 for each mineral spring with a

free gas phase consisting of gas flux, isotopic and chemical gas composition, contents of HCO_3^- and dissolved CO_2 contents and water discharge.

According to Wendt (1968) the isotope balance for CO_2 in the free gas phase can be described by the following equation:

$$\delta^{13}C_{gas} = \delta^{13}C_{total} - \left(m_{diss}/m_{total}\right)\varepsilon_{w-gas} + -\left(m_{HCO_3}/m_{total}\right)\varepsilon_{HCO_3-gas}$$

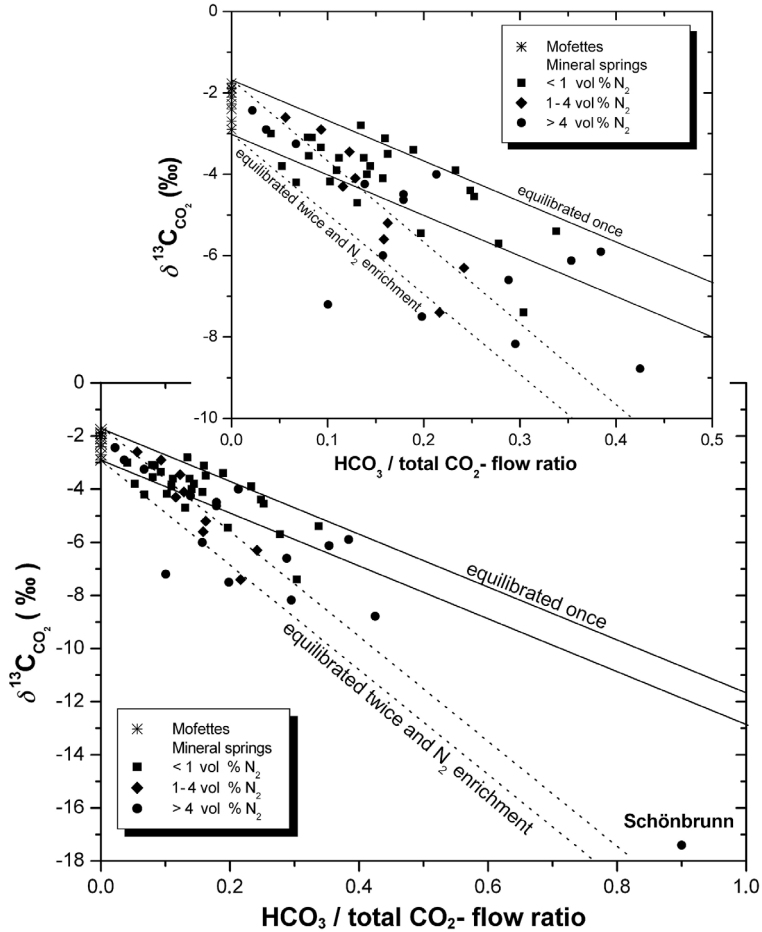**Fig. 5.** Dependence of $\delta^{13}C_{CO_2}$ values in free gas phase from the ratio of HCO_3^- transport (m_{HCO_3}) in water to total CO_2 flux in mineral springs and mofettes in the western Eger Rift with complete mass balances, according to the isotope balance formula (see text) (data of HCO_3^-, dissolved CO_2 and water discharge are taken from Kolářová and Myslil, 1979 and Weinlich *et al.*, 1999, 2003). Lines starting from the scattering range of the dry gas vents (on the *y* axis) in the mofettes wrap the field of theoretical fractionation according to the fractionation factor ε_{HCO_3-gas} at 10°C. Between these lines, the $\delta^{13}C$ values for the free gas are exclusively a result of fractionation by the means of formed HCO_3^- during a single equilibration, without the necessity to assume an additional biogenic carbon. The $\delta^{13}C$ values below the lines can be explained by twice equilibration. This results in an increase of N_2. Multiple equilibrations with solely dissolved CO_2 and single equilibration with HCO_3^- result in occurrence of N_2-richer gases, which fall in between the fractionation lines.

Table I. Measured and calculated $\delta^{13}C$ values of CO_2 for springs in the vicinity of mofettes in North Bohemia demonstrate that the differences between mofettes and springs are solely caused by HCO_3^- fractionation. For the $\delta^{13}C_{primary\ (total)}$ − value the isotope signature of the neighbouring mofettes, the HCO_3^- as well as dissolved CO_2 and the water discharge of the respective spring were used according to isotope balance formula (data from Weinlich *et al.*, 1998, 1999).

| Locality, spring | CO_2 vol% | Gas flux l/h | Water discharge l/h | CO_2 - flux | | | | $\delta^{13}C\ CO_2$ | |
				Free gas mol/h	Dissolved mol/h	HCO_3^- mol/h	Total mol/h	Measured ‰	Calculated ‰
Cheb Basin									
Soos, mofettes	99.946	21100	0	941.46	0	0	941.46	**−2.9**	
Soos, Cisařský	99.941	7600	2520	339.08	143.18	60.7	542.96	−3.6	−3.64
Františkovy Lázně									
Kostelní spring	99.017	2500	8600	110.51	418.08	84.31	612.90	−3.6	−3.34
Mariánské Lázně									
Smrad'och mofettes	99.923	5200	0	231.96	0	0	231.96	**−2.27**	
Farská spring	99.610	149	1166	6.63	67.73	11.55	85.91	−2.8	−2.55
Mariiny mofette	99.990	87000	0	3883.54	0	0	3883.54	**−2.7**	
Ferdinand spring II	99.969	8240	1440	367.74	70.85	71.86	510.45	−4.0	−3.88
Křížový spring III	99.625	135.6	72	6.03	4.74	3.27	14.04	−3.9	−4.52
Martinov	99.280	4	90	0.18	5.28	1.06	6.52	−3.5	−3.22
Chotěnov	85.570	4.1	171.1	0.16	8.54	2.35	11.05	−4.0	−3.75
Dolní Kramolín	99.370	164	324	7.28	19.29	1.58	28.15	−2.6	−2.35

where m is the amount of CO_2 and ε the fractionation factors of −1.3 ‰ for $\varepsilon_{diss-gas}$ and 9.6 ‰ for $\varepsilon_{HCO3-gas}$ at 10°C (Wendt, 1968; Mook *et al.*, 1974; Zhang *et al.*, 1995).

In case of the mofettes the water discharge is 0, *i.e.* the ratios m_{diss}/m_{total} and m_{HCO3}/m_{total} are 0. Consequently, the measured $\delta^{13}C$ value of the free gas phase is identical to the total, *i.e.* the primary isotopic composition of magmatic CO_2 in this area. Therefore m_{HCO3}/m_{total} ratios near 0 can be used to identify the primary isotopic composition.

In the case of mineral springs with a continuous transport of leached cations, mainly Ca^{++} and Mg^{++}, isotopic fractionation occurs with contemporaneously formed HCO_3^- whereas remaining CO_2 in the gas phase becomes isotopically lighter and CO_2 contents can decrease. Figure 5 exhibits this dependency of the $\delta^{13}C$ value of CO_2 in the gas phase from the m_{HCO3}/m_{total} ratios in the springs. In cases of spring gases in the close vicinity of mofettes it can be demonstrated that the differences in the isotopic composition are solely caused by HCO_3^- fractionation (table I).

The spring gases, which are further away from the main gas release-centres, can be transported within more than one fault system and thus in different waters. Therefore, the equilibration between CO_2 in the gas phase and HCO_3^- can occur several times and the calculated $\delta^{13}C_{CO_2}$-values are consequently higher than expected in a single equilibration.

Changes in isotopic composition can also be explained by mixing with lighter biogenic CO_2. However, the common change in isotopic and chemical composition (fig. 6) points to fractionation processes caused by multiple equilibrations as increasing nitrogen contents are not linked with biogenic CO_2 admixtures. In the gases of the western Eger Rift a correlation between N_2 and He contents can be observed (fig. 7) which indicates one source and
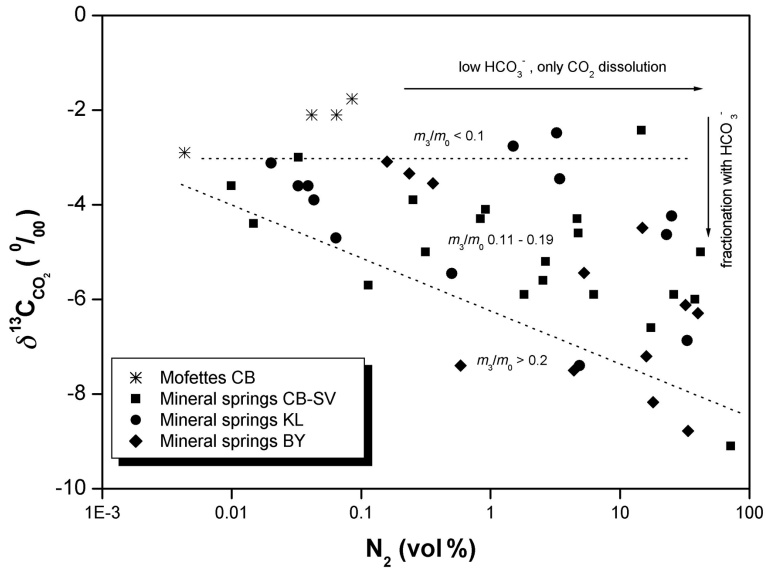
Fig. 6. Plot of N_2 content *versus* $\delta^{13}C$ values displays the common variations in gas and isotope composition of gases from the Eger Rift area, *e.g.*, from the Cheb Basin/South Vogtland area (CB-SV), Konstantinovy Lázně area (KL) and Bavaria (BY). These variations are caused by fractionation (CO_2 solution and HCO_3^- formation). In the case of waters with low TDS contents and without HCO_3^- formation, the fractionation can only take place with dissolved CO_2 and the isotopic heavy CO_2 remains therefore in the gas phase.
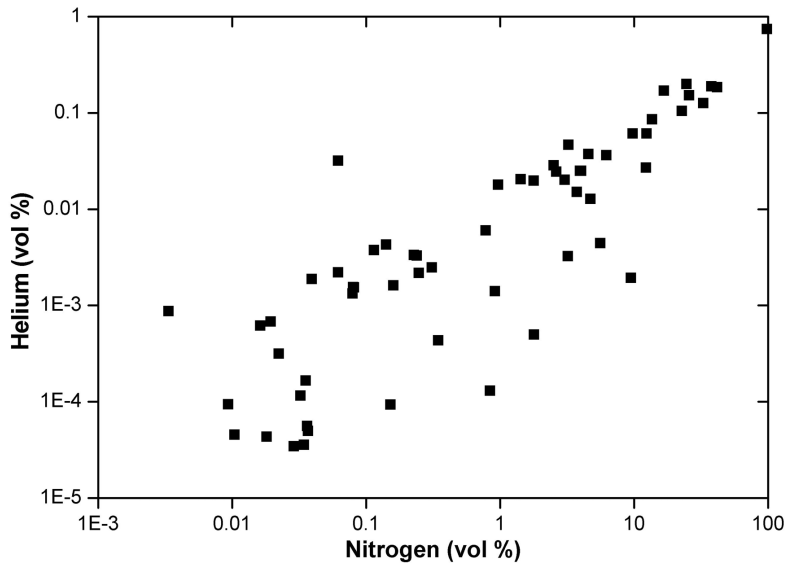

Fig. 7. Correlation between nitrogen and helium contents in gases of the western Eger Rift (data from Weinlich *et al.*, 1998).

a continuous enrichment by solubility fractionation (Weinlich *et al.*, 1998). The assumption of an additional N_2-source in case of the N_2-richer gases is therefore not necessary. Compared to the gas release centres the nitrogen flux decreases in the springs in the marginal areas. An exception is the water inflow about 500 m below the surface with 100 l/h N_2 in the Schönbrunn fluorite mine, caused by pressure release in this mine.

A special case of these fractionations are springs with very low Ca-Mg-HCO_3 contents and with isotopic composition of CO_2 being still nearly unchanged due to lack of extensive HCO_3^- fractionation and where the CO_2 contents are solely decreased by the solution of CO_2. This can be explained by fractionation processes. However, in case of an interpretation of isotopically lighter CO_2 in the gas distribution pattern of the western Eger Rift caused by mixing with lighter biogenic CO_2 there should be no reason to elucidate why the mixing should not occur in springs with low Total Dissolved Solids (TDS) contents.

Regarding longer migration pathways as mentioned above it is considered that the gas migration occurs within different hydrological systems and therefore these fractionations can take place repeatedly during the migration. This results in a drastic drop of the CO_2 contents and the $\delta^{13}C$ values in the remaining gas phase.

Figure 5 demonstrates the isotopic composition of the N_2-rich gases in the Fluorite mine of Schönbrunn (one of the most northern springs shown in fig. 1) with a $\delta^{13}C$ value of -17.4 ‰ which can be explained alone under the assumption that the CO_2-HCO_3^- system is equilibrated twice.

Certainly, an admixture of biogenic CO_2 cannot be excluded but in this mine about 3.6 m^3 of CO_2 gas and 3664 m^3 of dissolved CO_2 per year were released. Facing the fact that the granite surface is located only about 650 m below both the thermal water and gas inflows (Kuschka and Hahn, 1996) this amount is hardly explainable with noticeable proportions of biogenic CO_2. It is problematic to derive the nitrogen from crustal sources in terms of the 100 l/h N_2 in the free gas phase and about 450 l/h dissolved N_2 (air-free over dissolved Ar; procedure in Weinlich *et al.*, 1998) accompanied by 0.45 l/h He and 5.72 l/h dissolved He (in total 54 m^3/yr He). It should be

considered that due to the intrusion of Variscian granites the metamorphic rocks were exposed to far higher temperatures, as is the case today. Therefore, the N_2 is probably also mantle derived, because the N_2 gas release including metamorphic CO_2 sourced from these crustal rocks took place during the Variscian intrusions. The nitrogen isotope composition with $\delta^{15}N$ 0.7 (Weinlich *et al.*, 1999) exhibits a tendency to more positive values of a plume-like mantle (Marty and Dauphas, 2003) which occurs in Central Europe (Wilson and Downes, 1992).

Recalculating the CO_2 and N_2 in the gas phase together with the dissolved N_2, and CO_2 including the HCO_3 the whole fluid system contains about 90 vol% CO_2 (possible $CaCO_3$ precipitations would additionally increase this CO_2 content) and about 10 vol% N_2 and thus this system is comparable with the Eger Rift gases.

3.2. *The gases of the French Massif Central*

The distribution pattern and the isotopic signature of -23 up to -12 ‰ of the N_2-rich spring gases of the French Massif Central could be explained in the same way. As in the western Eger Rift, the CO_2-rich gases with $\delta^{13}C$ values of -7 up to -5 ‰ are linked with high gas fluxes in the concerned mineral springs. Figure 8 demonstrates this correlation between $\delta^{13}C$ values and the gas composition. Batard *et al.* (1982) calculated initial isotope composition for some gases in this area with mass balances according to a single equilibration CO_2-HCO_3. The authors concluded a biogenic or mixed origin for the CO_2 because the isotopic composition of the total carbon ranges between -16 and -11 ‰. However, due to multiple equilibrations, it cannot be excluded *a priori* but only the m_{HCO3}/m_{total} ratios near 0 should be used to avoid misinterpretations (the calculated $\delta^{13}C$ value of CO_2 for Schönbrunn assuming a single equilibration is also -11 ‰).

For the gases of the French Massif Central, it can be assumed that the gas of Royat with a $\delta^{13}C$ value of -6.4 ‰ is unfractionated owing to its m_{HCO3}/m_{total} ratio of 0.007 and displays the primary composition. Further, geothermometer calculations (Pauwels *et al.*, 1997) indicate that
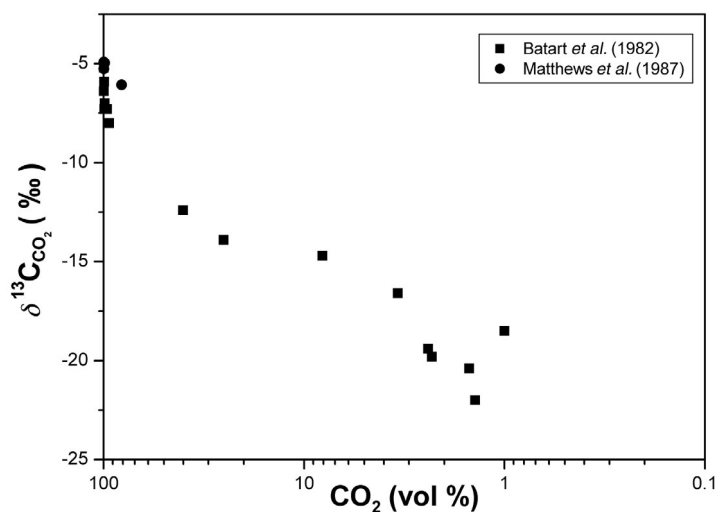
Fig. 8. Correlation of gas composition and isotopic composition of CO_2 in gases of the Massif Central (data from Batard *et al*., 1982 and Matthews *et al*., 1987).
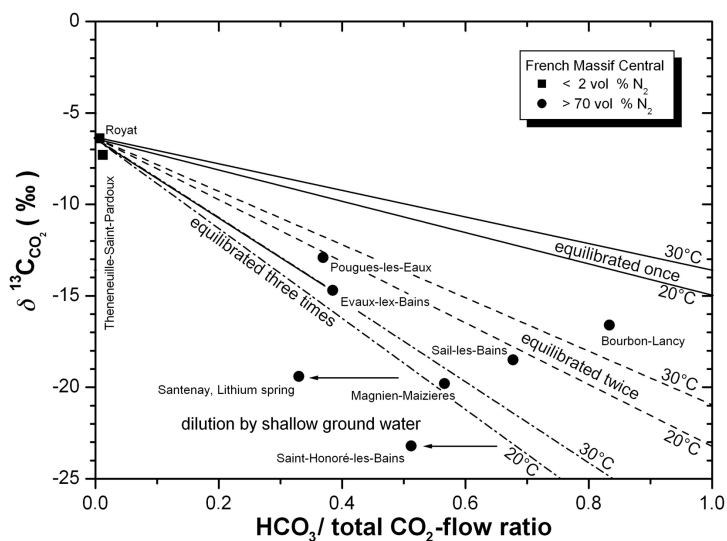

Fig. 9. Mass balance plot displays $\delta^{13}C$ values *versus* ratio HCO_3^- transport ($mHCO_3$) to total CO_2 flux (m_0) for gases of mineral springs in the French Massif Central (data from Batard *et al*., 1982).

these waters emerging in the Mont Dore area reach temperatures of about 100-130°C at depth and in Saint-Nectaire ($\delta^{13}C$ value CO_2 –7.0 ‰) temperatures of 160-175°C at depth respectively. According to Mook *et al*. (1974),

the fractionation between CO_2 and HCO_3^- at temperatures of around 120°C is zero. Based on the isotope composition of Royat it can be shown that the low values of –12 and –23 ‰ can be reached (fig. 9) under the assumption

that the equilibration between CO_2 and HCO_3^- takes place only twice and in two cases three times. Therefore, it is not absolutely necessary to assume biogenic contributions in the region as well as in the Eger Rift. Just two isotope values, which represent gases of Santenay and Saint Honoré, situated at the edge of the Morvan horst and which are associated with Na-SO_4 waters are lighter than those lying in the field of gases equilibrated three times. However, an uncertainty of these mass balances lies within the possibility of influence of non-mineralised groundwaters and/or mineral waters of different type, which «dilute» the HCO_3-rich mineral water in the respective springs.

In the Cézallier area, Négrel *et al.* (2000) demonstrate such mixtures of mineral waters with meteoric and different mineralised waters in line with the REE distribution and strontium isotope ratios. Pauwels *et al.* (1997) state similar processes in the Mont Dore region on the basis of the main element distribution in spring waters. This effect of «dilution» of these mineral waters can produce lower m_{HCO3}/m_{total} ratios, present during equilibration in deeper regions as higher m_{HCO3}/m_{total} ratios. Since the CO_2 of these N_2-rich gases is completely fixed as HCO_3^-, it is no longer possible to form new HCO_3^- in these waters. The $\delta^{13}C$ values were altered by the formed HCO_3^- and remained unchanged in less mineralised waters. This results in a shift of these gases in plot of the ratio of HCO_3 *versus* total CO_2 flow (fig. 9) and acts as if a thrice equilibration took place. According to Schoeller and Schoeller (1979) the TDS contents and especially the HCO_3^- contents decrease with increasing distances from the area of Vichy-Cantal-Devès.
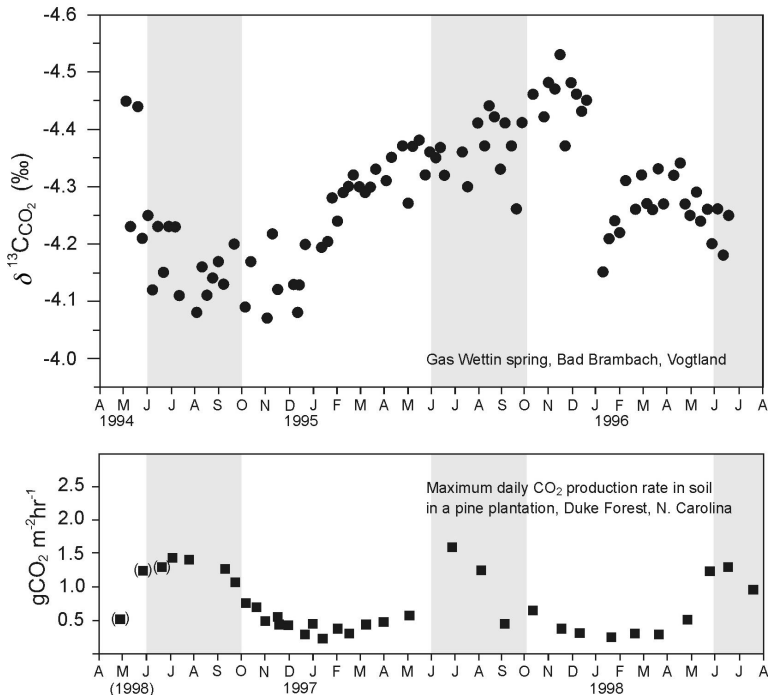

Fig. 10. Long-term observation of isotopic composition of the gas of the Eisen spring in Bad Brambach, Eger Rift (Weise *et al.*, 2002) and typical annual changes in the CO_2 production in soils (Andrews and Schlesinger, 2001). Growing seasons – light grew.

As in the western Eger Rift, the N_2-rich gases in the Massif Central are enriched in helium. The extreme enrichment of helium, whose contents are the highest in Europe, points rather to a complete fractionation than to a simple mixing with biogenic components. According to the gas flux measurement of Batard *et al*. (1982) 30 l/h of N_2 are also released in the CO_2-rich gases of Royat. On the other hand, N_2 release in the case of N_2-rich gases are *ca.* 2.8 l/h in Bourbon-Lancy, 29.6 l/h in Evaux-les-Bains, 0.5 l/h in Sail-les-Bains and 1.7 l/h N_2 in the Lithium spring in Santenay. Thus only the gas composition is fractionated and it is not necessary to assume additional N_2 sources.

An additional argument contradicting the influence of mixing processes is that outside these areas with magmatic CO_2 there are no springs with biogenic/organic CO_2 in the gas phase. The production rates of biogenic CO_2 in soils (Andrews and Schlesinger, 2001) are too small to nourish a free gas phase. A long-term measurement of isotope composition of CO_2 in the gas phase of the Wettin spring in Bad Brambach (Weise *et al*., 2001) compared with the biogenic CO_2 production rates (Andrews and Schlesinger, 2001) demonstrate that there is no influence (fig. 10).

It is also problematic to derive biogenic/organic CO_2 from sedimentary rocks, especially in areas of metamorphic rocks, since these waters and gases circulate within fault systems. There, either a far-reaching CO_2 exchange between the gases migrating along fault pathways and the surrounding country rocks is impeded or the ascending magmatic CO_2 saturates the groundwater with CO_2 gas, as it is the case in the Cheb Basin. The CO_2 concentration gradient in the close vicinity of the faults prevents the admixture of CO_2 from other sources like for example the biogenic/organic CO_2.

4. Conclusions

As demonstrated, it is possible to elucidate low $\delta^{13}C$ values with gas fractionation, *i.e.* by isotope fractionation with formed HCO_3^- and not necessarily and exclusively by mixing with biogenic or organic CO_2. However, without complete mass balances it is not possible to discriminate between either or give reasons to prefer one of the interpretations. In some cases, it will not be possible to educe the «last proof» for the interpretation. Therefore, it should always be considered that even enhanced CO_2-contents in the soil air encountered in the vicinity of fractured rocks can also represent completely fractionated magmatic CO_2.

However, if we have to assume that the isotopic composition and contents of CO_2 in the gas phase can be alternated by fractionation processes, an influence on the $C/^3He$ ratios should also be assumed. Marty *et al.* (1989) described abating $C/^3He$ linked with reduced CO_2 contents.

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