Gas Flux and Tectonic Structure in the Western Eger Rift, Karlovy Vary – Oberpfalz and Oberfranken, Bavaria

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ABSTRACT: The distribution pattern of gas flux as well chemical and isotopic composition of free gases in the western part of the Eger Rift allows to demonstrate the tectonic structure. A CO_2-free zone occurs between the main area of gas release in the Cheb Basin and the Mariánské Lázně area. The Y-structure splits the ascent of magmatic gas flux. As a result, it is possible to follow the Eger Rift main faults with the borders of this zone. NNW–SSE-striking faults shift the Litoměřice Deep Fault stepwise to the north and narrow the Eger Rift to the west.

KEY WORDS: Ohře Eger Rift, gas flux, CO_2, isotopic composition, gas fractionation.

Introduction

The Eger (Ohře) Rift reaches undoubtedly westward to the region of the Oberpfalz and Oberfranken in Bavaria, as shown among others by the occurrences of Tertiary basaltic volcanism, (Malkovský 1980, 1987, Huckenholz and Schröder 1985, Behr et al. 1992, Hirschmann 1992). Likewise there are CO_2-bearing mineral springs in the Bavarian part (Quentin 1970). The ascent of these gases is caused by crustal extension (Stettner 1975). The isotopic signature of the CO_2 (Lodemann 1992) and enhanced mantle-derived helium proportions up to 40 % (O'Nions et al. 1989) point to a magmatic origin.

It is problematic to locate the exact course of the main faults in the western part of the Eger Rift, especially in Bavaria. In the case of the Litoměřice Fault, the geophysical (gravimetric) survey failed yet in the area east of Mariánské Lázně because of the sharp boundary between the heavy Mariánské Lázně Amphibolite Complex and light Variscan granite intrusions. To the west of the Mariánské Lázně Fault, the exact course of the Litoměřice Fault was uncertain and it is fairly unclear west of the Cheb Basin.

With an extensive programme of investigations for spring gases in the western Eger Rift, it was possible to characterize these gases regarding their chemical and isotopic composition. Additionally, the gas flux and water discharge of the springs were measured (Weinlich et al. 1998, 1999). With the gas flux distribution it was possible to demonstrate the tectonic structure in the Czech part of the Eger Rift between Karlovy Vary and the southern Cheb Basin.

The distribution pattern of the spring gases in Oberpfalz and Oberfranken complete the picture and allow it to follow the Eger Rift main faults to Bavaria.

Investigation methods

Only the free gas phase was sampled with a funnel or, in some cases in Bavaria, with a gas separator and fed into gas vessels. Gas chromatography analyses were carried out with a Chrom 5 (Laboratorní Přístroje Praha).

During the ascent through the surface waters, the CO_2-rich gases strip atmospheric-derived proportions from air-saturated waters. The air-free calculation was transacted with the proportion of dissolved argon. The analysis of $\delta^{13}C_{CO_2}$ and $^{15}N_{N_2}$ isotope composition was performed with a Finnigan Mat Delta-S mass spectrometer and the $^3He/^4He$ ratios were determined with a VG MM 3000 mass spectrometer. These procedures were described in detail by Weinlich et al. (1998, 1999).

The gas flux was measured at most springs with large funnels of plastic sheet which could be adjusted to the diameter of the tapping of springs. The Bavarian springs are mostly in use and equipped with technical installations and it was only possible to measure the gas flux when springs were pumped (see Table).

Furthermore, the contents of dissolved CO_2 and HCO_3^- were determined for springs without newer data for an isotopic balancing of CO_2 (Weinlich et al. 1999).

The gas distribution pattern

The distribution pattern in the Czech territory was described in detail by Weinlich et al. (1998). Fig. 1 and 2 display the distribution pattern of gas flux, gas composition as well as the isotopic composition of CO_2 and helium of free gases including the Bavarian springs.

In the Czech territory, 4 gas escape centres with high gas fluxes could be distinguished – Cheb Basin (~90 m^3/hr), Mariánské Lázně area (~156 m^3/hr), the surroundungs of Konstantinovy Lázně (~2.7 m^3/hr) and Karlovy Vary (~356 m^3/hr).

The zone identified in the Cheb Basin of springs and mofettes with the highest gas flux can be followed with a northern line of springs of Hohenberg, Kothigenbibersbach and the Luisen spring in Bad Alexandersbad. The springs of Sophienreuth and the vicinity of Bad Steben lie north of these lines (not incorporated in Figs. 1 and 2). Likewise, it is possible to assemble the mineral springs with a free gas phase of Maiersreuth and Neualbenreuth, Kondrau, Großschlattengrün and of König Otto Spa near Wiesau to a southern zone. The flux of magmatic CO_2 in the Oberpfalz and Oberfranken decreases starting from the Cheb Basin to the west. Higher gas flows in the most westerly springs of

Nr.	Locality, spring	Samp1ing	Water	Gas flux			Gas-water	Gas composition								
		date	discharge	dissolved	gas	free gas	ratio									
				diss.CO_2	HCO_3	Vol.		CO_2	N_2	O_2	Ar	He	H_2	CH_4	C_2H_6	C_3H_8
			1/hr	mg/l	mg/l	1/hr	l/l	vol%	vol%	vol%	vol%	vol%	vpm	vol%	vpm	vpm
75	Maiersreuth, well MS	6.4.95	pumped	1994	2075	23.8	0.032	51.30	47.41	0.413	0.584	0.237		0.055		
76	Neualbenreulh,well E	6.4.95	pumped	2074	1279	235	0.100	65.31	33.77	0.161	0.523	0.194		0.038		
77	Kondrau, Diepholz spring	6.4.95	pumped	2650	1081			94.14	5.72	0.069	0.014	0.040		0.015	12.03	2.00
78	Gerwig spring	4.4.95	pumped	1320	518			41.87	56.47	0.419	0.768	0.212		0.260	17.96	
79	Grollschlattengrijn, Reichel pond	3.4.95	Gas bubles in surface water			1.5		78.85	14.42	6.025	0.260	0.029		0.418	1.00	
80	Wiesau, Neue Otto spring	3.4.95	pumped	2530	481.9	1017	0.743	99.12	0.83	0.005	0.013	0.004		0.023	0.88	0.06
81	Hohenberg, Carolinen spring	5.4.95	pumped	2624	448.3	638	0.545	99.22	0.75	0.012	0.016	0.002	0.94	0.005	0.20	
82	Kolhigenbibersbach	5.4.95	187	1368	1046	2.1	0.011	50.26	48.73	0.161	0.674	0.124		0.050	10.06	
83	Bad Alexanderbad, Luisen spring	6.4.95	pumped	2366	354	320	0.242	98.64	1.26	0.013	0.029	0.005	1.36	0.046	2.45	0.15
84	Sophienreuth, Sophien spring	4.4.95	34	2041	686.2	4.4	0.129	74.05	24.72	0.692	0.321	0.199		0.021	13.04	1.00
85	Hölle, Höllensprudel II	30.9.96	pumped	1584	649.9		0.186	86.00	13.60	0.084	0.256	0.045		0.010		
86	BadSteben, Wiesenquelle	30.9.96	pumped	3759	742.2		0.740	71.50	27.84	0.011	0.386	0.127		0.139		
87	Langenau, Max-Marien spring	30.9.96	480	2576	1560	I.0	0.002	97.35	2.54	0.044	0.053	0.005		0.007	1.02	

Nr.	**Locality, spring**	**Samp1ing**	**Gas composition, air-free**							**Air**	**Isotope ratios**			
		date								**content**	$\delta^{13}C_{CO2}$	$\delta^{15}N$	$^3He/^4He$	R/R_a
			CO_2	N_2	He	H_2	CH_4	C_2H_6	C_3H_8		‰	‰		
			vol%	vol%	vol%	vpm	vol%	vpm	vpm	vol%	(PDB)	(air)	$x10^{-6}$	
75	Maiersreuth, well M5	6.4.95	66.55	33.07	0.307		0.072			22.91	-8.78	0.60	3.02	2.19
76	Neualbenreulh, well E	6.4.95	82.01	17.70	0.244		0.048			20.36	-8.17	1.30	3.51	2.54
77	Kondrau, Diepholz spring	6.4.95	94.72	5.23	0.040		0.015	12.10	2.02	0.61	-5.44	-0.50		
78	Gerwig spring	4.4.95	59.94	39.38	0.303		0.373	25.71		30.15	-6.29		3.29	2.37
79	Grollschlattengrün, Reiche1 pond	3.4.95	93.90	5.57	0.034		0.497	1.19		16.03	-0.62	7.90		
80	Wiesau, Neue Otto spring	3.4.95	99.64	0.33	0.004		0.023	0.88	0.06	0.52	-3.55	4.50	4.07	2.91
81	Hohenberg, Carolinen spring	5.4.95	99.84	0.15	0.002	0.95	0.005	0.21		0.62	-3.09	3.10		
82	Kolhigenbibersbach	5.4.95	67.95	31.81	0.167		0.068	13.60		26.03	-6.12	0.10	4.69	3.39
83	Bad Alexanderbad, Luisen spring	6.4.95	99.77	0.18	0.005	1.37	0.046	2.47	0.15	1.13	-3.34	2.80	4.88	3.52
84	Sophienreuth, Sophien spring	4.4.95	85.14	14.61	0.228		0.024	14.99	1.15	13.02	-4.49	1.05		
85	Hölle, Höllensprudel II	30.9.96	95.60	4.34	0.049		0.012	0.00		10.05	-7.50			
86	Bad Steben, Wiesenquelle	30.9.96	84.07	15.62	0.149		0.164	0.00		14.95	-7.20			
87	Langenau, Max-Marien spring	30.9.96	99.41	0.57	0.006		0.008	1.04		2.07	-7.40			

Tab. 1. Gas flux, gas composition and isotopic composition of spring gases in the Oberpfalz/Oberfranken, Bavaria.

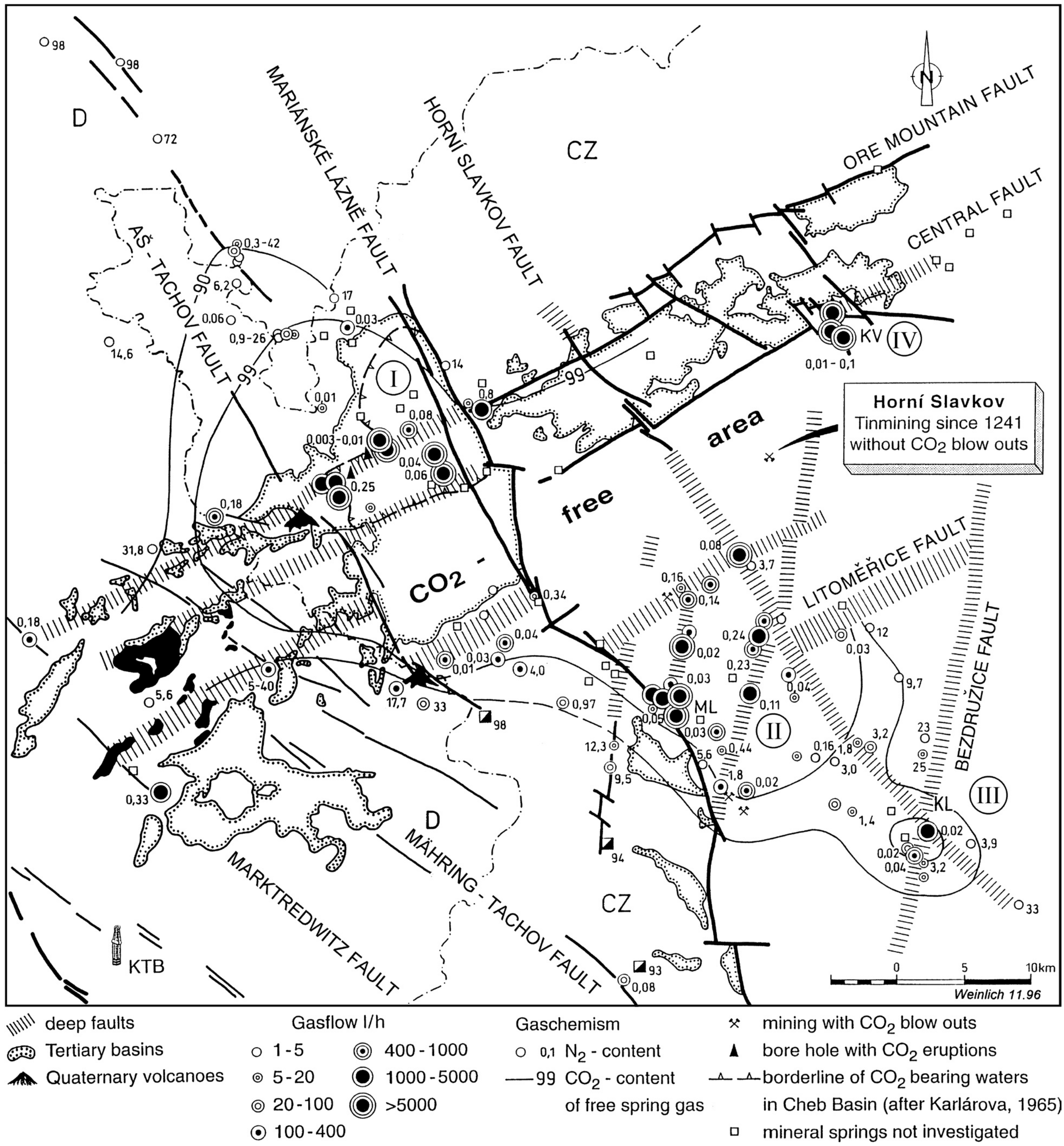

Fig. 1. Distribution pattern of gas flux (free gas) and gas composition (air-free) of gases in the western Eger Rift; gas escape centres: I – Františkovy Lázně/Cheb Basin, II – Mariánské Lázně (ML), III – Konstantinovy Lázně (KL) and IV – Karlovy Vary (KV); half-filled squares – uranium mines; Litoměřice Deep Fault in the Czech territory according to gas geochemical mapping (Weinlich et al. 1998).

Bad Alexandersbad and Wiesau are merely a result of the pumping rate.

An important feature of the gas flux distribution is a CO_2-free zone within the Eger Rift. As there are no additional springs between the northern and southern line of mineral springs with CO_2, it is possible to follow the discovered gas-free zone in NW Bohemia from the Cheb Basin to Oberpfalz/Oberfranken as well (Figs. 1 and 2).

Geochemistry of the gases

The unchanged magmatic gases within the gas escape centres with the highest gas fluxes (Cheb Basin, Mariánské Lázně area, Konstantinovy Lázně and Karlovy Vary) are characterized by almost pure CO_2 with 99.5 to 99.9 vol.% CO_2 and with $\delta^{13}C$ values of −2.5 to −2.9 ‰ (against PDB) isotopic heavy CO_2. With R/R_a values of up to 5, these gases contain high proportions of mantle-derived helium. Isotopically heavy magmatic CO_2 is obviously typical for the Eger Rift, as indicated by the isotopic values of

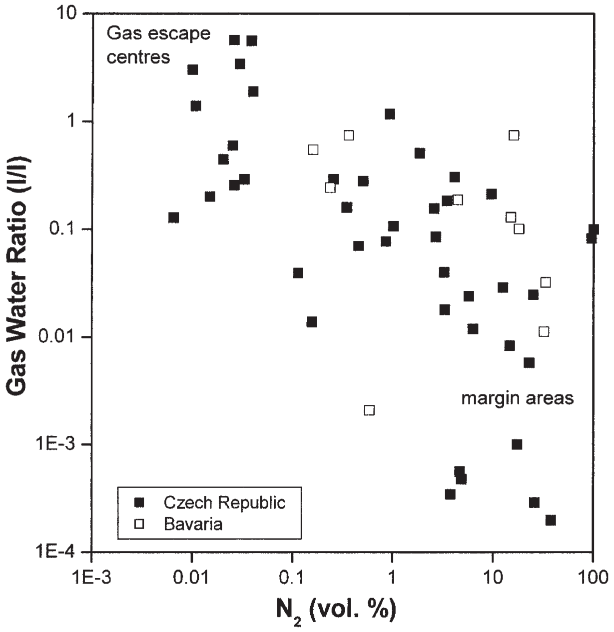

Fig. 2. Rise of N_2 (air-free) in gases with decreasing free gas-water ratio due to increased gas fractionation, i.e., selective CO_2 solution in water. The scatter of the data is inevitable because varying air proportions in the gases due to different partial pressures influence the bubble point pressure of the gas-water systems.

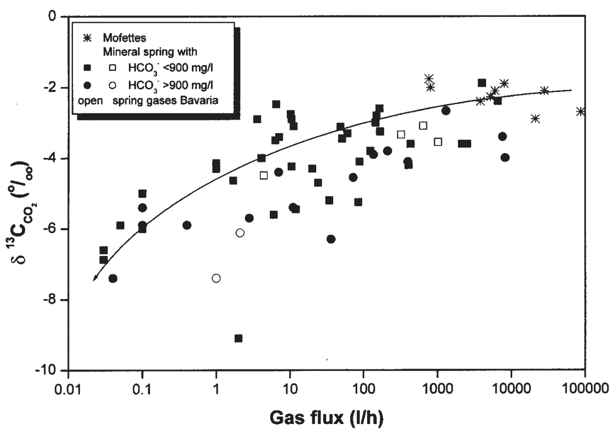

Fig. 4. Decreasing δ^{13}C values of CO_2 with decreasing gas flux at increasing distance from the gas escape centres of the western Eger Rift.

HCO_3^- data according Kolářová and Myslil (1979) and new data of the authors.

The scatter is caused by varying ratios in HCO_3^- and dissolved CO_2 and the opposing fractionations, $\varepsilon_{w\text{-}g}$ = -1.3 and $\varepsilon_{HCO3\text{-}g}$ = 9.6 (at 10°C) – see text.

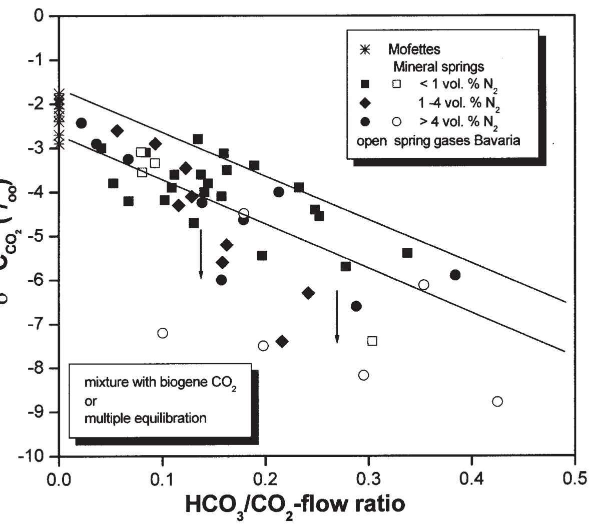

Fig. 5. Dependence of $\delta^{13}C_{CO_2}$ values in free gas phase from the ratio of HCO_3^- transport (m_{HCO3}) to total CO_2 flux in mineral springs from the western Eger Rift with complete mass balance, according to the isotope balance formula (see text).

HCO_3 and diss. CO_2 data and water discharge according to Kolářová and Myslil (1979) and new data of the authors.

Lines starting from the scatter ranges of the dry gas escapes in the mofettes wrap the theoretical fractionation according to the fractionation factor $\varepsilon_{HCO3\text{-}gas}$ at 10 °C. Between these lines, the δ^{13}C values for the free gas are exclusively a result of fractionation by HCO_3^- formed by non-repeated equilibration, without the necessity to assume additional biogenic carbon. The δ^{13}C values below the lines can be explained by twice repeated equilibration. This results in an increase in N_2. Multiple equilibrations only with dissolved CO_2 and non-repeated equilibration with HCO_3^- results in the occurrence of N_2-richer gases between the fractionation lines.

the carbonatite from Roztoky near Děčín (−3.0 ‰, Kopecký 1979). Starting from these centres, CO_2 in the gas phase becomes isotopically lighter and the CO_2 contents drop in favour of an increase in N_2 with increasing distance. Gases in the adjacent Bavarian area are not different from those in the Eger Rift in the Czech territory. Likewise, the highest CO_2 contents in NW Bohemia are liked with high gas fluxes.

The change in composition of the free gases, i.e., the increase in nitrogen contents with increasing distances from the gas escape centres, is a result of selective solution of CO_2 according to its better solubility in water, displayed in Fig. 3. Likewise, the δ^{13}C value of CO_2 decreases to the marginal areas with lower gas fluxes (plotted in Fig. 4).

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

$$\delta^{13}C_{gas} = \delta^{13}C_{total} - (m_{diss.}/m_{total})\ \varepsilon_{w\text{-}gas} - (m_{HCO3}/m_{total})\ \varepsilon_{HCO3\text{-}gas}$$

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

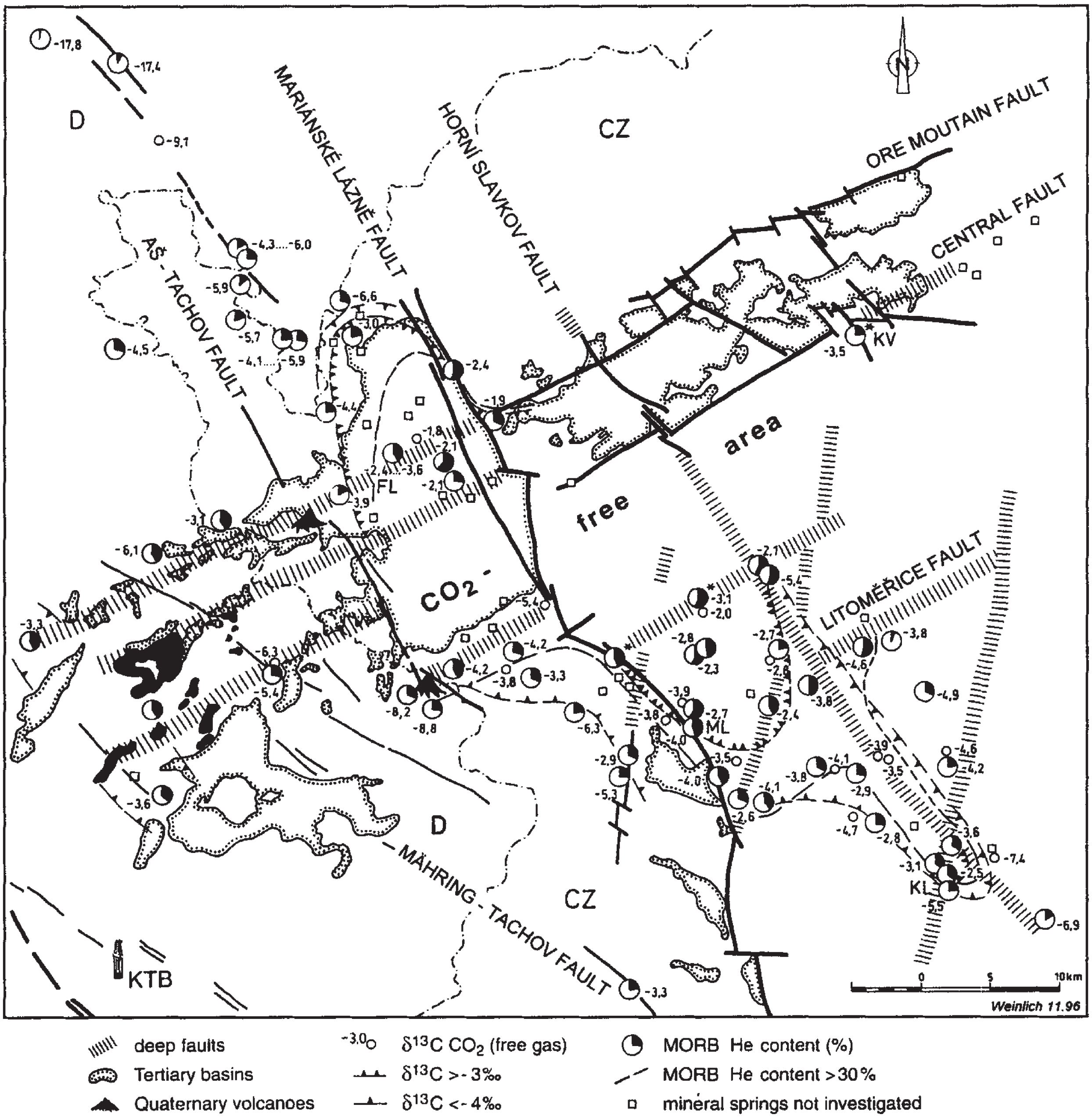

Fig. 3. Distribution pattern of $\delta^{13}C_{CO_2}$ values and proportions of mantle-derived He in gases from the western Eger Rift. He data are given as the proportion of MORB-He: R/R_a MORB = 8 and crust R/R_a= 0.02. For gas escape centres see Fig. 1. * data from O'Nions et al. (1989)

In the case of mofettes, the water discharge is 0, i.e., the ratios $m_{diss.}/m_{total}$ and m_{HCO_3}/m_{total} are 0. This means that the measured $\delta^{13}C$ value of the free gas phase is identical with the total, e.g., the primary isotopic composition of magmatic CO_2 in this area. This is different in the case of mineral springs. The isotopic fractionation with the formed HCO_3^- occurs with the supply on cations in the main Ca^{++} and Mg^{++}, and the remaining CO_2 in the gas phase becomes isotopically lighter (Fig. 5). Changes in isotopic composition can also be explained by mixing with lighter biogenic CO_2. But the common change of isotopic and chemical composition (Fig. 6) point to fractionation processes caused by multiple equilibrations, because increasing nitrogen content has nothing to do with biogenic CO_2.

Gas flux and tectonic structure

The principal feature of the gas flux distribution is a CO_2-free zone within the Eger Rift. No mineral springs (Laube 1884) or CO_2-bearing waters in wells (Kolářová 1965) are and were detectable between the gas escape centres of the Cheb Basin and

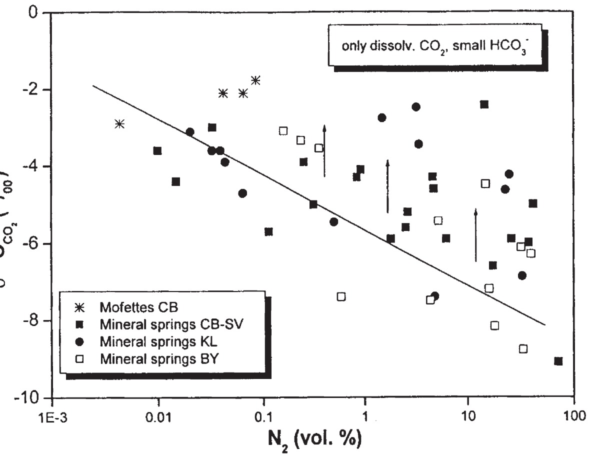

Fig. 6. A plot of N_2 content vs. $\delta^{13}C$ values displays the common variations in gas and isotope composition of gases in the Eger Rift area, specifically from the Cheb Basin/South Vogtland area, Oberpfalz and the Konstantinovy Lázně area.
These variations are controlled by fractionation (CO_2 solution and HCO_3^- formation). In the case of waters with low TDS contents, without HCO_3^- formation, a fractionation can only take place with dissolved CO_2 and isotopically heavy CO_2 retains in the gas phase.

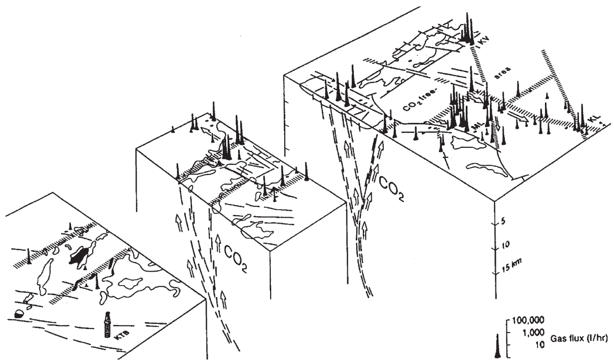

Fig. 7. Gas flux and tectonic structure of the western Eger Rift
Splitting of the magmatic gas flux by the Y-structure of the main faults of the Eger Rift, resulting in the formation of a central CO_2-free zone.

the area NW of Mariánské Lázně. Not even in the tin mines of Horní Slavkov did CO_2 occur.

Whereas fractionated gases with higher N_2 contents and $\delta^{13}C$ values of -7 to -17 ‰ occur in the marginal areas to the north and south, the occurrences of mineral spring on the borders of the gas-free zone with unchanged CO_2-rich gases with isotopically heavy CO_2 and high mantle-derived He proportions disappear immediately. The lack of any fractionations points to a tectonically caused boundary. According to the deep structure of the Eger Rift (Kopecký 1979, Šťovíčková 1980, Conrad et al. 1983), the opposite dip of the master faults as a Y-structure splits the gas flux and shields the zone in between from CO_2, i.e., the lines of mineral springs on the edge of the CO_2-free zone reflect the course of the main faults (Fig. 7). These zones can be followed especially in areas with insufficient geophysical results.

Fig. 1 clearly displays that the zone of the highest gas fluxes in the Cheb Basin represents the course of the Krušné hory Fault and the southern border of CO_2 appearances represents the Central Fault (of the České středohoří Mountains).

The Krušné hory Fault continues to Bavaria with a line of mineral springs of Hohenberg, Kothigenbibersbach and Bad Alexandersbad. In addition, the formation or preservation of smaller Tertiary basins of Schirnding, Dietersgrün and Göpfersgrün supports the assumption of a deep fault. Likewise the continuation of the Central Fault can be seen in the basins of Seedorf, Heiligenfurth and Brand.

Correspondingly, the southern edge of the CO_2-free zone is formed by the Litoměřice Deep Fault.

The NNW–SSE-striking faults of Horní Slavkov and Mariánské Lázně narrow the Eger Rift stepwise to the west. West of Mariánské Lázně, the Litoměřice Deep Fault follows the southern edge of the Cheb Basin. The position of the Quaternary basaltic volcanoes of Komorní Hůrka and Železná Hůrka gives evidence of the deep reach of these elements and supports the postulation of the main faults of the Eger Rift.

South of the Cheb Basin, the gases of mineral springs are CO_2-rich (>99 vol.% CO_2) and have $\delta^{13}C$ values of about −4 ‰. On the Bavarian side in Maiersreuth and Neualbenreuth the gas composition changes abruptly, with 17 vol.% N_2 and 33 vol.% N_2 as well as δ ^{13}C values of -8.2 and -8.8 ‰, respectively. With this characteristic these gases are obviously different from those along the main faults and are comparable with gases in the marginal areas. Therefore it has to be assumed, judged by the gas composition, that these gases are tectonically separated from those on the Bohemian side.

Gases with distinctly higher CO_2 contents of up to 99.6 vol.% and $\delta^{13}C$ values of −5.4 to −3.6 ‰ occur in the mineral springs of Kondrau and Wiesau. The migration path of these gases, which followed the northern edge of the Tertiary Mitterteich Basin can be interpreted as a continuation of the Litoměřice Deep Fault. This indicates a further northward shift of the Litoměřice Deep Fault on the Aš – Tachov Fault (sensu Conrad et al. 1983).

This interpretation is supported by the detection of photolineaments by remote sensing indicating ENE–WSW-striking fault sets, Neusorg-Waldershof and Waldeck-Teichelsberg Zug (Hirschmann 1992). Additionally, Peterek and Schröder (1997) have found Pliocene block movements in this area.

It can be clearly seen that the Eger Rift is stepwise narrowed by younger NNW–SSE-striking faults. In the vicinity of the Franconian Line, the influence of parallel NW–SE-striking elements on the magmatic gas flux becomes stronger and, therefore, the course of the ENE–WSW-striking Eger Rift structures becomes increasingly insecure.

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References

BEHR H.-J., 1992. Lineare Krustenstrukturen im Umfeld der KTB-Lokation. *KTB Report 92-3*, Nds. Landesamt f. Bodenf., Hannover, 3-82.

CONRAD W., HÄNING D., HAUPT M., SCHEIBE R., POLANSKÝ J., POKORNÝ L. and ŠŤOVÍČKOVÁ N., 1983. Ein geologisch-geopysikalisches Schema der Grenzregion zwischen der DDR und der ČSSR. *Z. Geol. Wiss.*, 11: 669-686.

HIRSCHMANN G., 1992. Das Bruchstörungsmuster im KTB-Umfeld. *KTB Report 92-3*, Nds. Landesamt f. Bodenf., Hannover, 85-124.

HUCKENHOLZ H.G. and SCHRÖDER B., 1985. Tertiärer Vulkanismus im bayrischen Teil des Eger Grabens und des mesozoischen Vorlandes. *Jber. Mitt. oberrhein. geol. Ver., N.F.*, 67 107-124.

KOLÁŘOVÁ M., 1965. Hydrogeologie chebské pánve. Sborník geol. Věd, HIG, 3, 7-101.

KOLÁŘOVÁ M. and MYSLIL V., 1979. *Minerální vody Západočeského kraje.* Ústř. úst. geol. Praha, 286 p.

KOPECKÝ L., 1979. Magmatism of the Ohre rift in the Bohemian Massif, its relationship to the deep fault tectonics and to the geologic evolution, and its ore mineralisation. In *Czechoslov. Geol. and Global Tectonics.* Bratislava, pp. 167-181.

LAUBE G.C., 1884. Geologische Exkursionen im böhmischen Thermalgebiet. Leipzig.

LODEMANN M., 1992. Salinare Fluide in der KTB-Vorbohrung (KTB-VB), Isotopengeochemische Untersuchungen im Rahmen des Kontinentalen Tiefbohrprogrammes der Bundesrepublik Deutschland. Inst. Hydrol., GSF-Bericht 42/93 (Thesis).

MALKOVSKÝ M., 1980. Model of the origin of the Tertiary basins at the foot of the Krušné hory Mts.: volcano-tectonic subsidence. *Věst. Ústř. Úst. geol.*, 55 (3): 141-150.

MALKOVSKÝ M., 1987. The Mesozoic and Tertiary basins of the Bohemian Massif and their evolution. *Tectonophysics*, 137: 31-42.

PETEREK A. and SCHRÖDER B., 1997. Neogene fault activity and morphogenesis in the basement area north of the KTB drill site (Fichtelgebirge and Steinwald). *Geol. Rdsch.*, 86: 185-190.

O'NIONS R.K., GRIESSHABER E. and OXBURGH E.R., 1989. Rocks that are too hot to Handle. *Nature*, 341: 391.

QUENTIN K.-E., 1970. Die Heil- und Mineralwässer Nordbayerns. *Geol. Bavarica*, 62: 1-312.

STETTNER G., 1975. Die Beziehungen der kohlensäureführenden Mineralwässer Nordostbayerns und der Nachbargebiete zum rhegmatischen Störungssystem des Grundgebirges. *Geol. Bavarica*, 64: 385-394.

ŠŤOVÍČKOVÁ N., 1980. Tectonic Stresses as Determined from the Character of Fault Systems in the Bohemian Massif. *Rock Mechanics*, Suppl. 9: 125-138.

WEINLICH F.H., TESAŘ J, WEISE S.M., BRÄUER K. and KÄMPF H., 1998. Gas flux distribution in mineral springs and tectonical structure in north-west Bohemia. *J. Czech. Geol. Soc.*, 43 (1-2): 91-110.

WEINLICH F.H., BRÄUER K., KÄMPF H., STRAUCH G., TESAŘ J. and WEISE S.M., 1999. An active subcontinental mantle volatile system in the western Eger rift, Central Europe: Gas flux, isotopic (He, C and N) and compositional fingerprints. *Geochim. Cosmochim. Acta*, 63: 3653-3671.

WENDT I., 1968. Fractionation of carbon isotopes and its temperature dependence in the system CO_2-Gas-CO_2 in solution and CO_3-CO_2 in solution. *Earth Planet. Sci. Lett.*, 4: 64-68.

ZHANG J., QUAY P.D. and WILBUR D.O. 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO_2. *Geochim. Cosmochim. Acta*, 59: 107-114.