

A review of the geology and origin of CO₂ in mineral water springs in east Belgium

RENATA BARROS^{1*}, AGATHE DEFOURNY^{2,3}, ARNAUD COLLIGNON³, PATRICK JOBE³, ALAIN DASSARGUES², KRIS PIESSENS¹ & KRIS WELKENHUYSEN¹

¹ Royal Belgian Institute of Natural Sciences, Geological Survey of Belgium, Jennerstraat 13, 1000 Brussels, Belgium.

² University of Liège, Hydrogeology, Urban and Environmental Engineering, Quartier Polytech 1, Allée de la Découverte, 9, Bât. B52 - Sart Tilman 4000 Liège, Belgium.

³ Spadel S.A., Water resource department, Rue Auguste Laporte 34, B-4900 Spa, Belgium.

* corresponding author: rbarros@naturalsciences.be.

ABSTRACT. Naturally CO₂-rich mineral water springs (pouhons) in east Belgium occur in the context of the Rhenohercynian domain of the Variscan fold-and-thrust belt, mostly within the Cambro-Ordovician Stavelot-Venn Massif. The origin of the CO₂ is still unclear, although different hypotheses exist. In this review study, we show pouhon waters are of the calcium bicarbonate type (~310 mg/l HCO₃⁻ on average), with notable Fe (~15 mg/l) and some Ca (~43 mg/l). Pouhon waters are primarily meteoric waters, as evidenced by H and O isotopic signature. The δ¹³C of CO₂ varies from -7.8 to +0.8‰ and contains up to ~15% He from magmatic origin, reflecting a combination of carbonate rocks and mantle as CO₂ sources at depth. Dinantian and Middle Devonian carbonates at 2–6 km depth could be potential sources, with CO₂ generated by dissolution. However, carbonates below the Stavelot-Venn Massif are only predicted by structural models that assume in-sequence thrusting, not by the more generally accepted out-of-sequence thrust models. The mantle CO₂ might originate from degassing of the Eifel magmatic plume or an unknown shallower magmatic reservoir. Deep rooted faults are thought to act as preferential pathways. Overall low temperatures of pouhons (~10 °C) and short estimated residence times (up to 60 years) suggest magmatic CO₂ is transported upwards to meet infiltrating groundwater at shallower depths, with partial to full isotopic exchange with carbonate rocks along its path, resulting in mixed magmatic-carbonate signature. Although the precise role and interaction of the involved subsurface processes remains debatable, this review study provides a baseline for future investigations.

KEYWORDS: pouhon, CO₂-rich waters, geogenic CO₂, Spa, Stavelot-Venn Massif, carbonated water springs, natural mineral water.

RÉSUMÉ. Synthèse de la géologie et des hypothèses sur l'origine du CO₂ dans les sources carbogazeuses de l'est de la Belgique. Dans l'Est de la Belgique, au sein du Massif de Stavelot-Venn, il existe une multitude de sources d'eaux souterraines naturellement carbogazeuses, appelées « pouhons » dans la région. Bien que plusieurs hypothèses aient été émises, l'origine du CO₂ présent dans ces eaux est encore incertaine. Dans cette synthèse, nous montrons que l'eau des pouhons est de type bicarbonatée calcique (~310 mg/l HCO₃⁻ en moyenne), avec des concentrations notables en Fe (~15 mg/l) et Ca (~43 mg/l). L'analyse des isotopes de l'eau a montré que l'eau souterraine étudiée est d'origine météorique. Le ratio δ¹³C du CO₂ varie entre -7.8 et +0.8‰ et jusqu'à ~15% d'hélium mantellique a pu être identifié dans les gaz dissous. Ces valeurs, comparées à celles existant dans la littérature, suggèrent que l'origine du CO₂ est une combinaison entre une source liée à la dissolution de roches carbonatées en profondeur et un apport direct de CO₂ mantellique. Pour la première hypothèse, les roches carbonatées du Dinantien et du Dévonien Moyen, probablement présentes entre 2 et 6 km de profondeur, pourraient être la source de carbonates générant du CO₂ par dissolution et/ou métamorphisme. La présence de carbonates sous le Massif de Stavelot-Venn peut être supposée sur base des modèles structuraux de la zone qui impliquent un chevauchement en séquence mais est peu réaliste selon la majorité des représentations structurales qui suggèrent, elles, un chevauchement hors-séquence. Pour la seconde, du CO₂ d'origine mantellique peut provenir du dégazage des panaches magmatiques de l'Eifel ou d'un autre réservoir moins profond, encore inconnu. Les failles de charriage profondes présentes dans la zone permettent une remontée préférentielle de l'eau souterraine vers la surface. La température relativement basse des pouhons (~10 °C) ainsi que le faible temps de résidence estimé (jusqu'à 60 ans) des eaux suggèrent que le CO₂ magmatique est transporté vers la surface où il rencontre l'eau souterraine à faible profondeur. Un échange isotopique plus ou moins important entre le gaz et des roches carbonatées pourraient conduire à la signature isotopique mixte qui est observée. Même si le débat sur l'origine du CO₂ reste ouvert, cet article offre une base de discussion et de travail pour de futures recherches.

MOTS-CLÉS : pouhons, eaux carbogazeuses, CO₂ géogénique, Spa, Massif de Stavelot-Venn, sources d'eaux carbogazeuses, eau minérale naturelle.

1. Introduction

The area located in the northern part of the Stavelot-Venn Massif, including the High Fens and the tectonic window of Theux, is touristically denominated 'blue Ardenne' due to the abundance and diversity of springs. Particularly in the areas of Spa, Malmedy and Stoumont, numerous occurrences of naturally ferruginous and CO₂-rich springs, locally referred to as 'pouhons', have been documented (Goemaere et al., 2016). There are also various dry CO₂ sources (mofettes) historically mapped in the region (Liégeois, 1929, 1931). These waters have attracted economic and touristic interest for centuries, being exploited since the 14th century and bottled and exported since the 16th century.

Different terminologies are used for waters naturally enriched in CO₂. These are often referred to as 'naturally carbonated' waters or 'high CO₂' waters in literature, and in Belgium the legal denomination of 'naturally carbonated natural mineral water' is applied for the product of exploited water. For clarity and brevity, in this text these are being referred to as 'CO₂-rich' waters.

Waters enriched in CO₂ also attract scientific interest for various reasons. Carbon dioxide concentrations in natural freshwaters are often 10 to 100 times greater than concentrations in pure water in equilibrium with atmospheric CO₂ (Karol, 2019), therefore acting as manifestations of geological processes in the subsurface. However, the hydrogeochemical processes involved are not often fully understood.

Additionally, these geomanifestations are natural laboratories to study processes and effects of CO₂ migration, which has great potential for enhancing knowledge about underground CO₂ storage sites. Carbon dioxide geological storage involves capturing CO₂ generated by fuel combustion or industrial processes and subsequent injection of CO₂ into geological formations for long-term storage and removal from the carbon cycle (IPCC, 2005; Bickle & Kampman, 2013). This is seen as a critical strategy towards a carbon-neutral society (Bickle & Kampman, 2013; IPCC, 2014). Carbon dioxide-rich springs can provide valuable information on CO₂ accumulation and leakage in the subsurface (e.g. Burnside et al., 2013; Karolytė et al., 2017). Residence times and sources of CO₂ in

groundwater are also important for improving our understanding of the global CO₂ cycle.

Geological studies targeting CO₂-rich water sources in east Belgium can be dated back to the 1600s (Van den Broeck, 1888). Different theories for the origin of CO₂ in these waters have been formulated over the years based on geochemical studies and developments in the knowledge of the structural setting (e.g. Van den Broeck, 1888; Defosse & Wery, 1975; Geukens, 2007). Isotopic compositions of naturally occurring gases dissolved in these distinctive groundwaters (e.g. CO₂ and He) provide some hints on their origin (e.g. Griesshaber et al., 1992; Harris et al., 1997; Cartwright et al., 2002).

However, there have been no attempts to link the information available into a single comprehensive model, and especially the recent advancements in the physico-chemical characterisation of spring waters and the understanding of the geotectonic evolution of the region remain largely unrelated. The link with other well-studied occurrences of the Rhenish Massif (e.g. May et al., 1996; May, 2005) is also poorly explored. Moreover, limited geochemical data that underpin the genetic models proposed for this area are publicly available, especially regarding isotopic signatures of the waters.

In this paper we therefore present a review of previous studies about the CO₂-rich waters in east Belgium, with a focus on the region between Spa, Stoumont and Malmedy. We present results of elemental and isotope geochemistry analysis that have been made accessible by Spadel for this study. The different proposed models regarding the origin of such waters are presented. We also compare the findings of this state-of-knowledge exercise with the well-studied CO₂-rich waters in the neighbouring Eifel region in Germany. We finally endorse an integrated model for a mixed crustal-mantle origin for CO₂ in these waters.

2. Geological setting

2.1. Regional geology

The area of interest is located in the eastern part of Belgium, which is dominated by Palaeozoic rocks of the Rhenohercynian zone of the Variscan orogeny. The Rhenohercynian zone extends through France, Belgium, Luxembourg and Germany and characterises a fold-and-thrust belt at the northern boundary of the Variscides in central Europe formed during the Carboniferous collision (e.g. Vanbrabant et al., 2002). The Rhenohercynian zone crops out in the Rhenish Massif (Fig. 1).

The Belgian part of the Rhenish Massif is dominated by the Ardenne Allochthon, consisting of a Cambro-Ordovician basement unconformably overlain by Devonian-Carboniferous sandstone and limestone deposits and separated from the Brabant foreland to the north by the Midi fault zone (Hance et al., 1999), known as Eifelian fault in the Liège area. The basement was possibly reworked during the Caledonian orogeny (~450 Ma) (Fourmarier, 1931; Michot, 1980). Basement rocks and the Devonian-Carboniferous cover were then deformed during the Variscan orogeny (~350 Ma) (Belanger et al., 2012). This deformation resulted in the NE-SW trending Ardenne Anticlinorium, with the massifs of Rocroi, Givonne, Serpont, and the largest Stavelot-Venn (Fig. 1) located on anticline crests. These massifs configure inliers with similar thick siliciclastic (often turbiditic) sequences from the Lower Cambrian to the Middle Ordovician (Verniers et al., 2001). The Dinant Synclinorium to the northwest and the Neufchâteau Synclinorium to the southeast (which continues into the Eifel Synclinorium in Germany) consist predominantly of clastic sediments deposited from Lower Devonian (Bultynck et al., 2000). The Stavelot-Venn Massif is crosscut by the NE-SW Malmedy Graben (Geukens, 1957). The graben is filled with

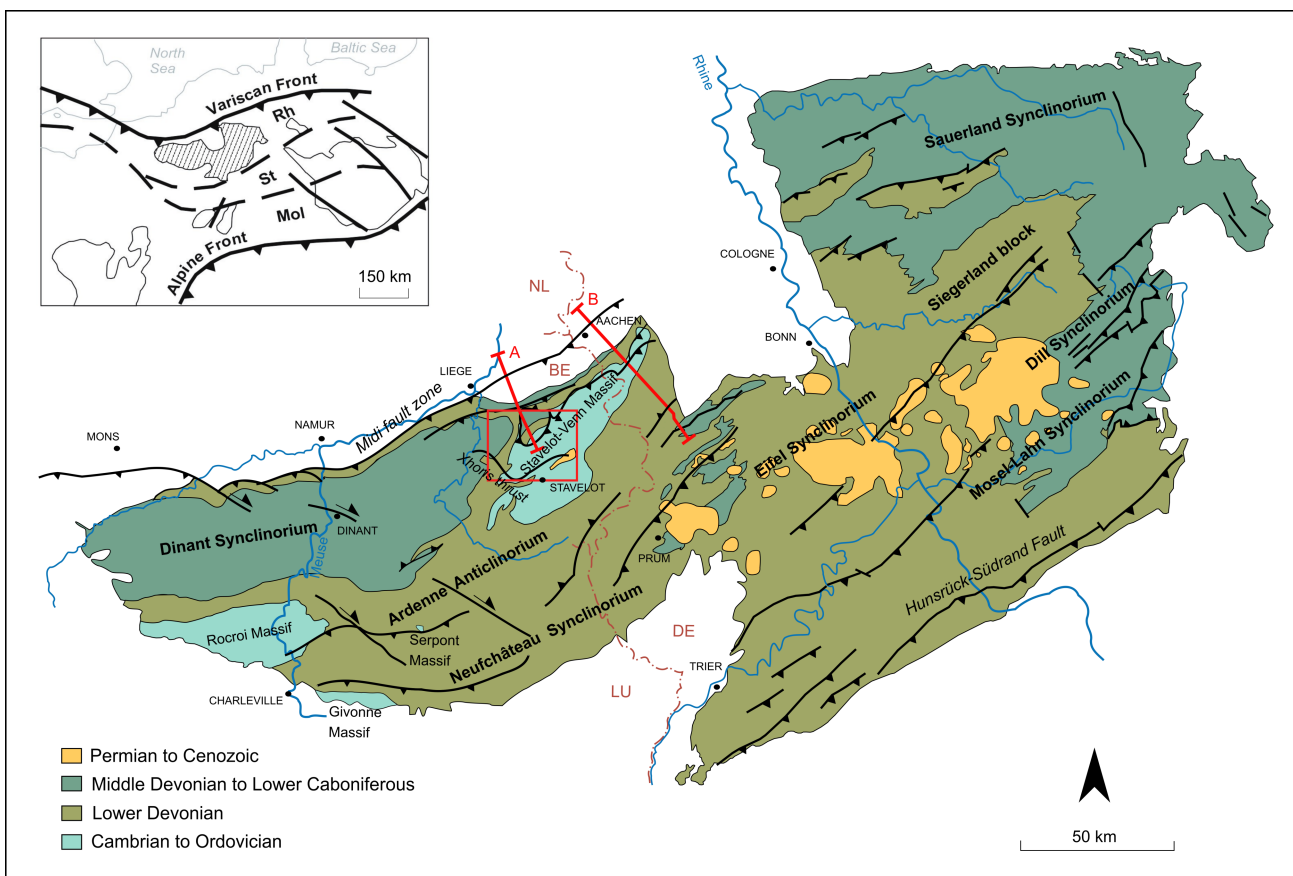


Figure 1. Simplified geology of the Rhenish Massif after Fielitz & Mansy (1999) and Meschede (2018). Red rectangle shows the area represented in Fig. 2; red cross sections are represented in Fig. 9. Inset: configuration of the Rhenohercynian zone within the Variscides (after Vanbrabant et al., 2002). Rh: Rhenohercynian zone; Mol: Moldanubian zone; St: Saxothuringian Zone.

conglomeratic beds of Permian age and lies between a predominant general NE-SW strike to the north and a more frequent W-E strike parallel to Caledonian structures to the south (Geukens, 1995).

The Eifel area to the east of the Stavelot-Venn Massif (Fig. 1) is part of the European Cenozoic Rift System, an almost continuous system of extensional structures with spatially related volcanism and uplifting (Goes et al., 1999). The development of the European Cenozoic Rift System began during the late Eocene, mainly by reactivation of late Variscan, Permo-Carboniferous and Mesozoic crustal discontinuities (Schumacher, 2002). The causal relations between these features are still a matter of scientific debate. Nonetheless, mineral waters may contain information on the processes in the lower crust or mantle in the form of minerals or elements dissolved in fluids and gases (May et al., 1996).

2.2. Geology and hydrogeology of the Spa-Stoumont-Malmedy area

The studied area is focused on the western part of the Stavelot-Venn Massif, including the Theux Window and the Malmedy Graben, as well as within the Devonian to Carboniferous rocks of the Dinant Synclinorium and Ardenne Anticlinorium located to its west (Figs 1, 2). The bedrock of the area consists of a 2500 m thick siliciclastic sedimentary sequence from the Cambrian to the Middle Ordovician. The sequence is mainly composed of an alternation of slates and quartzite beds of varying thicknesses, ranging from a few millimetres to a few metres (Goemaere et al., 2016). The slate beds act as less permeable barriers isolating aquifer compartments from each other.

The oldest rocks of the Stavelot-Venn Massif are subdivided into the Deville, Revin and Salm Groups, and the Petites Tailles Formation, detailed below (according to Verniers et al., 2001 and references therein; Herbosch et al., 2020); the detailing of magmatic rocks is according to Corin (1965).

- Deville Group: lower to middle Cambrian sequence subdivided, from oldest to youngest, into the Hour Formation, composed of >150 m of light coloured to greenish quartzite and green slate, and the Bellevaux Formation, composed of a 150 m thick sequence of alternating greenish and purple slate and shale and white quartzite.
- Revin Group: middle to upper Cambrian sequence subdivided into the following formations, from base to top:
 - Wanne Formation: dominated by dark coloured slate and greyish-green quartzite (at times micaceous) with rare conglomerate beds (10–15 cm thick) and interstratified volcanic lavas or tuffs; presence of black graphitic silty slate (locally called quartzophyllade) at the base with localised accumulations of pyrite or marcasite.
 - La Venne Formation: 500 m thick sequence of alternating black slate and dark quartzite, the latter at times clayey and micaceous, and rhyolitic to rhyodacitic volcanic intrusions. Feldspar is often chloritised, and the intrusions are at times enriched in pyrite.
 - La Gleize Formation: sequence of around 300 m thickness of black and silty slate (locally called quartzophyllade), minor dolomite nodules in the upper part and occasional acid intrusions and lava flows.
- Salm Group: Ordovician sequence subdivided into the following formations, from base to top:
 - Jalhay Formation: over 400 m thick sequence of blue-green slate, sandstone and silty slate (locally called quartzophyllade), often micaceous or graphitic towards the base.
 - Otré Formation: 150 m thick purplish and silty slate (locally called quartzophyllade), occasionally with calcareous nodules or garnet-bearing slates (Meuville Member) or with calcareous levels with iron and

manganese nodules (Les Plattes Member).

- Bihain Formation: over 180 m thick sequence of black silty slate (locally called quartzophyllade) and greenish sandstone, often rich in pyrite (Salm-Château Member).
- Petites Tailles Formation: over 75 m thick sequence of whitish quartzitic sandstone of unknown age, covering the Salm Group.

The lower part of the Devonian-Carboniferous sequence deposited above the Cambro-Ordovician basement and outcropping at the western border of the Stavelot-Venn Massif and hosting the pouhons includes the following formations (according to Bultynck & Dejonghe, 2001 and references therein; Geukens, 2008), from base to top:

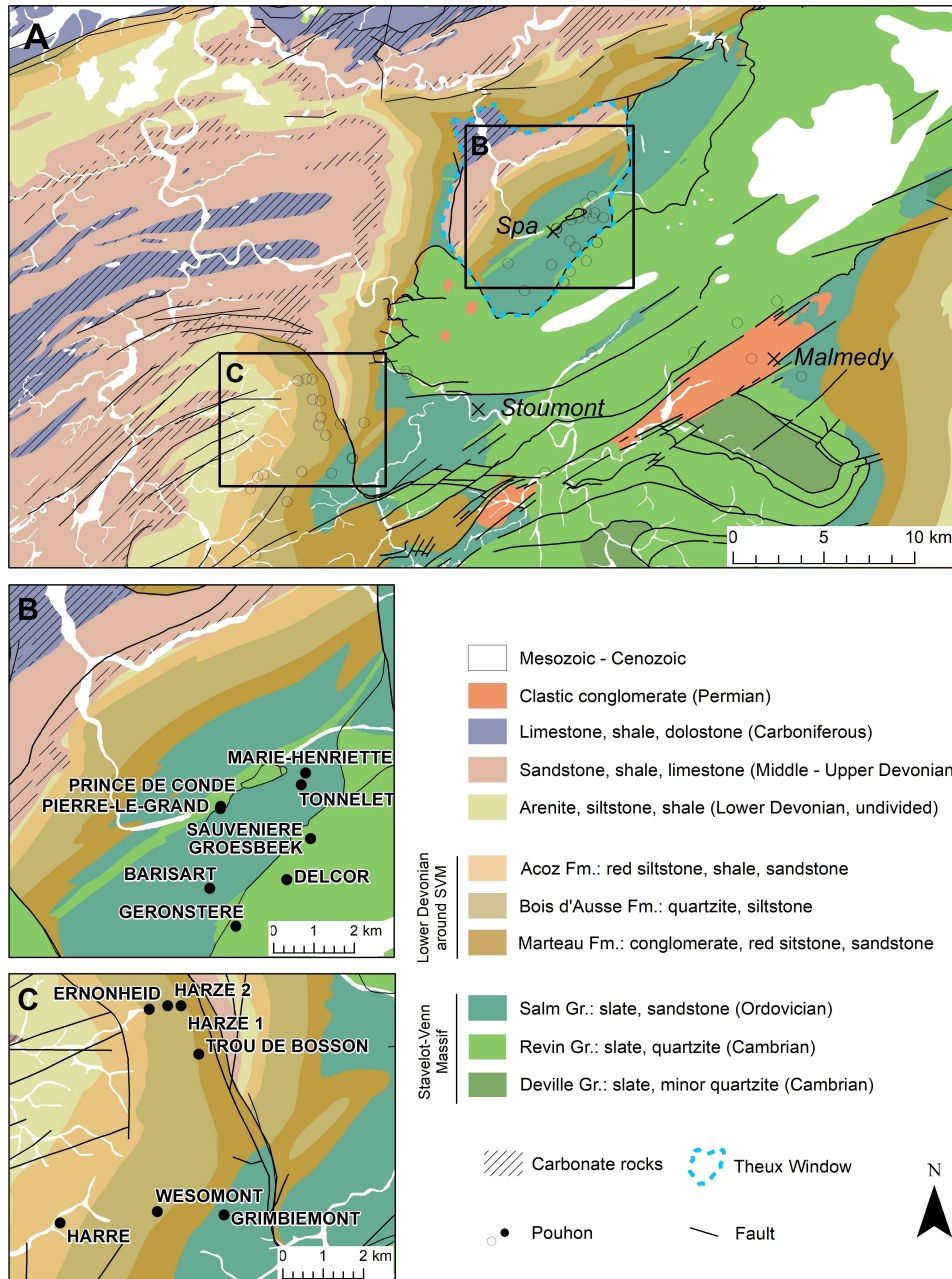
- Marteau Formation: basal conglomerates (1.5 to >10 m thick, often 2 to 3 m) overlain by maroon-red siltstones and argillaceous sandstones (>150 m thick), with occasional concentration of carbonate nodules in some beds.
- Bois d’Ausse Formation: sequence of 100 to 360 m thickness of grey or beige quartzites with cross-stratification (Bôlia Member), overlain by alternating siltstones and green argillaceous siltstones (Tréko Member), topped by lenticular grey or beige quartzite banks (Masuis Member).
- Acoz Formation: detrital rocks of predominantly maroon-red colour; 140 m thick base of siltstones and shales (Bième Member), followed by 160 m thick of sandstones and light-coloured quartzite layers (Ruisseau d’Hanzinne Member).

Younger units in the studied region (Fig. 2) include Middle to Upper Devonian sandstone, shale and limestone, Carboniferous limestone, shale and dolostone, Permian clastic conglomerates and Mesozoic-Cenozoic sedimentary cover including Quaternary peat (Bless et al., 1990; Pirson et al., 2008 and references therein).

Regarding the hydrogeology, the local aquifer character depends mainly on the fracturation of the quartzite and sandstone rocks in depth, and on the degree of superficial weathering in the shallow zone, and these two zones can be considered as two different aquifer types. The term ‘aquifer’ is used here in a relative way because ‘an aquifer formation of low permeability can be considered as an aquifer when, locally, all surrounding geological formations are less permeable and the considered formation can be used for water supply’ (Dassargues, 2018). Consequently, the hydraulic conductivity (K [m/s]) values measured by Spadel during pumping tests in different wells in the area differ by up to four orders of magnitude from one well to another, depending on local fracturation and faulting. This value varies from 10^{-8} m/s in low permeability zones up to 10^{-4} m/s for wells located along major fractures.

Deep aquifer zones correspond to fractured quartzites and sandstones. They have variable extensions, and permeability and porosity properties are largely influenced by the fracture frequency, opening, filling and interconnections. Wells into those aquifers rarely exceed 100 m in depth. Large-scale faults can play an important role as in the more quartz-rich zones they act as drains, while in mixed or alternated lithologies, their filling is more clayey, inducing a partitioning of the aquifer zone (Debbaut et al., 2014). The most productive aquifer zones in the area are located within the most quartzitic zones in faults and fractures.

Shallow aquifers are located in the alteration mantle and/or peatland areas. This type of aquifer zones corresponds to unconfined aquifers in which direction of flow is mainly topographically driven, and saturated thickness is limited to a few metres and the water table varies over time following winter recharge and summer depletion. Those aquifers have a low productivity and their water storage capacity is low. Often exploited using drains and galleries, they may dry up at the end of the summer. Sources are often located at the transition



between a permeable alteration mantle (on a mostly quartzitic bedrock) and a lower permeable clayey alteration mantle (on the shales and slates).

Pouhons are a geological manifestation at the surface of this complex geological and hydrogeological context. They are often located in topographic lower zones (Monjoie, 1995) corresponding also more probably to fractured/faulted zones. Most are located at less than a 100 m distance from riverbeds. In those locations, the pressure conditions and thus the local piezometric level tends to equilibrate with the topographic level, favouring the formation of springs. These particular springs are rich in ferrous iron (Fe^{2+}), which oxidises with oxygen from the atmosphere to the less soluble ferric iron (Fe^{3+}) giving the waters a distinct orange-red colour. Bacterial mats are also commonly developed in the pouhons, causing biologically-driven iron oxidation (Papier et al., 2016). Hydrogen sulphide often accompanies CO_2 resulting in the typical smell near the pouhons.

The most productive aquifer zones in the area are located within the most quartzitic zones in faults and fractures. The presence of the pouhons is most often interpreted as linked to

particular geological features that act as pathways enabling the ascent of the deep groundwater: the Theux Window, the Malmedy Graben and the Lower Devonian unconformity. In Spa, for example, sources are located along SW-NE axes, corresponding to the limit of the different thrust sheets that have been superposed in the region. The Theux Window (Fig. 2) results from the erosion of one of the thrusting sheets, revealing underlying younger (Ordovician and Devonian) rocks (Geukens, 2007). In Malmedy (Fig. 2), it is believed that the presence of the pouhons is linked to the different normal faults that have led to the opening of the Permian Malmedy Graben (Lamberty et al., 2017). These faults have NE-SW orientation across the Stavelot-Venn Massif and the graben is filled by Permian conglomerates (Geukens, 1995). Some of the pouhons in the Stoumont region (Fig. 2C) are spatially linked to the unconformity existing between the Stavelot-Venn Massif (Cambrian to Ordovician) and the Dinant Synclinorium (lower Devonian), together with the major thrust fault of Xhoris (Lamberty et al., 2016).

Table 1. General chemical composition of pouhon waters (internal data from Spadel). Analyses for the period 2012-2013. * measured at 25 °C. When below detection limit, detection limit is given. Empty cell means no data. For the location, see Fig. 2.

Name of the pouhon		Marie-Henriette	Tonnelet	Pierre Le Grand	Prince de Condé	Géronstère	Delcor	Barisart	Groesbeek	Sauvenière	Trou de Bosson	Ernonheid	Harzé 1	Gribiémont	Wésomont	Harre	Average	Std deviation
		O	O	O	O	C	C	O	C	C	D 1	D 3	D 2	O	D 1	D 3		
Outcropping bedrock																		
Ca	mg/l	11.3	11.1	38.4	29.1	14.7	21.5	16.1	23.4	28.3	108.9	39.1	53.8	151.4	64.4	38.6	43.3	38
Mg	mg/l	6.5	6.9	34.8	24.7	7.1	13.7	11.6	10.4	13.5	47.0	31.0	16.3	23.7	123.0	38.0	27.2	28
Na	mg/l	10.5	6.2	63.0	38.2	7.1	8.9	19.5	11.8	8.9	12.9	104.9	30.9	37.8		42.4	28.8	27
K	mg/l	1.0	0.8	4.3	4.9	4.3	8.4	1.5	5.8	4.8	2.2	5.1	4.0	3.5	4.2	2.9	3.8	1.9
Cl	mg/l	6.7	10.4	39.7	27.8	6.5	4.0	<1	19.1	5.8	4.6	61.7		4.0	12.2	26.8	17.6	17
NO₃	mg/l	0.6	2.0	<0.1	<0.1	0.1	0.8	<0.1		<0.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	0.7
SO₄	mg/l	4.9	0.9	10.3	11.5	4.2	4.8	2.5	1.9	0.2	<5	<5	<5	<5	<5	<5	4.6	3.7
HCO₃	mg/l	96.1	72.9	402.5	265.3	81.6	172.6	105.6	131.1	201.0	597.5	430.0	279.0	585.0	861.0	353.0	310	223
SiO₂	mg/l	17.6	16.7	65.1	47.2	9.1	10.2	30.7	8.5	8.8	17.5	9.0	11.0	32.8	13.9	32.0	22	16
pH	-	5.2	5.1	5.7	5.7	5.5	5.9	5.9	5.3	5.6	5.9	5.9	6.6	5.9	6.1	5.6	5.7	0.36
EC*	µS/cm	209.0	176.7	798.1	589.3	183.6	304.7	233.9	346.0	375.0	878.0	845.0	545.0	867.0	1235.0	638.0	550	312
Fe	mg/l	19.7	14.7	15.4	17.7	3.0	7.3	9.2	18.6	28.0	33.2	9.9	0.9	16.7	15.3	16.2	15	8.2
Mn	mg/l	0.4	1.0	1.8	3.3	0.2	0.2	1.3	0.6	0.7	2.5	0.7	1.6	3.9	1.0	0.7	1.3	1.1
CO₂	g/l	1.8	1.9	2.3	2.4	0.7	1.4	1.8	2.0	2.1	3.0	2.5	0.5	2.2	2.2	2.2	1.9	0.63

C = Cambrian, Revin Group; D 1 = Devonian, Marteau Formation; D 2 = Devonian, Bois d'Ausse Formation; D 3 = Devonian, Acoz Formation; O = Ordovician, La Salm Group.

3. Characterisation of groundwaters in the studied area

In the studied area, both CO₂-rich and non-carbogaseous groundwaters are present. Their quality and specific composition result from their particular geological history.

The non-carbogaseous groundwaters are weakly mineralised. The top 50 to 100 m layer of rocks forming the upper part of the Ardenne Anticlinorium are composed mainly of quartzites and slates, rocks that are weakly soluble or reactive. Moreover, groundwater pathways and residence times are expected to be relatively short. This kind of groundwater consequently presents low mineralisation, with an electrical conductivity (EC) ranging from 40 to 80 µS/cm in the Spa area.

Several hundreds of naturally CO₂-rich groundwater springs are mapped in the Stavelot-Venn Massif and surroundings. The groundwater composition at the springs is variable (Table 1). They present high mineralisation, with EC varying by a factor of almost 10 between the lowest (around 177 µS/cm at Tonnelet) and highest (around 1,235 µS/cm at Wésomont) values. Waters are rich in bicarbonate (around 70 mg/l) and present a high content of dissolved CO₂ (3.8 g/l) that degasses at atmospheric pressure. This indicates that the water is carbonated under pressure at depths greater than around 50 m below water table. The residence time of this kind of water has been estimated to be around 60 years in the region of Spa (Monjoie, 1997) on the basis of isotopic investigations. Groundwater from the region of Stoumont is more mineralised and carbonated than in Spa (EC around 340 µS/cm, 4.4 g/l dissolved CO₂).

Observed chemical composition differences can be explained by the local geology (Figs 3 and 4). The pouhons in the area of the Stoumont region can be geochemically distinguished from those of the Spa region, due to variations in bedrock geology (Devonian in Stoumont, Cambrian and Ordovician in Spa, Fig. 2). All outcropping lithologies have

similar anion content, presenting a major proportion of carbonates and bicarbonates and a small proportion of chlorides. In general, all pouhons have similar proportions of cations and bicarbonates are the dominant anions. Specifically, the cation signature of the springs located in Cambrian and Ordovician rocks is similar in terms of cation proportions, resulting in clear composition clusters on the Piper diagram (Piper, 1944). In contrast, those from the outcropping Devonian (Stoumont) are less clearly defined with strongly varying Ca and Mg proportions.

Besides general geochemical variations between different pouhon waters, the groundwater composition of an individual pouhon also slightly varies over time, although the averaged compositions have been approximately stable throughout the last decade (Fig. 5).

4. Overview of models and theories

Pouhons have been studied for a long time by several authors, but important unknowns are still remaining. Although there is some consensus on the infiltration and upward transport mechanisms, the source of CO₂ at depth is still unresolved and will be discussed in the following sections. Isotopic analyses can be a key element to answer these questions. Besides water isotopes to determine age and origin of groundwater, one of the methods used to determine the origin of CO₂ in groundwaters globally, and the main method used in the Belgian Ardenne, is C isotope analysis. Carbon-13 traces carbon sources and reactions for a multitude of interreacting organic and inorganic species (Clark & Fritz, 1997).

Limited isotope data for the studied region were published by Defosse & Wery (1975), Langguth & Plum (1984), Wollast (1985), Smets & Wollast (1988), and Monjoie (1997). Most information available is on ratios of stable H ($\delta^2\text{H}/^1\text{H}$, or $\delta^2\text{H}$) and O ($\delta^{18}\text{O}/^{16}\text{O}$, or $\delta^{18}\text{O}$) isotopes of pouhon and rain samples,

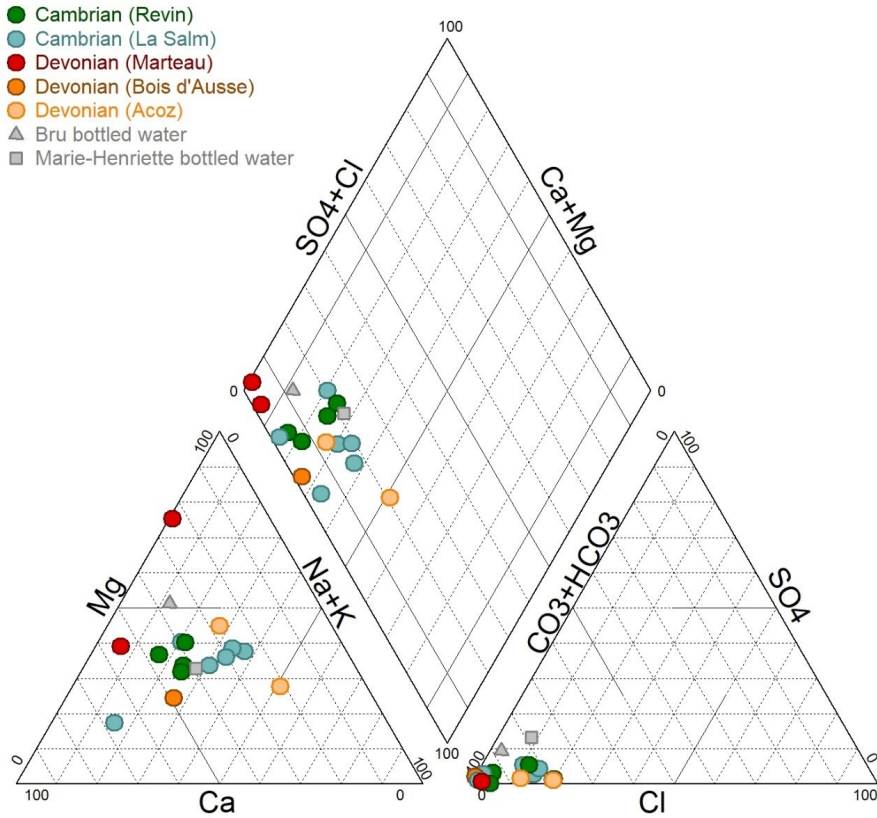


Figure 3. Relationship between chemical compositions and bed-rock geology for 15 pouhons from the Stavelot-Venn Massif and for two types of CO₂-rich waters bottled in the area.

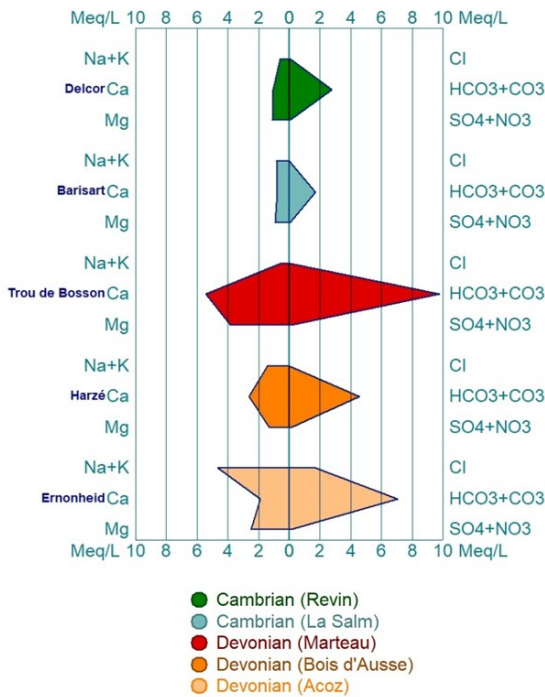


Figure 4. Stiff diagram representing one sample from each geological formation from the study area. All samples present a similar anion signature, but the cations signature differs depending on the geological formation. Sample mineralisation is strongly correlated to their bicarbonate content.

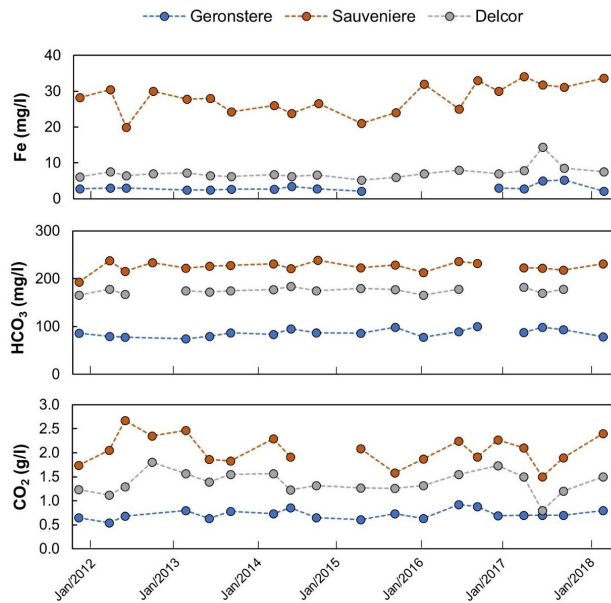


Figure 5. Evolution of HCO₃⁻, Fe and CO₂ concentrations in Geronstere, Sauveniere and Delcor pouhons in the Spa region (Fig. 2B) between 2011 and 2018. Internal data from Spadel.

Table 2. Summary of isotope data of CO₂-rich waters in the Ardenne. Detailed data and references presented in the Supplementary Material online. TU for Tritium Units.

Sources	$\delta^{18}\text{O}$ range	$\delta^2\text{H}$ range	TU range	$\delta^{13}\text{C}$ range	$\delta^{34}\text{S}$ range
Stoumont region	-8.32 to -7.89	-57.1 to -53.3	1.6 to 17.7	-7.76 to 0.80	-
Spa region	-8.04 to -7.79	-57.0 to -54.7	5.3 to 22.6	-7.2 to -3.8	+5.4 to +6.7
Malmédy region	-8.62 to -8.10	-58.8 to -56.0	1.8 to 5.2	-4.74 to -2.70	+7.2
Bernister region	-8.20 to -7.90	-58.0 to -57.4	10 to 17.3	-5.80 to -4.18	-

C isotopes ($\delta^{13}\text{C}/^{12}\text{C}$, or $\delta^{13}\text{C}$) and tritium (^3H) content of pouhon samples, as summarised in Table 2 and presented in full in the Supplementary Material. These historical data are being presented and discussed with caution, considering the limitations of analytical methods at the time of the analyses. Such limitations are reflected e.g. in large errors.

Moreover, the spatial correlation between water sources and major faults in the Ardenne was noted by various authors, but is still debated. Laurent (1987) and Graulich (1969) highlighted the occurrence of a network of major faults in the region, some of them apparently reactivated as recently as during the Quaternary. Graulich (1969) describes that a 250-metre deep coal mine gallery in Limburg (The Netherlands) intercepted a fault with as result a large inflow of thermal water (50 °C) with a high CO₂ content, suggesting that this was acting as a main preferential pathway for groundwaters at depth. Monjoie (1995) noted that pouhons occur preferentially at the intersection of traces of N-S faults with NNE-SSW or NW-SE faults. Geukens (2007) argues that the majority of water sources in Spa can be interpreted as linked to the thrust fault corresponding to the southern border of the Theux Window. Those faults are presumed to be preferential pathways that enable CO₂-rich waters to reach the surface (e.g. Monjoie, 1995). A commonly mentioned mechanism is that, after infiltrating through the bedrocks and acquiring the CO₂ at depth, rapid ascent through the faults or faulted zones would have to happen to allow the conservation of the CO₂ concentration acquired at depth, and avoid the release of CO₂ due to the pressure decrease (e.g. Monjoie, 1995).

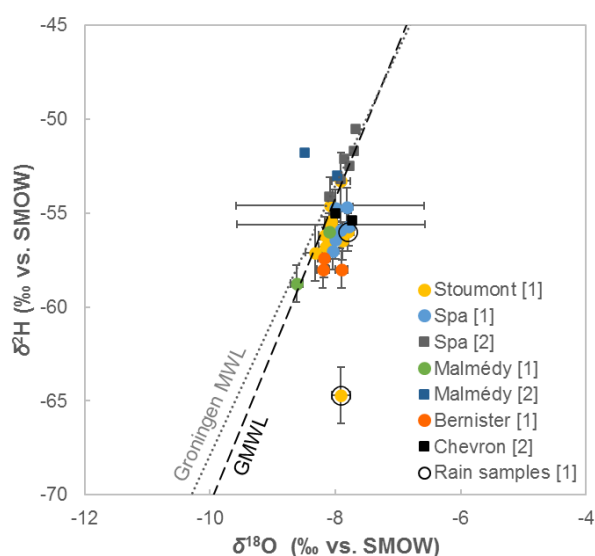


Figure 6. Available $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data for CO₂-rich waters in the Ardenne after [1] Monjoie (1997) and [2] Langguth & Plum (1984). Global Meteoric Water Line (GMWL) after Rozanski et al. (1993). Data for the local meteoric water line (Groningen) after IAEA/WMO (2019).

4.1. Origin and estimated age of groundwaters

Data obtained for H and O isotopes in water samples from the Ardenne (Table 2) are presented in Figure 6. The largest observed variation lies in the $\delta^2\text{H}$ signature, mostly between -58 and -60‰ away from the Standard Mean Ocean Water (SMOW). Results of all water samples are close to the Global Meteoric Water Line (Fig. 6), indicating limited isotopic re-equilibration with the bedrocks. Shifts in $\delta^2\text{H}$ between analysed rainwater and pouhon waters could indicate an isotopic exchange with gas species such as H₂S, inducing an increase of $\delta^2\text{H}$ and/or precipitation of hydrated minerals, combined with high temperature groundwater-rocks interactions, inducing an increase of $\delta^{18}\text{O}$. Nonetheless, the groundwater that will be later enriched in CO₂ is thought to be from meteoric origin. However, it should be noted that one rain sample collected in Stoumont during the spring period presented the most negative $\delta^2\text{H}$ signature around -65‰ vs. SMOW.

For this aspect, a general and widely accepted hydrogeological conceptual model that most authors agree upon is then that meteoric water infiltrates through mostly horizontal Quaternary peat and/or colluvia, Cenozoic residual sands and Cretaceous residual clays on top of the High Fens plateau, and then penetrates the underlying altered Lower Palaeozoic quartzites and slates and percolating through fissures in the unaltered Lower Palaeozoic rocks, the waters meet the CO₂ source at depth.

Data for tritium dating were analysed considering the peak of tritium input to groundwater during testing periods of thermonuclear bombs, the most significant around 1952 and 1963. Although ^3H values are variable (Table 2), most CO₂-rich water sources present clear contribution of post-nuclear water input inferred by relatively high TU (Tritium Units). Dating of HCO₃⁻ and CO₂ of the Pierre le Grand pouhon using the ^{14}C method (Langguth & Plum, 1984) yielded an age of $\leq 24,000$ years. However, the authors emphasize large uncertainties in this estimate due to low ^{14}C concentrations.

Mixing processes are mentioned to explain co-existing presumably older groundwater with TU < 5 (Monjoie, 1997), and the discrepancy between ^{14}C and tritium ages (Langguth & Plum, 1984). Mixing is also inferred from the variation of $\delta^{34}\text{S}$ isotopic signature (Langguth & Plum, 1984).

4.2. Origin of CO₂ in groundwaters

The nature of the CO₂ source at depth in the Ardenne is contentious. Several theories, some of them abandoned, have been proposed and discussed for over the decades. Most of them are supported or discarded based on the measured $\delta^{13}\text{C}$ isotopic signature of groundwaters (Table 2). The hypotheses of the origin of CO₂ and mineralisation processes are summarised as follows.

Atmospheric origin. Given the meteoric origin of groundwaters in the Ardenne (Monjoie, 1995) and considering that atmospheric CO₂ is in equilibrium with rainwater prior to infiltrating the ground, the concentration of CO₂ (equivalent to the concentration of carbonic acid H₂CO₃) in rainwater is

estimated at 0.53 mg/l. Even when we exclude here the bicarbonate equilibria, this estimated concentration is very small when compared to the typical CO₂ contents observed in pouhon waters that range between 0.5 and 3.0 g/l (Table 1), therefore demonstrating atmospheric CO₂ can only be a minor source of the CO₂ in those groundwaters.

Organic origin. The presence of extensive peatlands in the High Fens area in eastern Belgium was suggested as possible organic CO₂ source for the groundwaters (Defosse & Wery, 1975). The decomposition of organic matter by bacterial activity in the first metres of soil produces CO₂ that would lead to a concentration of 15.6 mg/l of H₂CO₃ in water. This value is too low to consider an organic source as the only origin of CO₂ for groundwater.

Furthermore, results obtained from C isotope analyses (Table 2) discard the possibility of CO₂ origin by organic matter decomposition, for which values of δ¹³C are -18‰ and below (e.g. Hoefs, 2009). Moreover, except for the Spa area, peat makes a small proportion of the studied region.

Dissolution and/or metamorphism of carbonate rocks. Dissolution of carbonate rocks by acidified groundwater that would solubilise bicarbonate and carbonate ions is currently one of the most accepted explanations for the origin of the CO₂ in pouhon waters.

Many authors suggest that a first source of rainwater acidification is from organic acids due to infiltration through superficial layers rich in organic matters (peat/colluvium) (Defosse & Wery, 1975; Laurent, 1987; Wollast & Wollast, 1987). Then, in the bedrock, oxidation of pyrite (FeS₂), a common mineral in the local geology (Lamberty et al., 2016), forming sulphuric acid may also increase water acidity. This hypothesis could possibly explain high Fe concentrations in pouhon waters, but is not consistent with the low sulphate contents (<12 mg/l, Table 1) and would assume sufficiently strong oxidising conditions below the water table.

Acidification of groundwater would then be sufficient to dissolve carbonate rocks. However, carbonate rocks are not common in the Stavelot-Venn Massif. Laurent (1987) mentions the presence of calcite and siderite in Cambrian and Ordovician dark slates. Carbonated nodules have also been observed in the basis of the Marteau Formation (Lamberty et al., 2016) that

forms the discordance between Ordovician and Lower Devonian. However, it is unlikely that the dissolution of this finite stock of nodules would suffice to originate high quantities of CO₂ over a prolonged period. The most often cited source of carbonates are therefore the Middle to Upper Devonian and Carboniferous limestones outcropping to the north of the Massif and which could possibly be found also at depth, being overthrust by the older rocks of the Stavelot-Venn Massif (e.g. Fielitz, 1992). A third possible source, for the Malmedy area, is the Permian filling of the Malmedy Graben. The graben is filled by a conglomerate with locally a significant amount of Carboniferous carbonate pebbles and carbonate cement (Lamberty et al., 2017). However, the current level of erosion is probably already close to the roots of this graben, limiting the current depth and volume of its infill.

Results obtained for δ¹³C in CO₂ of pouhon samples (Table 2) show some variations between water sources, but mostly comprised within -8 and -2‰ δ¹³C, with a few samples yielding δ¹³C between -1.96 and 1‰ δ¹³C (Fig. 7). The range between -8 and -5‰ is found both in magmatic-derived CO₂ (e.g. Deines, 1970; Cartigny et al., 1998; Hoefs, 2009) and bulk crustal / atmospheric carbon (e.g. Hoefs, 2009), and this overlap is represented in Figure 7. The isotopically heaviest sources of carbon are marine carbonates (δ¹³C between -4 and 4‰), which configure one of the main carbon reservoirs (Hoefs, 2009). The isotopic signature of some pouhon waters could possibly result from carbon sources from carbonate rocks, or a combination of CO₂ from magmatic and bulk crustal origins.

Other possible source of CO₂, proposed by Laurent (1987), are metamorphic reactions involving kaolinite (Al₂Si₂O₅(OH)₄), quartz (SiO₂), rhodocrosite (MnCO₃) and siderite (FeCO₃) to generate spessartine (Mn₃Al₂Si₃O₁₂) or chloritoid (FeAl₂SiO₅) at estimated P-T conditions of 360–450 °C and 2 kbar. Minerals involved are often observed in the Cambrian and Ordovician rocks forming the Stavelot-Venn Massif (e.g. Schreyer et al., 1992; Theye et al., 1996). These reactions would then lead to the formation of CO₂ at depth. Metamorphic reactions as source of CO₂ were also mentioned by Wollast & Wollast (1987). Depending on the position within the Stavelot-Venn Massif, such conditions were reached during the Caledonian and Variscan metamorphic events and indeed resulted in the

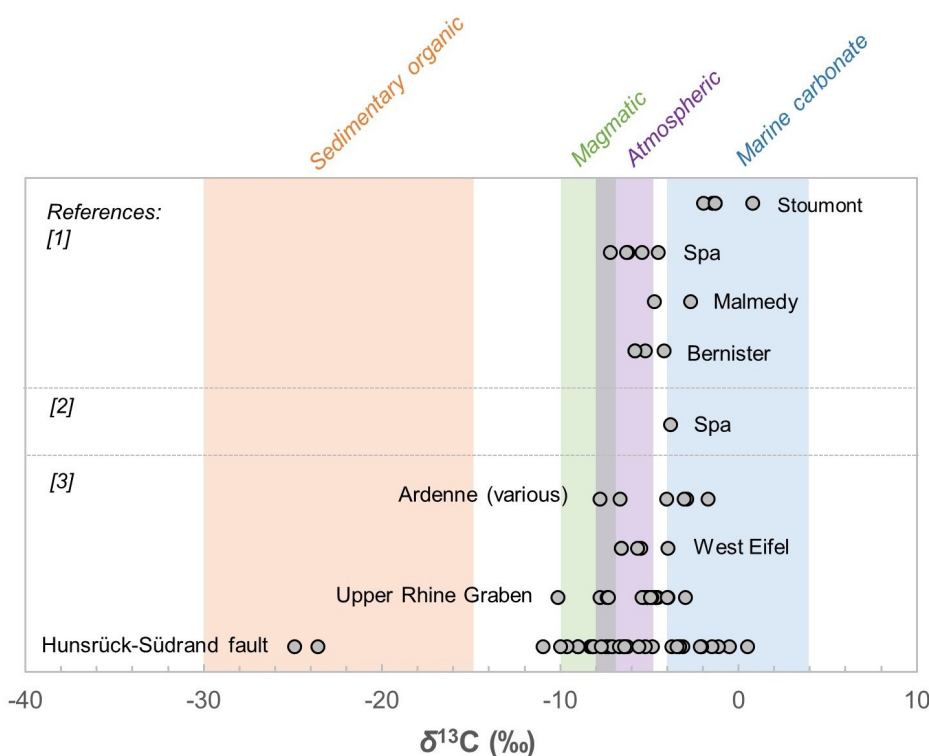


Figure 7. Available δ¹³C data for carbonated waters in the Ardennes (Belgium) and Eifel, Rhine Graben and Rhenish Massif (Germany) from [1] Monjoie (1997), [2] Langguth & Plum (1984) and [3] Griesshaber et al. (1992). Ranges of isotopic signatures for sedimentary organic and marine carbonate carbon (Hoefs, 2009), magmatic (mantle) CO₂ (Deines, 1970) and atmospheric CO₂ (Veizer, 2009) are also presented for comparison—note the overlap between mantle and atmospheric signatures. Error bars are smaller than symbols.

generation of CO₂ rich fluids (Schroyen & Muchez, 2000). It is however doubtful that CO₂ from those events would to-date still be available as fluids, other than trapped in fluid inclusions.

Monjoie (1995) concluded that the positive to weakly negative $\delta^{13}\text{C}$ of CO₂ in groundwaters sampled in Stoumont exclude the hypotheses of magmatic or organic CO₂ (Fig. 7) and can only be explained by dissolution of carbonate rocks at depth as described above. However, most samples from other areas have a range that may represent partial magmatic origin, or bulk crustal / atmospheric origin (Fig. 7). Therefore, identifying a source based solely on carbon isotopes is not possible.

Magmatic origin. The relative proximity of the Stavelot-Venn Massif to the volcanic area of Eifel has driven several authors to suggest a volcanic or juvenile origin of the CO₂ (Van Beneden, 1947; Wollast & Wollast, 1987; Monjoie, 1995, 1997), although little geochemical evidence was provided. Defosse & Wery (1975) are the main authors arguing against a volcanic origin for CO₂. Reasons mentioned include the lack of a negative trend in measured CO₂ concentrations over time, which should be observed since these authors considered the Eifel volcanic activity to be extinct and CO₂ reserves stored in host rocks would be slowly and irreversibly decreased, and the lack of CO₂-rich water occurrences in other areas close to the extinct volcanoes such as in Saint-Vith or Schöneberg areas.

However, recently the Eifel activity has been shown as not extinct, with ongoing migration of magma or magmatic fluids (e.g. Ritter et al., 2001; Schmincke, 2007; Hensch et al., 2019) and therefore a magmatic origin for the CO₂ is probable. Furthermore, a decrease in CO₂ concentrations in groundwaters should first of all be observable in the Eifel area itself, as being closest to the CO₂ source. Griesshaber et al. (1992) reported results for C and He isotope analyses for the Rhenish Massif, including Fays, Spa, Chevron and Harre in the Ardennes, and the Hunsrück-Südrand Fault, besides various locations in the Rhine Graben and Black Forest (Fig. 7). The percentage of mantle He in total dissolved He varies between sources: around 14% for Spa, between 30 and 35% for Chevron, and around 12% for Harre; these should, however, be considered as minimum values, since the authors consider the mantle-derived R/R_a (³He/⁴He of sample normalised to that of the atmosphere) for the Eifel area similar to MORB values, whereas in reality this was

demonstrated to be lower (i.e. R/R_a around 5 according to Bräuer et al., 2013).

The same authors favoured the hypothesis of a mixed origin from mantle and crustal C sources for the CO₂ in the Ardennian pouhons, noticing separate trends in $\delta^{13}\text{C}$ and percentage of mantle He (Fig. 8): a) magmatic He and C and crustal, radiogenic He mixed with organic-derived C, and b) magmatic He and C to radiogenic He mixed with carbonate-derived carbon. The second trend is based on a small number of samples enriched in ¹³C, implying the presence of an additional component of crustal carbon to these groundwaters. Pouhons and springs along the Hunsrück-Südrand Fault to the southeast are isotopically indistinguishable and show similar mixing trends (Fig. 8). Most samples from the Eifel area show a stronger magmatic component (over 35% mantle He).

A magmatic origin for the CO₂ is in agreement with interpretations by other authors for CO₂-rich (Ca-Mg-HCO₃ type) waters in the western part of the Rhenish Massif (e.g. Plum, 1989; May et al., 1996).

4.3. The crustal component: occurrence of carbonate rocks in the Ardennes

Based on isotope data discussed earlier, it is believed that the CO₂ in the pouhons originates at least partially from dissolution of carbonate rocks, which in the Ardennes are predominantly represented by Dinantian and Middle Devonian carbonates. If this model is correct, it therefore implies that carbonate rocks, part of this sequence, occur at depth within the complex fold-and-thrust belt of the Variscan front in the Ardennes.

The structural evolution of the Variscan front zone in Belgium and western Germany has been widely studied over the years (e.g. Le Gall, 1992; von Winterfeld, 1994; Hance et al., 1999, Vanbrabant et al., 1999, 2002). The interpretation of the deformation history can be separated in two contrasting models: in-sequence forward thrust propagation and out-of-sequence thrust propagation. The first is a standard model of thrust systems formed progressively and in order in one direction, based on the understanding of sequences dominated by competent rocks such as the Appalachians, while the second is characterised by unpredictable trajectories in heterogeneous sequences with a lower proportion of competent rocks (McClay,

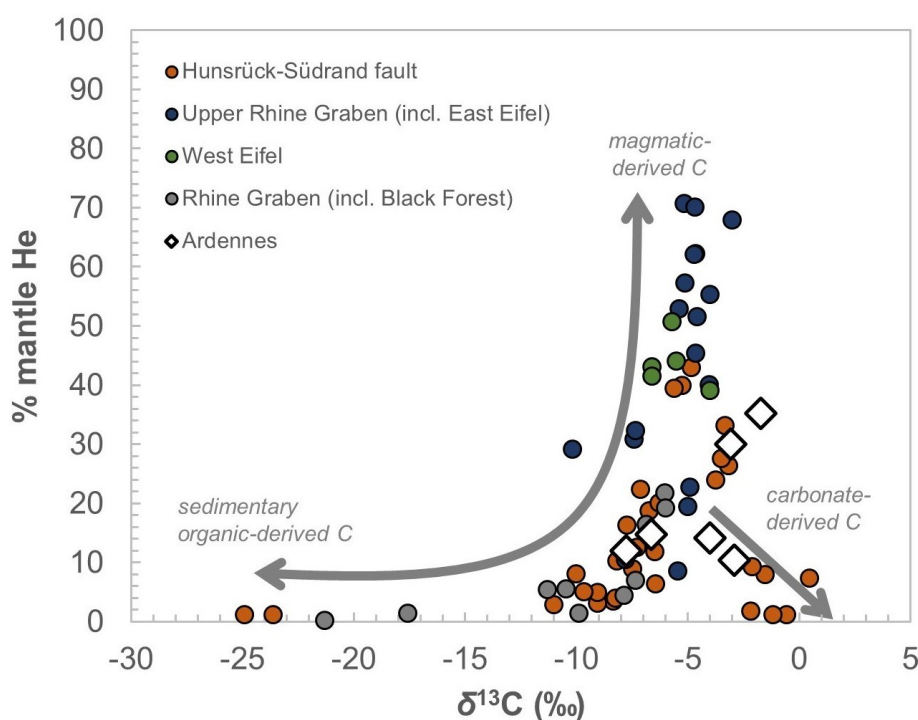


Figure 8. Variation of percentage mantle He and $\delta^{13}\text{C}$ values for CO₂-rich groundwaters in Belgium (Ardennes) and Germany (other data) after Griesshaber et al. (1992). Error bars are smaller than symbols. For location of the Hunsrück-Südrand Fault and Eifel region refer to Fig. 1.

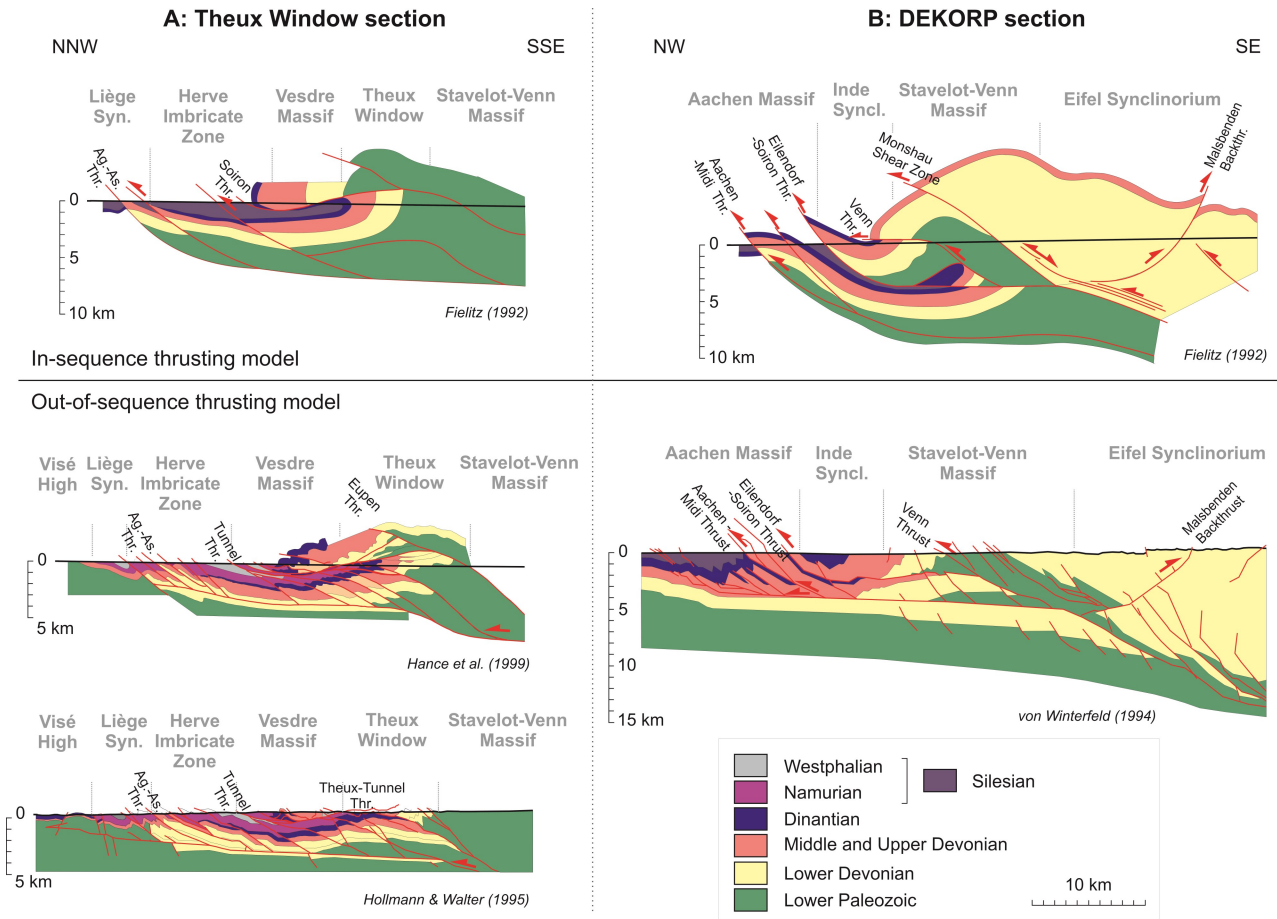


Figure 9. Comparison between geological cross sections demonstrating different interpretations of the geotectonic evolution of eastern Belgium (from Vanbrabant, 2001). Carbonate rocks occur in Dinantian and Middle Devonian sequences. Syn. = Synclinorium; Ag.-As. Thr. = Aguesse-Asse Thrust. Location of cross sections as indicated in Fig. 1.

1991; Hance et al., 1999).

Different interpretations of deformation history in the region have led to distinct interpretations of subsurface geology, as shown by the comparison between geological cross sections (Vanbrabant, 2001; Fig. 9). Of special interest to the discussion around the possible CO₂ source of the pouhons is the extension of carbonate-containing Dinantian and Middle Devonian sequences at depth to the south of the Theux Window in the Stavelot-Venn Massif. Geological interpretations based on out-of-sequence thrusting restrict these sequences to the north of the Massif, particularly in its northwestern part (see different interpretations for section B). Alternatively, interpretations based on in-sequence thrusting allow for carbonates at depths between 2 and 6 km over a larger extension below the Stavelot-Venn Massif (Fig. 9).

It is therefore possible to tie the crustal C component identified in the CO₂ from the pouhons to the dissolution of carbonates occurring below the Stavelot-Venn Massif, especially when considering geotectonic evolution through in-sequence thrusting in the Ardenne. In this case, it is assumed groundwater would currently need to circulate to at least 2 km deep to reach the carbonates. This seems to require a deep network of open fractures or faults facilitating water infiltration and subsequent upward transport.

However, if groundwaters ascend rapidly in order to preserve their high CO₂ content, as assumed in previous studies (e.g. Monjoie, 1995), this does not seem in line with the overall low temperatures (around 10 °C) of the pouhon waters and absence of thermal waters in the region. Moreover, given the unaltered meteoric δ¹⁸O of pouhons, it is inferred that there is no isotope

exchange between infiltrating meteoric water and bedrocks; water-rock reactions, if occurring, are at low temperatures, below 200 °C (Karolytè et al., 2017). Infiltration of meteoric water must therefore be limited to 6 km depth. Additionally, the concentration of Ca ions is relatively low in pouhon waters, mostly between 10–55 mg/l (Table 1). If carbonate rocks have dissolved to contribute for a part of the dissolved CO₂, it is then assumed that Ca ions precipitated prior to water resurfacing.

Given the above, the CO₂-rich waters in the Ardenne are most likely resulting from upward CO₂ flow from deeper levels reaching local flow systems with short underground residence times, similarly to what is observed in similar water types in the Eifel region (e.g. May et al., 1996). This discards the premise that waters need to circulate as deep as where carbonate rocks may occur to acquire the CO₂.

4.4. The mantle component: possible links with Eifel, Germany

The carbon isotopic signature of the pouhons cannot be explained solely by CO₂ originated from carbonate rocks, since a magmatic component was demonstrated (Griesshaber et al., 1992). As mentioned previously, CO₂-rich waters are also common in the neighbouring Eifel area in Germany (Fig. 10). Evidences for mantle upwelling under central Europe include thinning of the lithosphere in regions of Cenozoic volcanism (Babuska & Plomerova, 1992), the identification of a low seismic velocity structure 660 to 2000 km deep on tomographic images (Goes et al., 1999), among others. Mantle plumes possibly fed by this main upwelling system have been identified in the Eifel area (Ritter et al., 2001; Kreemer et al., 2020), and

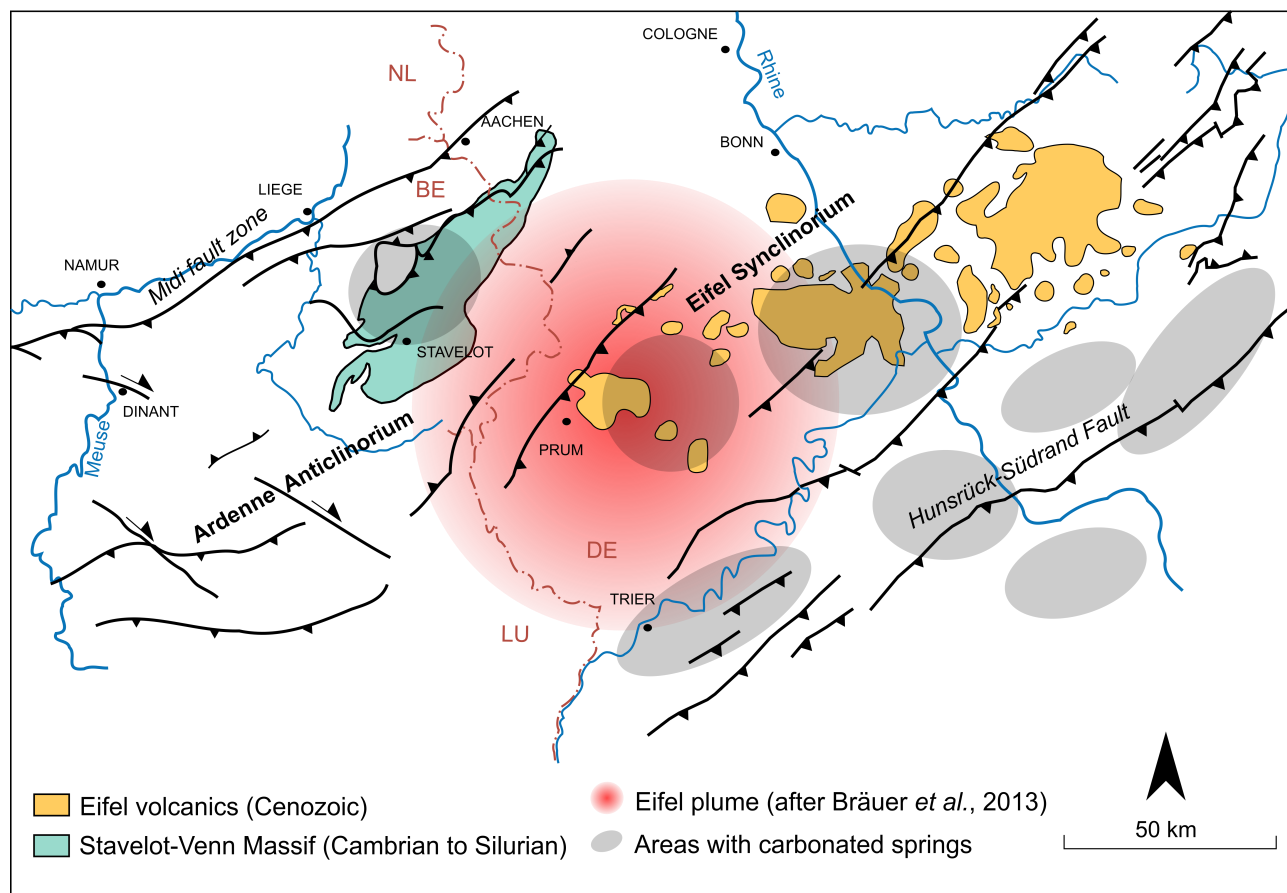


Figure 10. Occurrence of naturally carbonated springs in Belgium and Germany. The shaded red circle shows the presumed extension of the Eifel plume (>50 km depth) at the surface (after Bräuer *et al.*, 2013). Areas of occurrence of CO₂-rich springs in Belgium according to this study, and in Germany after Griesshaber *et al.* (1992), Bräuer *et al.* (2013) and May *et al.* (1996). Full geological setting in Fig. 1.

in other areas such as the Massif Central (France) (Granet *et al.*, 1995). The existence of a plume is, however, not a consensus in the scientific community (e.g. Meier *et al.*, 2016).

Contribution from the mantle in degassing locations (springs and mofettes) is well established in the area (e.g. Aeschbach-Hertig *et al.*, 1996; Schmincke, 2007). Most studies are based on He isotopes given the markedly different isotopic signatures between their three main reservoirs, atmosphere, Earth's crust and mantle (White, 2015).

Regional studies were carried out by Bräuer *et al.* (2004, 2013, 2017), obtaining $\delta^{13}\text{C}$ and $^3\text{He}/^4\text{He}$ ratios for CO₂-rich springs and mofettes in Cenozoic volcanic areas in the Eifel, as well as around the Massif Central and the Eger Rift in Czech Republic. Isotopic signatures in gas samples of the three areas overlap the characteristic range of the subcontinental lithospheric mantle and the authors suggest that CO₂ upflows from the degassing magmatic reservoirs through deep faults (Bräuer *et al.*, 2013). According to the same authors, these magmatic reservoirs presumably fed the intra-continental Eifel volcanism in the past.

The contribution from mantle CO₂ identified in the Belgian pouhons (Griesshaber *et al.*, 1992) could possibly be linked to the supposed extension of the Eifel plume area (after Bräuer *et al.*, 2013), which is occurring at depths between 50 and 410 km (Ritter *et al.*, 2001; Fig. 10). The mantle component is presumably dominantly gaseous, since coupled H-O isotopic signature for pouhons does not show large deviations from the GMWL towards magmatic fluid signature. This implies that the contribution of CO₂ from the mantle either a) diffuses from the plume at 50 km depth or deeper and is transported upwards to the depth reached by percolating groundwater of meteoric origin, and/or b) diffuses and is transported upwards from shallower magmatic reservoirs still to be identified in the lower

crust below the Ardennes. Based on CO₂ flux density in the Eifel, it is likely that both mechanisms happen simultaneously (May, 2002).

5. Towards an integrated model

A mixed crustal-mantle origin for the CO₂ in the Ardennian pouhons has been suggested by previous authors. This is also considered by us as the most plausible at present. In this respect, the processes that form CO₂-rich pouhons waters are schematically described and summarised in Figure 11. Supporting evidence compiled and discussed in the present study can be summarised as follows:

- Meteoric water infiltrates in the areas of higher altitude and travels through geological layers with relatively low rock-water interactions until around 400 metres depth ('demineralisation limit' of Monjoie, 1992), and with different bedrock lithologies beyond that. There is no isotope exchange between infiltrating meteoric water and bedrocks along shallower and deeper pathways, since the ^2H and ^{18}O isotopic signature is largely unchanged (path D in Fig. 11).
- Infiltrating deeper, water acquires a high CO₂ content. This is thought to have two main contributing components:
 - The crustal component of the CO₂ could be generated through dissolution of carbonate rocks at depth possibly enhanced by water acidification by pyrite oxidation.
 - The magmatic component of the CO₂ could be associated with the degassing of the Eifel plume, with the top located at 50 km depth, or from an unknown shallower magmatic reservoir.
- CO₂ originating from dissolution of carbonate rocks implies that water circulates to at least 2 km depth, based on the assumed possible location of carbonate rocks within Dinantian and Middle Devonian sequences according to the

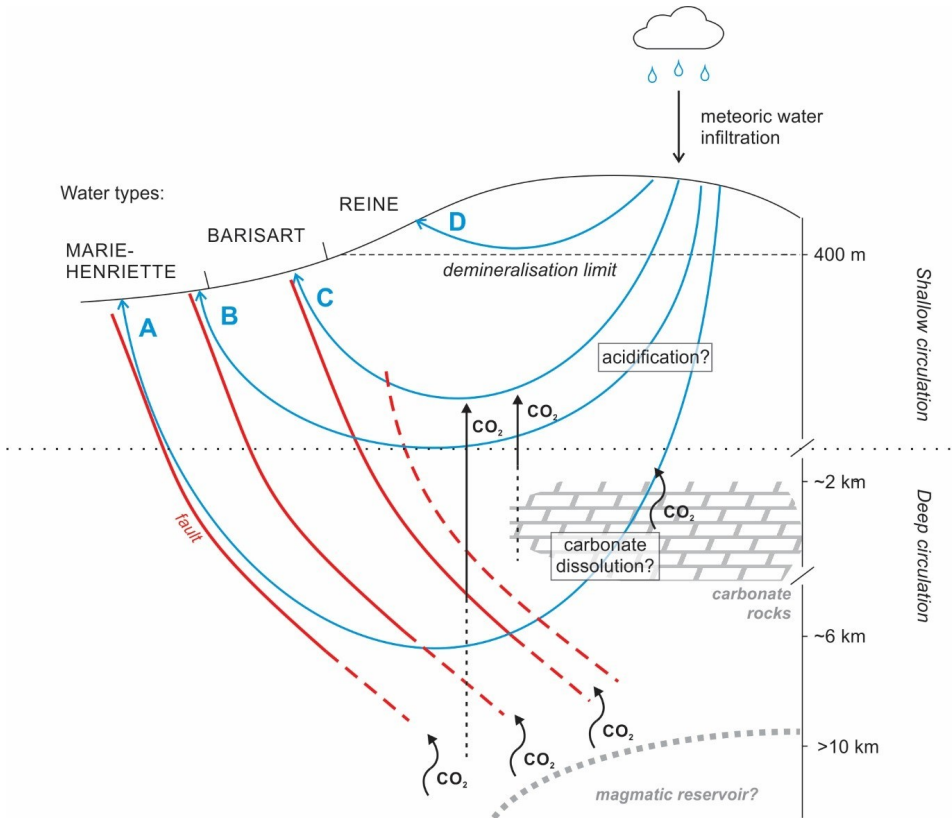


Figure 11. Schematic cross section in the Spa region. Uppermost part modified from Goemaere et al. (2016) and Monjoie (1995). Possible deep circulation (A) and shallow circulation (B) paths for pouhon waters are represented. C and D represent possible water circulation paths for Barisart and Reine waters, respectively. Presence of carbonate rocks at depth requires in-sequence Variscan thrusting.

structural cross sections of the Stavelot-Venn Massif that assume in-sequence thrusting (Fig. 9). Structural models based on out-of-sequence thrusting are not able to explain the occurrence of carbonate rocks under the Stavelot-Venn Massif. Deeper circulation is unlikely, given the cold temperature of the pouhon waters when reaching the surface.

- Most likely, the meteoric water does not infiltrate as deep, which would be in line with relatively short estimated residence times (up to 60 years) and low temperatures of pouhons. This implies that magmatic CO_2 could be transported upwards to meet infiltrating groundwaters at shallower depths. The presence of mofettes in the region, although much rarer than pouhons, could be evidence of such upward transport of CO_2 . When the magmatic fluid along its path would encounter carbonate rocks, partial to full isotopic exchange would explain the mixed magmatic-carbonate signature.

6. Conclusions

Iron-rich cold CO_2 -rich mineral water springs called pouhons occur in East Belgium. They represent an opportunity to investigate and understand geological processes involving CO_2 in the subsurface. Although for over a century various studies have focussed on these occurrences and models for their origin, there have been no recent attempts to integrate different models and data available. In this study, we have compiled physico-chemical parameters and isotopic compositions of Belgian pouhons, reviewed the possible sources of CO_2 and processes that may lead to formation of CO_2 -rich waters.

Most pouhon waters are of the calcium bicarbonate type (~310 mg/l HCO_3^- on average), with Fe (~15 mg/l), Ca (~43 mg/l on average), Mg (~27 mg/l) and Na (29 mg/l). The pouhons from the Stoumont region, occurring where Devonian bedrocks outcrop, are geochemically distinguishable from the pouhons from the Spa region, occurring in the area where Cambrian and Ordovician bedrocks outcrop. While the Spa groundwaters have no dominant cation type, the Stoumont groundwaters vary between dominant Ca, Mg or Na+K.

Based on previous studies, a primarily meteoric origin of the pouhon waters is evidenced by ^2H and ^{18}O isotopic signature with little deviation from the GMWL. The $\delta^{13}\text{C}$ ratios for different sources are between +0.8 and -7.76‰. Signatures of the pouhon waters overlap with C sourced from carbonate rocks ($\delta^{13}\text{C}$ between -4 and 4‰) and mantle C ($\delta^{13}\text{C}$ between -8 and around -5‰). Moreover, the percentage of mantle He in total dissolved He varies between sources, with minimum estimates of around 14% for Spa, between 30 and 35% for Chevron, and around 12% for Harre. This suggests that CO_2 in pouhons results from a combination of CO_2 from magmatic and crustal origins.

Carbonate rocks in the Ardenne that might represent the crustal component in CO_2 could be represented by Dinantian and Middle Devonian carbonates. These rocks possibly occur at depths of at least 2 km, based on in-sequence geological cross sections of the Stavelot-Venn Massif. Liberation of CO_2 from these rocks could be achieved through dissolution by acidified water. However, this is in contradiction with the more generally accepted out-of-sequence thrust models.

The magmatic component in dissolved CO_2 could be associated with the degassing of the Eifel plume, with top located at depths over 50 km, or from an unknown shallower magmatic reservoir. The magmatic fluid can migrate to shallower levels, changing its isotopic composition when encountering carbonate rocks, before mixing with groundwater. Deeper groundwater circulation is less likely because elevated temperatures would result in isotopic exchange and deviation from a meteoric isotopic signature.

The upward transport of CO_2 -rich water is thought to be facilitated by pathways formed by faults in the region. Overall low temperatures of the pouhons (around 10 °C) refute the generally accepted idea that the water ascent is rapid. Water circulation restricted to shallower depths is in line with estimated residence times of less than 60 years. This shallow circulation would imply that magmatic CO_2 is transported upwards to meet groundwaters at depths that may be less than a

few km. The occurrence of mofettes evidences such transport is happening.

Although this only partly solves the precise origin of the CO₂ in pouhon waters, we consider this review study provides a much-needed base for future investigations bringing together previously unrelated data and interpretations. Moreover, our model is a step forward from previous studies and contributes to the understanding of the complex subsurface cycle that involve water infiltration, CO₂ assimilation and water resurfacing happening in east Belgium. Future work aims to provide new results on the isotope geochemistry of pouhon waters to determine the origin of CO₂ with greater detail.

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