

Isotopically light carbon dioxide – result of mixing or fractionation? The distribution pattern in the western Eger Rift, in the Eifel and the French Massif Central

F. H. Weinlich

Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany

Abstract. Based on the example of the western Eger Rift gases, it can be demonstrated that gas fractionation controls the distribution pattern of gas composition and isotopic composition of CO₂ instead of mixtures with biogenic CO₂. The processes of isotopic and chemical solubility fractionations control apparently the gas distribution pattern also in other regions.

1 Introduction

In areas with low CO₂ abundance and contents we encounter very often CO₂ with isotopic compositions of $\delta^{13}\text{C}$ values lesser than -10‰ . Usually such values are interpreted as biogenic CO₂ or mixtures between magmatic and biogenic CO₂. It seems that, occurrences of CO₂ gases with low $\delta^{13}\text{C}$ values confirm this in the margin areas of regions with ascending magmatic CO₂ like for example in mineral springs of the western Eger Rift, the Eifel or the French Massif Central. Another way of interpreting such low $\delta^{13}\text{C}$ values is a comprehensive gas fractionation concerning both gas composition and isotopic composition of CO₂.

2 Gas distribution pattern in areas with magmatic CO₂

In the western Eger Rift the main release of magmatic gas is bounded to gas release-centres north and south of the main structures of Eger Rift (Weinlich et al., 1998). The gas of the mofettes and springs with the highest gas fluxes in these areas is characterised by high CO₂ contents up to 99.99 vol. % and $\delta^{13}\text{C}$ values of -1.9 up to -3.9‰ (Fig. 1). With increasing distances from these gas release-centres the gas flux falls and related with it the CO₂ becomes isotopically lighter whereas the CO₂ contents decrease and are compensated by a rise of the N₂ and He contents (Weinlich et al., 1999).

In the Eifel (Rhine Graben), Griesshaber et al. (1992) report isotopic compositions of CO₂ ranging from -3‰ up to

Correspondence to: F. H. Weinlich (falk.weinlich@bgr.de)

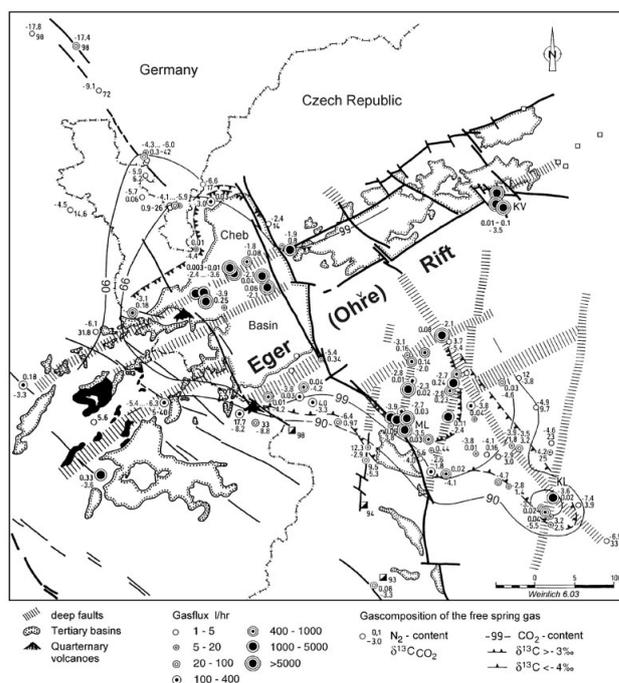


Fig. 1. Distribution pattern of gas flux (free gas), gas composition (air-free) and $\delta^{13}\text{C}_{\text{CO}_2}$ values of the gases from mineral springs and mofettes in the western Eger Rift; ML – Mariánské Lázně, KV – Karlovy Vary, KL – Konstantinovy Lázně.

-7.8‰ . The lighter isotopic values are explained according to lower R/R_a values due to mixing of magmatic and biogenic CO₂. May (2002) describes the occurrence of CO₂-rich gases linked with higher gas fluxes within the central Eifel and the decrease of the CO₂ contents in its margin areas.

In the French Massif Central CO₂ occurs with $\delta^{13}\text{C}$ values ranging from -4‰ up to -23‰ . Gas flux measurements (Batard et al., 1982) carried out on these spring gases show also in this region that the CO₂-rich gases are linked with

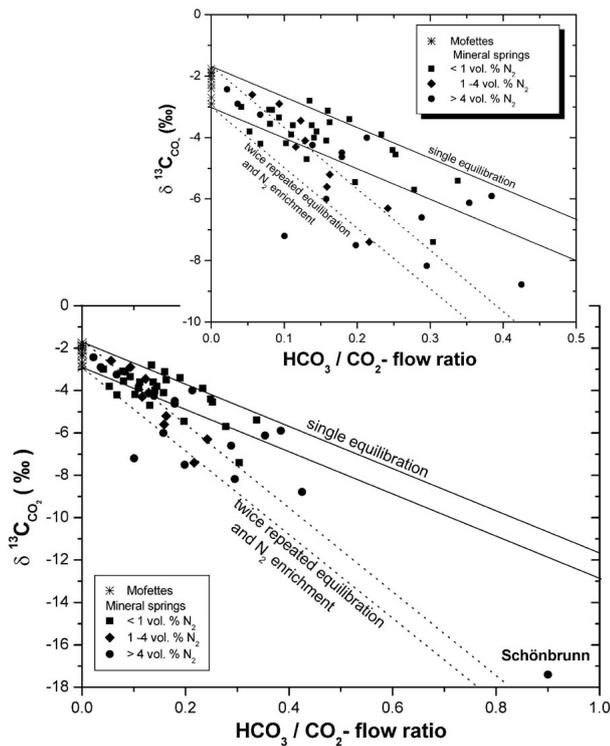


Fig. 2. Dependence of $\delta^{13}\text{C}_{\text{CO}_2}$ values in free gas phase from the ratio of HCO_3^- transport ($m_{\text{HCO}_3^-}$) in water to total CO_2 flux in mineral springs and mofettes in the western Eger Rift with complete mass balances, according to the isotope balance formula (see text). Data of HCO_3^- , dissolved CO_2 and water discharge are taken from Kolářová and Myslík (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 $\epsilon_{\text{HCO}_3^- - \text{gas}}$ at 10°C . Between these lines, the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values below the lines can be explained by twice repeated 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 inbetween the fractionation lines.

high gas fluxes. According to the data by Batard et al. (1982) and Matthews et al. (1987) the same distribution pattern prevails there. In the central part the isotopically heavy CO_2 also occurs linked exclusively with CO_2 -rich gases whereas CO_2 with $\delta^{13}\text{C}$ values ranging from -12 up to -23 ‰ is linked with N_2 -rich gases in the margin areas. The latterly values are in the range of “typical” biogenic CO_2 .

3 CO_2 fractionation

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, it can alter the gas composition solely by solubility fractionations. This results

in enrichment of the inert gases. Secondly, linked with the solution of CO_2 are decreasing pH values of these waters resulting in the leaching of cations from the adjacent rocks and formation of HCO_3^- ions. An isotope fractionation of about 10‰ (at 10°C) exists between HCO_3^- and CO_2 in the gas phase. With ongoing HCO_3^- formation, the remaining CO_2 in the gas phase becomes isotopically lighter. The key for discriminating mixing or fractionation is the compilation of complete mass balances for CO_2 for each gas occurrence: 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:

$$\delta^{13}\text{C}_{\text{gas}} = \delta^{13}\text{C}_{\text{total}} - (m_{\text{diss.}}/m_{\text{total}})\epsilon_{\text{w-gas}} - (m_{\text{HCO}_3^-}/m_{\text{total}})\epsilon_{\text{HCO}_3^- - \text{gas}}$$

where as m are the amounts of CO_2 and ϵ the fractionation factors of -1.3 ‰ for $\epsilon_{\text{diss.}-\text{gas}}$ and 9.6 ‰ for $\epsilon_{\text{HCO}_3^- - \text{gas}}$ at 10°C (Wendt, 1968; Mook et al., 1974).

In case of the mofettes the water discharge is 0, i.e. the ratios $m_{\text{diss.}}/m_{\text{total}}$ and $m_{\text{HCO}_3^-}/m_{\text{total}}$ are 0. Consequently, the measured $\delta^{13}\text{C}$ value of the free gas phase is identical with the total, e.g. the primary isotopic composition of magmatic CO_2 in this area. In the case of mineral springs gases with a continuous transport of leached cations, mainly Ca^{++} and Mg^{++} , isotopical fractionation occurs with contemporaneously formed HCO_3^- whereas remaining CO_2 in the gas phase becomes isotopically lighter (Fig. 2) and CO_2 contents can decrease. In the case of spring gases in the vicinity of mofettes it can be demonstrated that the differences in the isotopic composition are solely caused by HCO_3^- fractionation. The spring gases, which are further 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. Changes in isotopic composition can be also explained by mixing with lighter biogenic CO_2 . However, the common change of isotopic and chemical composition in the Eger Rift gases point to fractionation processes caused by multiple equilibrations as increasing nitrogen contents are not linked with biogenic CO_2 admixtures. In these gases a correlation between N_2 and He contents can be observed which points to one source and 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.

In case of longer migrations pathways as mentioned above it is to consider that the gas migration occurs within different hydrological systems and therefore these fractionations take place repeatedly during the migration. This results in a drastic drop of the CO_2 contents and the $\delta^{13}\text{C}$ values in the remaining gas phase. Figure 2 demonstrates that yet the assumption of a twice repeated equilibration $\text{CO}_2 - \text{HCO}_3^-$ can explain the isotopic composition with a $\delta^{13}\text{C}$ values of -17.4 ‰ of the N_2 -rich gases in the Fluorite mine

of Schönbrunn (one of the most northern springs shown in Fig. 1). Certainly, an admixture of biogenic CO₂ cannot be excluded but in this mine about 3.6 m³ of CO₂ gas and 3664 m³ of dissolved CO₂ per year were released. Facing the fact that the granite surface is located only about 650 m below the thermal water and gas inflows (Kuschka and Hahn, 1996) this amount is hard to explain with larger proportions of biogenic CO₂. In the same way the isotopic signature of –12 up to –23‰ of the N₂-rich spring gases of the French Massif Central could be explained. Batard et al. (1982) calculated mass balances according to a single equilibration CO₂ - HCO₃⁻ for some gases in this area and concluded a biogenic or mixed origin of CO₂ because the isotopic composition of the total carbon range between –11 and –16‰. With the assumption of only a twice and in two cases a thrice repeated equilibration between CO₂ and HCO₃⁻ these values can be achieved so that it is also not absolutely necessary to assume biogenic contributions in the region. Like in the western Eger Rift, the N₂-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.

An additional argument contradicting the influence of mixing processes is: outside these areas with magmatic CO₂ there are no springs with biogenic CO₂ in the gas phase. The production rates of biogenic CO₂ in soils (Andrews and Schlesinger, 2001) are too small to nourish a free gas phase. It is also problematic to derive biogenic CO₂ from sedimentary rocks since these waters and gases circulate within fault systems. There, either a far-reaching CO₂ exchange between the gases migrating along fault pathways and the surrounding country rocks is impeded or the ascending magmatic CO₂ saturates the groundwater with CO₂ gas, as it is the case in the Cheb Basin. The CO₂ concentration gradient in a close vicinity of the faults prevents the admixture of CO₂ from other sources like the biogenic CO₂.

4 Conclusions

As demonstrated, it is possible to elucidate low δ¹³C values with gas fractionation and not necessary exclusively with mixing. However, without complete mass balances it is not possible to discriminate between both or give reasons to prefer one of the interpretations. In some cases, it will be not possible to educe the “last proof” for the interpretation.

Therefore, it should be always considered that even the enhanced CO₂-contents in the soil air in the vicinity of fractured rocks can also represent completely fractionated magmatic CO₂.

References

- Andrews, J. A. and Schlesinger, W. H.: Soil CO₂ dynamics, acidification, and chemical weathering in a temperate forest with experimental CO₂ enrichment, *Global Biochem. Cycles*, 15, 149–162, 2001.
- Batard, F., Baubron, J. C., Bosch, A., Marcé, A., and Risler J. J.: Isotopic identification of gases of a deep origin in French thermomineral waters, *Jour. Hydrol.*, 56, 1–21, 1982.
- Griesshaber, E., O’Nions, R. K., and Oxburgh, E. R.: Helium and carbon isotope systematics in crustal fluids from the Eifel, the Rhine Graben and Black Forest, *F. R. G., Chem. Geol.* 99, 213–135, 1992.
- Kolářová, M. and Myslík, V.: *Minerální vody Západočeského kraje. - Ústřední Ústav Geol. (Geol Surv.)*, Prague 286 p., 1979.
- Kuschka, E. & Hahn, W.: *Flußspatlagerstätten des Südwestvogtlandes: Schönbrunn, Bösenbrunn, Wiedersberg, Bergbau in Sachsen Bd. 2, Landesamt Umwelt u. Geol, Sächs. Oberbergamt 281 p.*, 1996.
- Mathews A., Fouillac C., Hill R., O’Nions, R. K., and Oxburgh, E. R.: Mantle-derived volatiles in continental crust: the Massif Central of France, *Earth and Plant. Sci. Lett.* 85, 117–128, 1987.
- May, F.: *Quantifizierung des CO₂-Flusses zur Abbildung magmatischer Prozesse im Untergrund der Westeifel*, Shaker Verlag 170 p., 2002.
- Mook, W. G., Bommerson, J. C., and Staverman, W. H.: Carbon isotope fractionation between dissolved bicarbonate and gaseous Carbon dioxide, *Earth Plant. Sci. Lett.* 22, 169–176, 1973.
- Weinlich, F. H., Tesáň, J., Weise, S. M., Bräuer, K., and Kämpf, H.: Gas flux distribution in mineral springs and tectonical structure in the western Eger Rift, *Jour. Czech Geol. Soc.* 43, 91–110, 1998.
- Weinlich, F. H., Bräuer, K., Kämpf, H., Strauch, G., Tesáň, J., and Weise, S. M.: 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, 1999.
- Weinlich, F. H., Bräuer, K., Kämpf, H., Strauch, G., Tesáň, J., and Weise, S. M.: Gas flux and tectonic structure in the Western Eger Rift, Karlovy Vary – Oberpfalz and Oberfranken, Bavaria, *Geo-Lines* 15, 171–177, 2003.
- Wendt, I.: Fractionation of carbon isotopes and its temperature dependence in the system CO₂-Gas-CO₂ in solution and CO₃-CO₂ in solution – *Earth Planet. Sci. Lett.* 4, 64–68, 1968.