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Carbogaseous spring waters, coldwater geysers and dry CO_2 exhalations in the tectonic window of the Lower Engadine Valley, Switzerland

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Key words: Lower Engadine, Swiss Alps, Scuol-Tarasp, tectonic window, carbon dioxide (CO_2), radon, carbogaseous springs, coldwater geyser, dry mofette

ABSTRACT

In the region of Scuol-Tarasp in the Lower Engadine Valley in the Eastern Swiss Alps, there are a variety of phenomena related to a geogenetic CO_2 production, including carbogaseous mineral springs, previously active coldwater geysers and dry gas exhalations from the ground via mofettes. Previous isotopic studies revealed that the CO_2 originates from the metamorphic decomposition of carbonate rocks in the crust. This paper presents an inventory of the springs, geysers and mofettes, and proposes a conceptual model on the regional gas and water circulation. Based on hydrochemical criteria, it was possible to identify six main groups of spring waters, three of which are carbogaseous mineral springs. Most of the carbogaseous springs and gas exhalations are bound to the Bündnerschiefer fractured aquifer. The different water types originate from mixing of groundwater and highly mineralised carbogaseous fluids from depth. Near-surface degassing of CO_2 from the fluid phase creates the dry gas exhalations. CO_2 and radon measurements in 178 soil boreholes suggest that the gas exhalations occur at a limited number of point-like anomalies, and there is no evidence for regionally important diffuse CO_2 discharges from the ground.

RESUMAZIUN

En la regiun da Scuol-Tarasp en l'Engiadina bassa, en l'orientala part dallas alps svizras cumparan antgins fenomens, che coreleschan cun la producziun da CO_2 en la profunditad. Ei dat fontaunas mineralas carbonicas, antruras geisirs activs d'aua freida e sortidas da gas schetg da mofettas. Anteriuras retschercas d'isotops han mussau, ch'il CO_2 deriva dalla decumposiziun metamorfosa da caltschina en la crusta dalla tiara. Questa lavur presenta in inventari da fontaunas, geisirs e moffettas e fa ina proposta per in model concepziunal per la circulaziun regiunala da gas ed aua. Sin fundament da criteris hidrochemics han sis gruppas da fontaunas saviu vegni identificadas, dallas qualas treis gruppas cumprendan fontaunas mineralas carbonicas. Las pliras fontaunas carbonicas neschan egl aquifer dil sfendaglius platter Grischun. Ils differents tips d'aua da fontauna resultan entras la mischeida da liquidas profundas carbonicas fetg mineralisadas cun auas sutterranas giuvnas. Degasaziun dil CO_2 ord la fasa d'aua damaneivel da la surfatscha meina tier l'exhalaziun da gas. Mesiraziuns da CO_2 e radon en 178 ruosnas indicheschan, che l'exhalaziun da gas serestrenscha sin paucas anomalias punctualas. Ei dat negins indezis per ina impurtonta sortida regiunala da CO_2.

1 Introduction

1.1 Significance and origin of geogenetic CO_2

Carbogaseous springs and CO_2 exhalations from the ground are manifestations of geogenetic gas production at depth. Such phenomena are of socio-economic interest, as carbogaseous waters are often used as mineral water sources, as well as for medicinal cures and spas (Vrba 1996). At the same time, dry and wet CO_2 exhalations provide insight into geochemical processes in the earth crust and mantle (e.g. Weise et al. 2001; Diliberto et al. 2002). As CO_2 is the most prominent greenhouse gas, a better understanding of its geogenetic sources and sinks is also relevant for climate change studies (Nesbitt et al. 1995; Kerrick 2001).

CO_2 discharges are often linked to areas of seismic activity and high heat flow. The world distribution of both dry and wet CO_2 discharges shows the highest densities in the Western US, Central Europe and Asia Minor (Barnes et al. 1978). Geogenetic CO_2 originates from three different sources: transformation of organic matter during oil, gas and coal formation (Battani et al. 2000; Butala et al. 2000), metamorphism of carbonatic rocks in the crust (Kerrick & Caldeira 1998; Derry et al. 2002), or degassing of the mantle. CO_2 exhalations are particularly frequent in volcanic and post-volcanic areas, where the CO_2 usually comes from the mantle but may also result from contact metamorphism of carbonate rocks (Giammanco et al. 1995; Seward & Kerrick 1996; Granieri et al. 2003; Werner & Brantley 2003). Carbon stable isotopes are helpful in deter-

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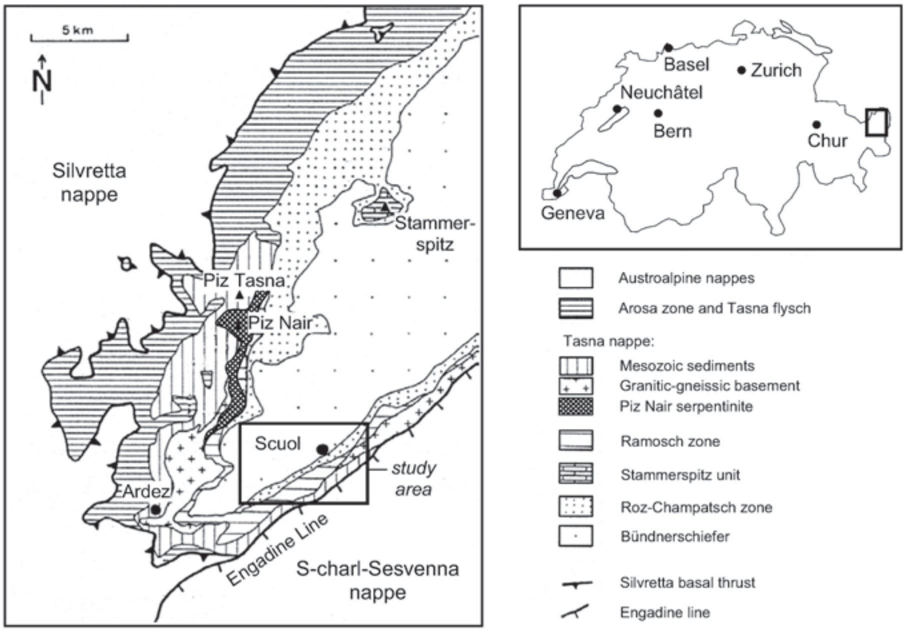

Fig. 1. Geological sketch of the Lower Engadine tectonic window (after Florineth & Froitzheim 1994).

mining the sources of CO_2, especially when there is no clear geological evidence (Sato et al. 2002). Regional surveys of the $^3He/^4He$ isotopic ratio make it possible to distinguish gas emissions of crustal and mantle origin (Marty et al. 1992).

1.2 A short history of the carbogaseous mineral springs of Scuol-Tarasp

The carbogaseous mineral springs of Scuol-Tarasp in the Lower Engadine Valley are famous for their particular characteristics for a long time. Remnants of prehistoric settlements were found near the springs. The Romans probably also used the water. The first historic document describing the springs' use dates from 1561, and the first springs were captured in 1841. Since then, they have been used for mineral water drinking cures (Stecher 1990). The so-called 'Trinkhalle' (drinking hall) was built in 1876 at the southern waterside of the River Inn. The two highest mineralised springs, Luzius and Emerita, can be degusted inside this hall. The Roman-Irish baths of Scuol use the waters from four intermediately mineralised springs. Today, most of the carbogaseous springs in the region are captured but only a few of them (Carola, Luzius, Emerita, Bonifazius, Sotsass) are used for small-scale mineral water production, i.e. some thousands of bottles per year, mainly for local hotels (pers. communic. R. Zollinger).

In 1930/31, two 100-m-deep wells were drilled on the northern waterside of the River Inn near Tarasp in order to gain additional mineral water. Unexpectedly, the boreholes showed periodical gas and water eruptions with up to 10-m-high water fountains. These 'coldwater geysers' became tourist attractions but could not be used for the mineral water production. Today, both geysers are in a bad state. Besides springs and geysers, dry CO_2 exhalations can be observed on the northern slope of the valley near Scuol. In analogy to similar phenomena in volcanic areas, these gas outlet points are referred to as 'mofettes'.

Since the 16th century, various scientists investigated the mineral springs. Nussberger (1914) compiled the results of early hydrochemical analyses; more detailed data were collected and published by Högl (1980). Nussberger (1899), Tarnuzzer & Grubenmann (1909) and Hartmann (1927) proposed different geological hypotheses of the origin of the carbogaseous water. In the late 1980s, detailed hydrochemical, isotopic and geophysical investigations made it possible to classify the different mineral water types, to identify the origin of the CO_2 and to propose a first conceptual model of the regional groundwater flow (Wexsteen & Müller 1987; Wexsteen 1988; Wexsteen et al. 1988). However, many questions still remained unresolved. The majority of the cited studies focused on the most prominent mineral springs, while small and remote mineral springs, as well as freshwater springs, were not sampled. Furthermore, the spatial extent of the CO_2 exhalations from the ground was not known, and their relation to the carbogaseous springs was thus not clear.

1.3 Framework and objectives of the study

The Centre of Hydrogeology (CHYN) launched two successive studies within the framework of postgraduate diplomas (Bissig 1997; Mayoraz 2004). Their main goals were:

- Providing an inventory and characterisation of the freshwater springs, carbogaseous mineral springs, coldwater geysers and mofettes;

Tab. 1. Hydrogeological units in the study area. [1]The springs were attributed to the main hydrogeological unit forming their catchment basin; the numbers in brackets refer to the number of springs that discharge via unconsolidated sediments. * No detailed investigations were made for this study.

	Hydrogeological unit	Lithology	Aquifer type	Number of springs [1]
1	Bündnerschiefer formation	Shale, sandy and calcareous phyllites	Fractured aquifer	29 (12) +2 drillings
2	Roz-Champatsch and Ramosch zone	Granite, gneiss, ophiolite (serpentinite, metagabbro, metabasalt), flysch type sedimentary rocks	Low-permeability fractured rocks	3 (1) + 1 drilling
3	Tasna nappe – crystalline basement	Granite, gneiss	Low-permeability fractured rocks *	2 (2)
4	Tasna nappe – sedimentary cover	Quartzite, limestone, calcareous slate	Partly fractured aquifer; partly karstified aquifer*	3
5	Silvretta nappe – crystalline basement	Gneiss	Low-permeability fractured rocks *	–
6	Silvretta nappe – sedimentary cover	Limestone, dolomite, carbonate breccia	Karst aquifer*	2 (1)
7	Unconsolidated sediments	Sand and gravel	Porous aquifer	(16)

- Proposing an improved conceptual model of regional CO_2 production and water circulation, to better understand both the springs and the CO_2 exhalations;
- Determining whether or not there is a regional CO_2 anomaly in the area, i.e. if the CO_2 exhalations are restricted to a limited number of mofettes or fault zones or if important quantities of this gas escape diffusely through the soil on larger surfaces;
- Identifying possible locations to drill a new coldwater geyser.

The investigation program included the evaluation of data and information from the literature, geological and hydrogeological mapping, measurement of physicochemical parameters at springs, water sampling and laboratory analyses for major and trace elements, and, above all, CO_2 and radon gas measurements, both in the water and soil gas.

2 Description of the study area and origin of the CO_2

2.1 Location, topography and climate

The villages of Scuol and Tarasp are located in the Lower Engadine Valley, the valley of the River Inn, in the Canton of Grisons (GR) in the eastern Swiss Alps. The river flows in a WSW-ENE direction and is at an altitude of 1165 m near Scuol; the highest summits on both sides of the valley exceed 3000 m and are scarcely glaciated. The valley is asymmetric with much steeper slopes on the southern (right) than on the northern (left) side. The Engadine Valley is characterised by a relatively dry and cool alpine climate. The average annual precipitation at Scuol is 795 mm, much less than in most other parts of the Alps, and the average annual air temperature is 5 °C.

2.2 Geological framework

In the Lower Engadine Valley, the Austroalpine nappes are regionally eroded so that the Penninic nappes are exposed, forming a large tectonic window (Fig. 1). The Engadine Window is 54 km long (SW-NE) and up to 17 km wide (SE-NW). The highest tectonic units are the Upper Austroalpine S-charl-Sesvenna and Silvretta nappes, which consist of a crystalline basement with parautochthonous sedimentary cover. These two nappes form the framework of the tectonic window. The Lower Penninic Bündnerschiefer (*schistes lustrés*) is the lowest tectonic unit and outcrops inside the window. The formation consists of metamorphosed, dominantly pelagic rocks, including grey and black shale, as well as sandy and calcareous phyllites. The Lower Engadine Mélange between the Penninic and Austroalpine nappes includes the Roz-Champatsch zone, the Tasna nappe with its Mesozoic sediments and crystalline basement, and the ophiolites and crystalline basement of the Ramosch zone (Cadisch et al. 1968; Florineth & Froitzheim 1994).

The structural reason for the tectonic window is an important regional uplift, which mainly occurred along a major fault at the SE margin of the window, the Engadine Line. This fault was active in the late Tertiary, after the main phase of alpine collision. It is a left-lateral extensional strike-slip fault (transtension) with a vertical displacement of about 6 km (Schmid & Froitzheim 1993). Regional uplift also formed a huge anticlinorium, which cumulates in the centre of the window. Its axis trends SW-NE and coincides with the axis of the tectonic window. In the area of Scuol-Tarasp, the anticlinorium is represented by an anticline; most of the carbogaseous mineral springs are located in this zone.

2.3 Hydrogeological framework

Based on lithological and hydrological field observations, Bissig (1997) defined seven major hydrogeological units in the study area (Tab. 1).

Most of the carbogaseous mineral springs discharge from the Bündnerschiefer fractured aquifer (unit 1), either directly or indirectly via overlying sediments (unit 7). In order to better characterise regional groundwater flow, Bissig (1997) carried out a fracturing study, which focused on the main aquifer but

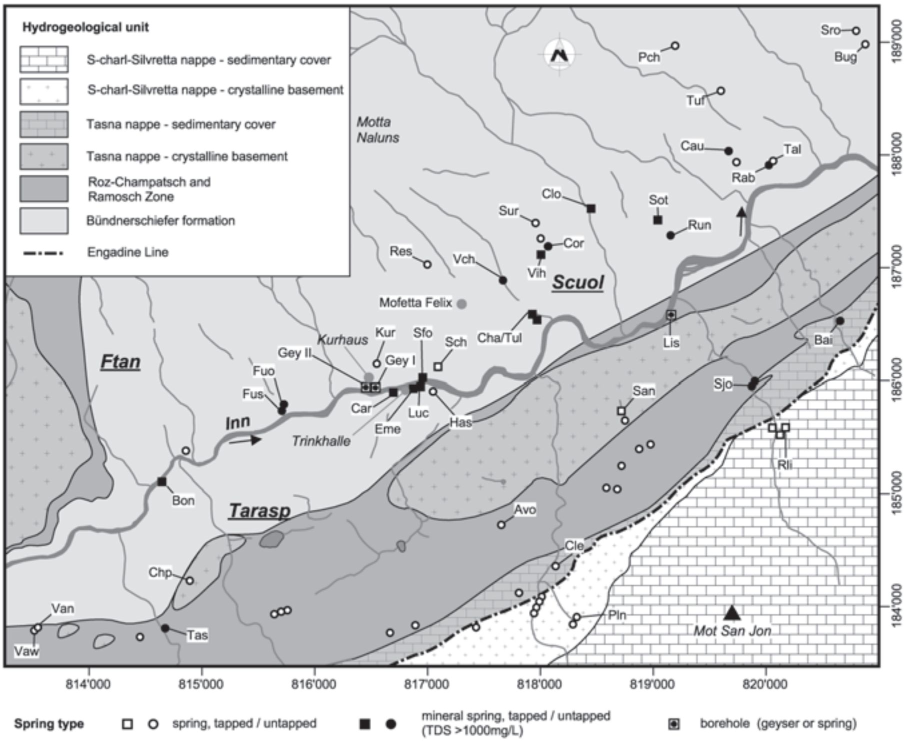

Fig. 2. Map of the springs in the region of Scuol-Tarasp. The location of the study area is shown in Fig. 1 and the shorthand symbols are defined in Tab. 2. The numbers at the margins represent the Swiss Topographic Grid (unit: metres).

also included a gneiss outcrop. It was possible to identify 8 families of joints, including release and shear joints, and 3 families of faults. Although there are no precise data on hydraulic fracture properties, such as aperture, connectivity or infillings, it was possible to demonstrate the importance of the joint pattern for groundwater flow and surface hydrology. Both the river network and geomorphological lineaments reflect the joint pattern. Mineral springs are often located at the intersection of such lines.

2.4 Origin of the CO2

Wexsteen et al. (1988) analysed the gas in selected mofettes and carbogaseous springs near Scuol-Tarasp in order to determine its origin. The gas is composed of CO_2 (> 93 %), N_2 (5–7 %), He (5 ppm) and traces of H_2S (1 ppm). The gas composition in the spring waters and mofettes is similar, suggesting that it has the same source. The $^{13}C/^{12}C$ and $^{3}He/^{4}He$ ratios indicate that the CO_2 originates from metamorphic reactions in the crust, while a mantle source can be excluded. During thermo-metamorphosis, CO_2 forms at 300–400 °C by the decomposition of carbonate minerals (Bucher & Frey 2002). For example, dolomite reacts with quartz to form talc, calcite and carbon dioxide:

$$3\,CaMg(CO_3)_2 + 4\,SiO_2 + H_2O = Mg_3(OH)_2Si_4O_{10} + 3\,CaCO_3 + 3\,CO_2$$

While calcite reacts with quartz to form wollastonite and carbon dioxide:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

3 Methods

3.1 Hydrochemical analyses

The water temperature (T), electrical conductivity (EC), pH and oxygen content (O_2) were measured at the springs using standard field instruments. The discharge (Q) was quantified using receptacles and a stopwatch, or estimated where this was not possible (Bissig 1997). Water samples were taken at all springs. The Cantonal Laboratory of Grisons measured the major water constituents using ion chromatography (DIONEX DX-120). The trace elements were analysed at the Institute of Geology and Hydrogeology (IGH) at the University of Neuchâtel by means of ICP-MS (Mayoraz 2004).

3.2 CO_2 and radon measurements in water

Bissig (1997) used a simple field method to estimate the CO_2 content in the spring waters, the ‘Karat’ tube. Mayoraz (2004) reinvestigated most of the spring waters in the study area. At each spring, two samples, one for CO_2 and one for radon, were taken in 20 mL Teflon lined silicone septum vials with no air bubbles left. The samples were analysed at the Environmental Radioactivity Laboratory at the CHYN within one week.

For the CO_2 measurement, air is bubbled in a closed circuit for 3 min at 200 mL/min through the sample. The CO_2 concentration in the air circuit is then measured by IR absorption (Texas Instruments CO_2 Sensor 9GS-1-5-ZC). The initial con-

Tab. 2. Overview of the springs and their characteristics in the region of Scuol-Tarasp.

Group	Water type	Sampling Point name	symbol	Altitude [m]	TDS [mg/L]	Q [L/s]	T [°C]	Data period for TDS, Q, T	CO_2 [1] [mg/L]	Radon [1] [Bq/L]	Remarks	Hydro. unit *see Tab. 1*
1	$Na\text{-}HCO_3\text{-}Cl$	Luzius	Luc	1182	16'100-17'700	0.05-0.10	5.2-6.7	1900-1997	2500-2600	0.8		1
		Emerita	Eme	1182	15'500-16'300	0.02-0.07	5.4-7.6	1900-1997	2500	0.6		
	$Na\text{-}Ca\text{-}HCO_3\text{-}Cl$	Sfondraz	Sfo	1185	7'340-9'270	0.04-0.10	7.2-8.7	1958-1997	2500	0.7		
		Geyser I	Gey I	1189	7'550-7'620	m.n.p.	7.1-7.8	1997	2400	n.m.	borehole	
	$Na\text{-}HCO_3$	Geyser II	Gey II	1191	4'310	m.n.p.	8.2	1945	2200 [2]	n.m.	borehole	
2	$Ca\text{-}Na\text{-}HCO_3$	Bonifazius	Bon	1210	5'620-5'820	0.05-0.17	5.2-6.9	1899-1997	2900	0.5		1
	$Ca\text{-}HCO_3$	Untere Fuschana	Fus	1205	3'990-4'370	0.02-0.03	5.8-9.1	1902-1997	2200	0.4		
		Obere Fuschana	Fuo	1260	2'310-2'570	0.01	9.9	1902/1997	1200	n.m.		
	$Ca\text{-}HCO_3\text{-}SO_4$	Carola	Car	1190	1'230-2'910	m.n.p.	5.0-8.4	1958-1997	2200	3.6		1/7
3	$Ca\text{-}HCO_3$	Runa	Run	1200	3'090	0.1	11.5	1997	2100	n.m.		1
		Vih	Vih	1320	2'040-2'240	0.05-0.7	7.5-8.7	1853-1997	2300	1		
		Sotsass	Sot	1285	2'260-2'510	0.06-0.55	8.8-10.0	1951-1997	2300	9.6		
		Rablönch	Rab	1185	2095	n.m.	9.0-10.2	2003	1910	10.5		
		Clozza	Clo	1290	1'410-1'670	m.n.p.	n.m.	1951-1997	2200	1.6		
		Chauennas	Cau	1335	1'470	0.2-0.5	n.m.	1997/2003	190-620	7.4		
		Corgnuns	Cor	1315	1'320	0.3-0.55	10.6-12.3	1997/2003	180-220	0.9		
		Val Chalzina oben	Vch	1315	1'340	0.06	6.8	1997	2300	n.m.		
		Chalzina	Cha	1225	1'110	1.1	8.8	1997	890	16.4		1/7
		Tulai	Tul	1230	1'015	0.8	9.0	1997	1300	30.4		
		Sur Vih	Sur	1370	700	0.04	11.8	1997	- [3]	n.m.		
4	$Ca\text{-}Mg\text{-}HCO_3$	S-Chürdüna	Sch	1235	830	0.5-0.7	8.0	1997	350	n.m.		1/7
		Hangquelle Schweizerhof	Has	1220	535	0.05-0.2	7.8-8.4	1997/2003	26	9.9		
		Bugl da Fontana	Bug	1380	625	0.7	9.1	2003	35	28.5		1
		Stron	Sro	1420	585	0.17	8.4	2003	53	1.1		
		Godda Rès	Res	1510	485	0.02-0.04	5.9-8.7	2003	20	1		1/7
		Tuffarola	Tuf	1510	415	0.3-0.5	7.9-8.4	2003	22	3.2		
		Plan de Chavas	Pch	1670	410	0.5	7.0-8.0	2003	24	4.7		
		Talur	Tal	1195	590	0.1-0.3	8.9-9.4	2003	58	23.8		
		Chaposch	Chp	1430	465	0.01	5.9-8.5	2003	35	5.4		3/7
		Avrona	Avo	1490	375	0.5	4.1	2003	14	1		2/7
5	$Ca\text{-}Mg\text{-}SO_4\text{-}HCO_3$	San Jon dadaint	Sjo	1470	1'310-2'090	0.06-0.3	5.2-7.1	1997/2003	33	13.9		4
		Rote Lischana, Cotschna	Rli	1555	975	5	6.4	1997	- [3]	6.6		6
	$Ca\text{-}Mg\text{-}SO_4$	Bain Crotsch	Bai	1470	1'670	0.5	4.6-5.8	2003	26	1.5		4
	$Ca\text{-}SO_4\text{-}HCO_3$	Vallatscha W	Vaw	1440	800	0.15-0.25	5.0-7.2	2003	22	33.4		1/2
6	$Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$	San Jon	San	1420	560	0.07-0.5	4.9-10.8	2003	12	1		3/7
		Plan de Funtanas	Pln	1460	255	15	4.9-5.0	1997/2003	- [3]	n.m.	karst spring	6/7(5)
		Clemiga dadaint	Cle	1350	640	0.2	4.8	1997	24	n.m.		4
		Kurhausquelle	Kur	1195	520	0.3	10.9	1997	- [3]	n.m.		1/7
		Vallatscha N	Van	1440	395	0.03-0.05	5.1-8.6	2003	14	2.3		1/2
7	$Na\text{-}Mg\text{-}HCO_3\text{-}SO_4$	Lischana	Lis	1164	7'790-9'320	n.m.	7.1-7.9	1984-1997	2300	6.1	borehole	2
8	$Ca\text{-}Na\text{-}CO_3\text{-}Cl\text{-}SO_4$	Tarasper Schwefelquelle	Tas	1496	300	0.1	6.0	1997	- [3]	4.0	pH 11-12	2

[1] measurements of CO_2 1997/2003 and Radon 2002/2003 [2] data from 1945 [3] not detectable with method "Karat" m.n.p. = measurement not possible n.m. = no measurement

centration in the sample is calculated using the known air/water volume ratio and the Bunsen coefficient. Measurements are reproducible within ± 2 mg/L. Calibration uncertainty of the sensor is estimated to be ± 20 %.

Radon (^{222}Rn) is measured by liquid scintillation counting: 10 mL of the water sample are added to 10 mL scintillator (Maxilight, Perkin Elmer). After a 3h delay, 7 mL of the scintillator are extracted and counted for 1000 s (Triathler, Hidex Oy, Finland, in alpha/beta separation mode). The detection limit is 0.3 Bq/L and the calibration uncertainty is < 5 %.

3.3 CO_2 and radon measurements in the soil gas

Mayoraz (2004) measured the CO_2 and radon concentration in the soil gas using a procedure proposed by Surbeck (1993): A hole is drilled manually to a depth of 30–50 cm using a 7 cm soil auger. A probe with an inflatable packer is introduced and fixed by pumping up the packer. The soil gas is sucked for 5 min at 1 L/min. The gas then passes through a ^{222}Rn monitor (RAD7, Durridge, Bedford, MA, batch mode) and a CO_2 detector (Texas Instruments CO2 Sensor 9GS-1-5-ZC). The CO_2 detector has a full range of 25 vol.%. Readings are reproducible within ± 0.2 vol.% and calibration uncertainty is estimated to be ± 20 % (1-sigma) for the full range. At typical values of several kBq/m^3, the radon monitor has a counting statistics uncertainty of ± 10 % (1-sigma). The calibration uncertainty given by the manufacturer is ± 2 % (1-sigma). A pressure gauge is connected to the tube leading from the soil gas probe to the pump (RAD7 internal pump). This allows for an estimation of the soil's gas permeability. However, no noticeable differences in the pressure have been observed for all the samples taken during this study. Therefore, the pressure readings were not used to normalise the radon and CO_2 data.

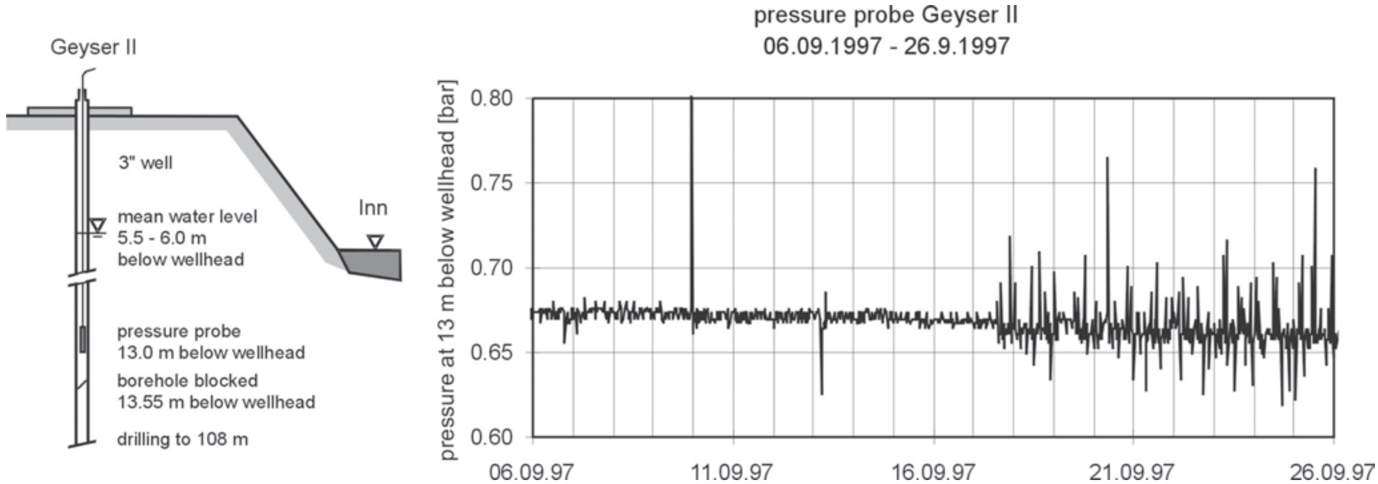

Fig. 3. Schematic illustration of Geyser II and the hydrodynamic behaviour observed in the borehole.

4 Carbogaseous springs and geysers

4.1 Overview

16 carbogaseous springs (> 500 mg CO_2/L), two formerly active carbogaseous geysers, and 23 other springs in the region of Scuol-Tarasp were observed and sampled (Fig. 2, Tab. 2). All carbogaseous waters discharge from the Bündnerschiefer fractured aquifer and are characterised by low temperatures (< 12.5 °C), a mineralisation of more than 1000 mg total dissolved solids (TDS) per litre, and CO_2 content that often exceed 2000 mg/L. The highest mineralised springs (> 5000 mg TDS/L) are situated along the River Inn. The springs at the northern slope of the valley often show intermediate mineralisation. Only two mineral water springs with relatively low CO_2 content occur at the southern slope.

4.2 Origin and functioning of the coldwater geysers

Normal geysers blow out hot water fountains when the heat of the rock brings the water near boiling. The pressure release during the eruption increases the steam production, which reinforces the eruption (Rinehart 1980). Most coldwater geysers are manmade phenomena, which may occur when a borehole is drilled into a carbogaseous aquifer. Liberation of CO_2 from the over-saturated water causes the eruption, and the pressure release increases the degassing. Both hot and cold geyser eruptions are thus self-amplifying processes, and the formation of gas bubbles is essential for the generation of eruptions. Glennon & Pfaff (2005) provide an overview of coldwater geysers. The world's largest one is located near Andernach in Germany. It was first created by a drilling in 1905, then destroyed due to road construction and reactivated in 2001 by a 350-m drilling. This geyser ejected 60-m-high fountains every 90 min. Soon after the drilling, the borehole had to be closed because there was unwarranted concern that the geyser could harm the environment (pers. communic. B. Krauthausen). Up to 30-m-high water and gas eruptions also occurred at a 1600-m-deep geothermal exploration borehole, which was drilled in 1991 in the Upper Engadine Valley (Aemissegger 1993).

The coldwater geysers in the region of Scuol-Tarasp were created by two 100-m-deep mineral water exploration wells. Geyser I was destroyed in 1934 during excavation works; however, the water can still be sampled. Geyser II is partly filled with sediments, and is blocked at 14 m depth. Only a few, small eruptions (< 2 m) have been observed since 1961.

Bissig (1997) investigated the geysers, including hydrochemical analyses (section 4.4) and recording of their hydrodynamic behaviour. The mean water level in the borehole of Geyser II is at 5.5–6.0 m below wellhead, i.e. 0.5–1.0 m above the level of the near River Inn (Fig. 3). The water level in the borehole was observed from July to October 1997 using a dip-meter for occasional measurements and a continuously recording pressure probe at 13 m below wellhead. This probe often showed lower water depths than the dip-meter, which can be explained by variable content of gas bubbles. The pressure data thus cannot be directly transformed into water-level data. During the first two months, the pressure recordings display stagnation periods that may last up to 7 days and short fluctuation phases. The fluctuations may exceed 0.1 bar in 10 min, i.e. more than 1 m of water-level variation. During the last month, the borehole showed permanent variations without stagnation periods, indicating that Geyser II is still active, although the borehole is in disrepair.

4.3 CO_2 and radon in the spring water

The available data on CO_2 in spring water for the region of Scuol-Tarasp (Mayoraz 2004, Deflorin 2004, a total of 38 samples) show a frequency distribution, which can be well fitted

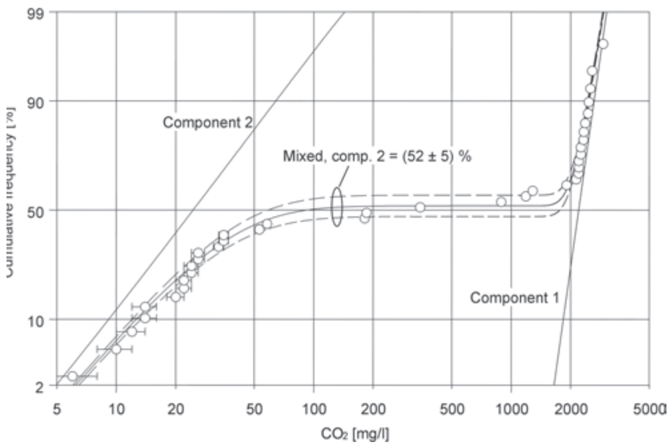

Fig. 4. CO_2 in spring water frequency distribution and approximation by a 2-component model. Component 1: geogenetic production; component 2: distribution to be expected for groundwater in equilibrium with the soil. Error bars are 1-sigma uncertainty estimations.

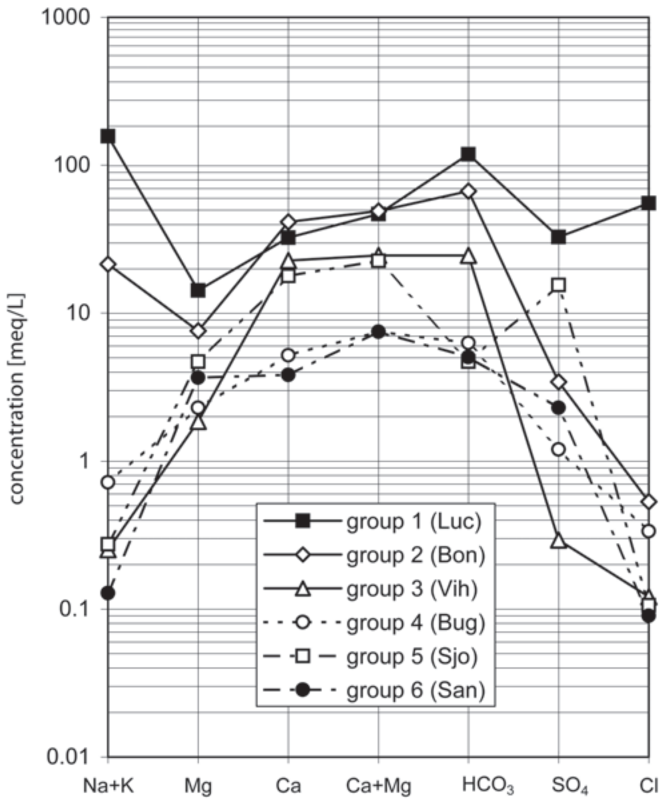

Fig. 5. SCHOELLER diagram of characteristic springs from the different hydrochemical groups.

using a two-component approximation Fig. 4. Component 1 with a median of 2200 mg/L is attributed to geogenetic production, whereas component 2 with a median of 24 mg/L shows a distribution expected for groundwater in equilibrium with the soil.

The data on radon in spring water (Mayoraz 2004; Deflorin 2004; a total of 32 samples) display a nearly perfect one-component lognormal distribution with a median of 5 Bq/L (not presented here). This corresponds to the median found by Deflorin (2004) for 360 samples taken in the Canton of Grisons. There is a deviation from the one-component behaviour at values above 20 Bq/L, with the highest value at 25 Bq/L. The origin of this second component is unknown, but there is no need to attribute it to radon upwelling with the CO_2 from depth. 25 Bq/L are still within the range for groundwater in contact with soil. Furthermore, there is no correlation between the concentrations of the two gases for the 18 water samples, for which both radon and CO_2 are known.

4.4 Hydrochemical classification of the spring and geyser waters

On the basis of the major-ion chemistry, the hydrogeological units and the location of the springs and geysers, it is possible to distinguish six groups of water types with various subgroups, and two special water types (Tab. 2). The water chemistry of one characteristic spring from each group is shown in the SCHOELLER diagram in Fig. 5; a detailed description of the spring groups is given in the following sections.

Group 1

The most famous carbogaseous mineral springs are situated along the gorge of the River Inn and discharge from the Bündnerschiefer formation. Luzius and Emerita are Switzerland's highest mineralised springs, with 15500–17700 mg TDS/L. These two springs, as well as Sfondraz and the geysers belong to the Na-HCO_3-Cl water type, which can further be classified according to the Ca^{2+} and Cl^- content (Tab. 2). Besides the standard major cations and anions, the mineral water also contains significant amounts of H_2S, boron acid, Li^+ and various trace elements. The CO_2 concentrations are within a range of 2200–2600 mg/L.

Group 2

Other carbogaseous mineral springs in the gorges of the River Inn are characterised by less highly mineralised water (1200–5800 mg TDS/L) with Ca^{2+} as the predominant cation and bicarbonate as the most important anion. The CO_2 content range from 1200 to 2900 mg/L. Hydrochemically, the spring waters can be considered as a result of mixing between groups 1 and 3. The Carola spring receives an additional contribution from the alluvial aquifer near the River Inn, which contains sulphate. About 3000 bottles of water from this spring are used each year for local hotels (pers. communic. R. Zollinger).

Group 3

These springs are located at the slope of Scuol and also discharge from the Bündnerschiefer formation. The spring waters show low to medium mineralisation (700–3100 mg TDS/L) and a simple Ca-HCO_3 chemistry. Iron and silicic acid are important minor water constituents at some springs. Most springs of this group are carbogaseous and contain more than 1000 mg CO_2/L. Tritium data (Högl 1980; Wexsteen et al. 1988) from some of these spring waters indicate relatively short residence time of less than 5 years.

Group 4

Low mineralised springs (TDS < 1000 mg/L) with a Ca-Mg-HCO_3 water type occur on both sides of the valley and most often discharge from the Bündnerschiefer formation; either directly or indirectly via an overlying shallow porous aquifer. The CO_2 content is most often < 60 mg/L, except for the S-Chürdüna spring with 350 mg/L.

Group 5

This group summarises springs that discharge from different hydrogeological units at the southern slope of the valley, which are characterised by higher sulphate than bicarbonate concentrations. The mineralisation of the spring waters is low to medium (800–1700 mg TDS/L) and the CO_2 content is always low (< 40 mg/L).

Group 6

This is another heterogeneous group of non-carbogaseous low mineralised springs, which are mainly situated at the southern valley slope and discharge from different aquifers, often indirectly via shallow porous aquifers. Unlike the springs of group 5, the waters of this group show higher bicarbonate than sulphate content (Ca-Mg-HCO_3-SO_4 water type).

Special water types (groups 7 and 8)

Two springs in the region show special hydrochemical characteristics that differ from the six other groups. The Lischana spring is a highly mineralised carbogaseous spring that was captured by a drilling in serpentinite near the River Inn. It is the only spring in the region that contains more magnesium than calcium. The major element composition is Na-Mg-HCO_3-SO_4. The water also contains high concentrations of boron and silicic acid.

The 'Tarasper Schwefelquelle' (sulphur spring) also discharges from serpentinite but has low mineralisation. The characteristics of this spring are very different from those of the Lischana spring because it contains no CO_2. As already observed by Pfeifer (1977), the water is strongly basic with a pH of about 11, which is typical for groundwater in ultramafic rocks. As a consequence of the high pH, inorganic carbon is present as carbonate (CO_3^{2-}). The geochemical water type is Ca-Na-CO_3-Cl-SO_4.

5 Mofettes and soil gas

5.1 Mofettes

On the northern slope of the valley, near Scuol, there are long-known spots of dry gas exhalations, which are called 'mofettes' in analogy to the volcanic phenomena. The largest one is known as 'Mofetta Felix'. As described above, the gas is mainly composed of CO_2 (> 93 %) but also contains other components, including traces of H_2S. Such high CO_2 concentrations are harmful. The mofettes can thus be recognised due to reduced vegetation, accumulations of dead insects and a slight smell of hydrogen sulphide (Schmassmann 1980).

All mofettes discharge from moraine overlying the Bündnerschiefer formation. Geophysical investigations (VLF-R) showed that the thickness of the moraine ranges between 15 and 20 m (Wexsteen & Müller 1987). In the zone of the Mofetta Felix, the gas outlets are aligned in a N60 direction, sub-parallel to the axis of the valley and the crest of the anticline. The geophysical investigations indicate conductive zones in a N150 direction, perpendicular to the mofette line. Those were interpreted as open fractures with diaclases allowing for degassing from depth. A second zone of mofettes is located nearby above the Vih spring and seems to follow a N100 direction.

5.2 CO_2 and radon in the soil gas

It was previously not known if the mofettes reflect an important regional CO_2 anomaly or if there are only a limited number of point-like gas outlets. Therefore, Mayoraz (2004) measured the CO_2 concentration in the soil gas along 7 profiles following a NW-SE direction, i.e. perpendicular to the mofette lines and structural axes, and 2 NE-SW profiles. The radon (^{222}Rn) concentrations were measured simultaneously. The main profile is 3745 m long, while the other profiles range in lengths between 45 and 518 m. The mean distances between the measurement points is 72 m for the main profile and 6–34 m for the others, and the number of points per profile is 53 for the main profile and 6–27 for the others. Furthermore, the gas concentrations in the soil gas were measured in the near environment of the carbogaseous springs and geysers. Altogether, the soil gas concentrations were measured in 178 boreholes along 5454 m of total profile length. The results are presented in Fig. 6.

The CO_2 measurements confirmed the long-known zones of gas exhalations, i.e. the mofettes near Scuol. Outside from these zones, the concentrations are often within a range of 0.2–2 vol.% – normal values for soil gas. Near the Mofetta Felix, increased concentrations (> 4 %) were detected in a 100-m-wide zone. Similarly, an 80-m-wide anomaly was detected in the mofette zone northerly uphill from the carbogaseous Vih spring. Locally, the range of the instrument (25 %) was exceeded. The 3745-m-long main profile only showed one small CO_2 anomaly, NW uphill from the Vih spring. Two detailed profiles, NW-SE and NE-SW, made it possible to better de-

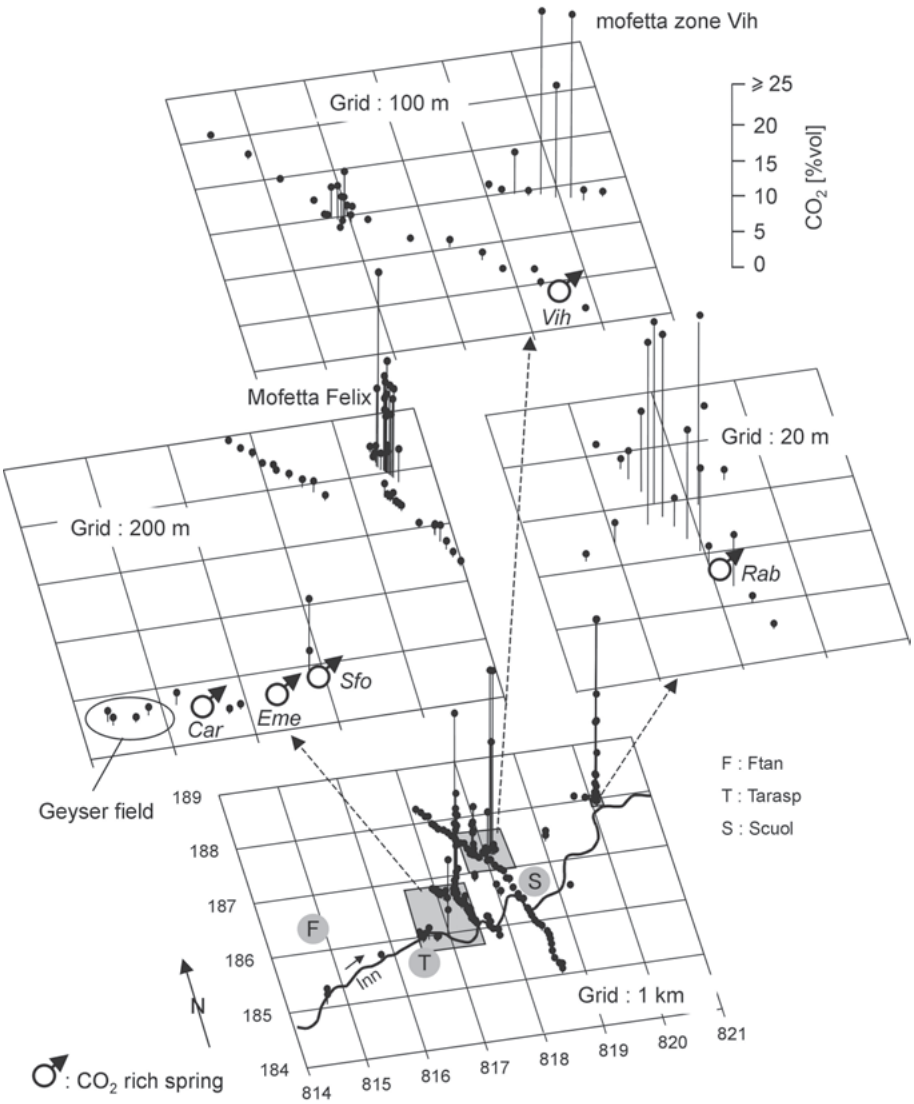

Fig. 6. Spatial distribution of the CO_2 concentrations in the region of Scuol-Tarasp (below) and in three zones that were investigated in great detail (above). The highest values were found near the known mofette zones (Felix and Vih) and some carbogaseous springs (Rab, Sfo, Vih). Apart from these small zones, no significant anomalies were detected, also not in the geyser field. The numbers at the margins represent the Swiss Topographic Grid (unit: km).

fine this anomaly, which is about 20 m x 20 m in size with a maximum concentration of 5.3 % CO_2.

The soil gas measurements near the carbogaseous springs and geysers most often showed CO_2 content of 0.2–2 %. Higher values were detected near two springs, Sfondraz and Rablönch. The near environment of the latter was investigated along two perpendicular profiles. Increased values were found in a zone of 50 m (NW-SE) x 40 m (NE-SW). The highest value, locally > 25 vol.%, were found 55 m uphill from the spring.

The radon concentrations in the soil gas range between less than 0.2 and 35 ± 3 Bq/L. Although high CO_2 content (> 10 %) always coincide with elevated radon content (> 1.5 Bq/L), there is no systematic correlation between the two gases.

The frequency distribution of the CO_2 concentrations in the soil can be approximated by two lognormal components (Fig. 7). About 70 % of all measured values can be attributed to CO_2 production in the soil, which confirms that there is no general regional CO_2 anomaly.

The ^{222}Rn in soil gas frequency distribution shows no indication for radon from depth (Fig. 8). 90 % of all values can be explained by radon produced in the soil, with a median of 2 kBq/m^3. A second component with a median of 0.5 kBq/m^3 may be due to leaky sampling.

6 Discussion and conclusions

6.1 Conceptual model of the regional gas and groundwater circulation

The previous isotopic studies showed that the CO_2 in the Lower Engadine originates from the metamorphosis of car-

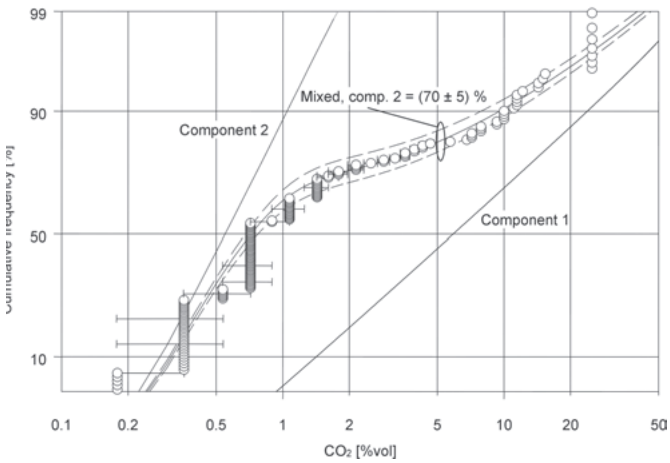

Fig. 7. CO_2 in soil gas frequency distribution and approximation by a 2-component model. Component 2: CO_2 production in the soil; component 1: geogenetic production. Maximum measured values are limited to 25 vol.%, the full scale of the instrument used. Error bars are 1-σ uncertainty estimations.

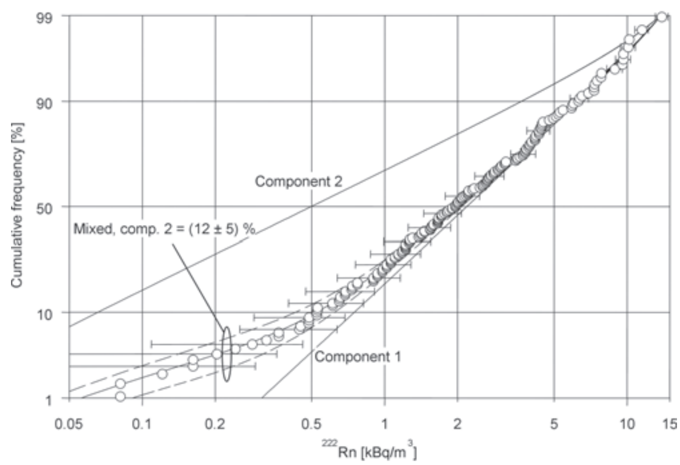

Fig. 8. ^{222}Rn in soil gas frequency distribution and approximation by a 2-component model. Component 1: typical radon production in an average Swiss soil. There is no need for any radon from deep down to explain the distribution. Component 2 with a lower median and a broader distribution may be due to leaky sampling. Error bars are 1-sigma counting statistics.

bonate rocks in the crust (Wexsteen et al. 1988). The results of the study presented in this paper made it possible to propose an improved conceptual model of the regional gas and water circulation (Fig. 9), and to better understand the relations between dry gas exhalations, carbogaseous mineral springs, and freshwater springs (Fig. 10).

Almost all carbogaseous phenomena are bound to the Bündnerschiefer fractured aquifer (unit 1 in Tab. 1). The tectonically higher hydrogeological units 2 and 3 act as a regional aquiclude limiting both groundwater and gas circulation. The River Inn forms the regional hydrological base level. Steep hydraulic gradients have to be expected in the fractured shale of the Bündnerschiefer formation so that the piezometric surface is high above the river on both sides of the valley. Below this level, all voids in the rock are fully saturated with water. It is thus clear that the CO_2 rises up from depth along water-saturated fractures, dissolved in the groundwater. Dry gas movement can only occur at shallow depth in the unsaturated zone. High CO_2 content in the groundwater favour both the dissolution of carbonate minerals and the transformation of silicate minerals (Krauskopf & Bird 1995), for example:

$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2\ HCO_3^-$

$2\ Na[AlSi_3O_8] + 2\ CO_2 + 3\ H_2O = Al_2[(OH)_4/Si_2O_5] + 4\ SiO_2 + 2\ HCO_3^- + 2\ Na^+$

Consequently, high CO_2 content causes high mineralisation. As the solubility of gas in water decreases with decreasing pressure, the carbogaseous fluids become over-saturated with gas when they rise up from depth. Near the River Inn, degassing of CO_2 and mineral precipitation can be observed at the springs. The soil gas measurement near these springs and the geysers displayed no significant CO_2 anomalies (exception: Sfondraz spring). This finding suggests that the degassing occurs directly at the outlet points of the springs and geysers.

On the northern slope of the valley, above the regional hydrologic base level, there is an important unsaturated zone, and thick moraines locally overlay the fractured aquifer. In this zone, degassing takes place near the groundwater surface, probably tens of metres below the land surface within the moraine. The long-known mofette zones are located in this area, and the soil gas measurements allowed the identification of two formerly unknown CO_2 anomalies uphill near the Rablönch and Vih carbogaseous mineral spring. These anomalies are tens of metres in size. The CO_2 content at some points exceed the measurement range of 25 %. The dry gas exhalations upgradient from the springs indicate the upwelling of carbogaseous water along fractures in the shale. In the moraine, a part of the CO_2 separates from the fluids and rises up through the unsaturated zone, while the carbogaseous mineral water mixes with fresh groundwater and flows laterally downwards to the springs (Fig. 10). Outside from these spatially restricted mofettes and anomalies, most of the 178 measurements gave CO_2 content of 0.2–2 vol.%, which is within the normal range for soil gas. The dry gas exhalations are thus locally restricted phenomena, which are, however, often aligned in a N60 or N150 direction.

Although all carbogaseous mineral springs, except one, discharge from the same aquifer, their hydrochemical characteristics are quite different and can only be understood within a wider hydrogeological framework. Natural tracers, i.e. the chemical and isotopic water composition, have been used to classify the spring waters and to obtain information on the groundwater circulation system. As described above, there are

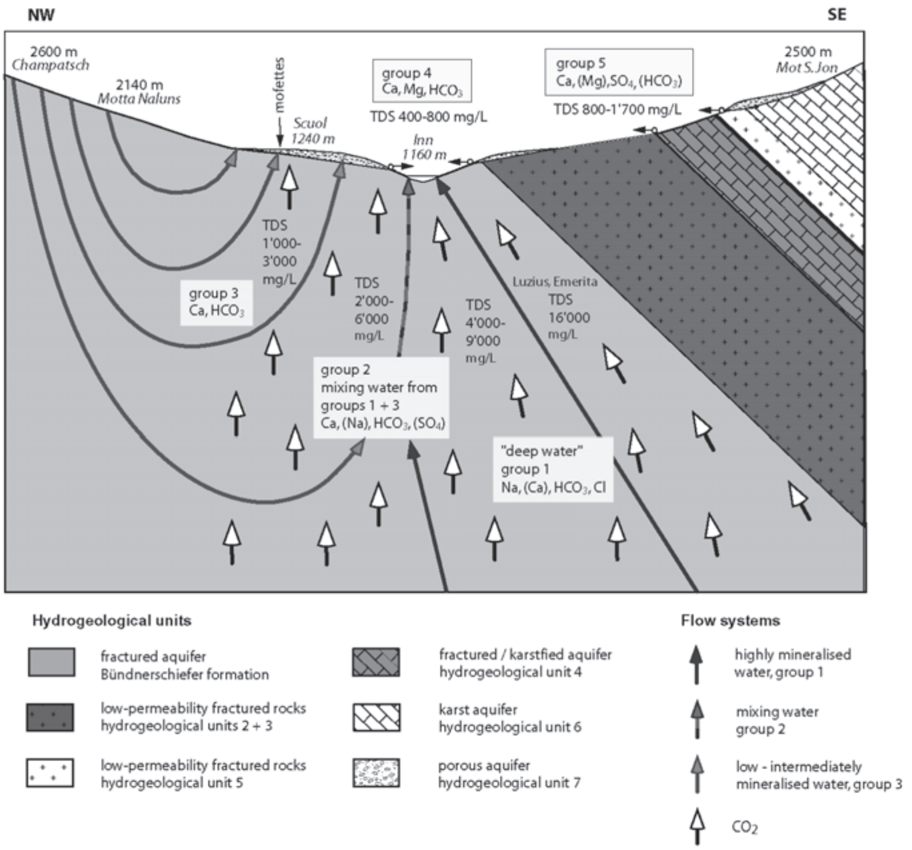

Fig. 9. Conceptual model of the CO_2 and groundwater fluxes in the region of Scuol-Tarasp.

six main hydrochemical groups of spring waters and two special water types (Tab. 2). Groups 1 to 3 are carbogaseous mineral waters that discharge from the Bündnerschiefer fractured aquifer, either directly or via overlying sediments. In a first approach, the different water types within these three groups can be explained by mixing of up to three main components:

1. Extremely mineralised Na-HCO_3-Cl water (Luzius and Emerita);
2. Highly mineralised Ca-HCO_3 water (Runa, Vih, Sotsass and Rablönch);
3. Fresh groundwater.

The origin of the Na-HCO_3-Cl water (comp. 1) is still debatable. Tritium data indicate that it is older than 32 years (Wexsteen 1988). The high content of Na^+, Cl^- and minor elements, like Li^+ and boron acid, cannot be derived from the Bündnerschiefer formation. These elements may originate from the dissolution of evaporitic rocks. Such formations have not been proven in the region. However, deep geophysical profiles across the Alps indicate the possible presence of evaporitic layers beyond the 10 km depth, within the sedimentary cover of the South Helvetic and North Penninic basement (Pfiffner et al. 1997). It is also possible that slices of Triassic evaporites occur in the hanging wall of the Bündnerschiefer formation at shallower depths. The radiocarbon method cannot be used for water dating, as the CO_2 is of metamorphic origin. Stable isotope data deviate from the meteoric water line. The water is enriched in ^{18}O, which may indicate water-rock interaction at more than 150°C (Schotterer et al. 1987; Wexsteen 1988). As the Bündnerschiefer consists of metamorphic marine sediments, the saline water could also originate from ancient marine formation waters, which is consistent with the deviation from the meteoric line (Högl 1980; Wexteen 1988). Up until now, the different hypotheses could neither be confirmed nor disproved.

According to Siegenthaler (in Högl 1980), the mean residence time of the highly mineralised Ca-HCO_3 water from the Vih and Sotsass springs (comp. 2) is less than 5 years. Wexsteen (1988) proposed that the spring water results from mixing of fresh groundwater with 5–50 % of very old components so that exact dating is not possible.

The fresh groundwater (comp. 3) includes a variety of different water types, which reflect the different hydrogeological units (Tab. 1). Groundwater from the Bündnerschiefer aquifer (unit 1) and the moraine (unit 7) predominantly contains Ca^{2+}, Mg^{2+} and HCO_3^-. Springs that discharge from the hydrogeological units 4 and 6 additionally contain sulphate.

The less mineralised waters within group 3 can be explained by mixing of highly mineralised Ca-HCO_3 water (comp. 2) and fresh groundwater (comp. 3). The highly miner-

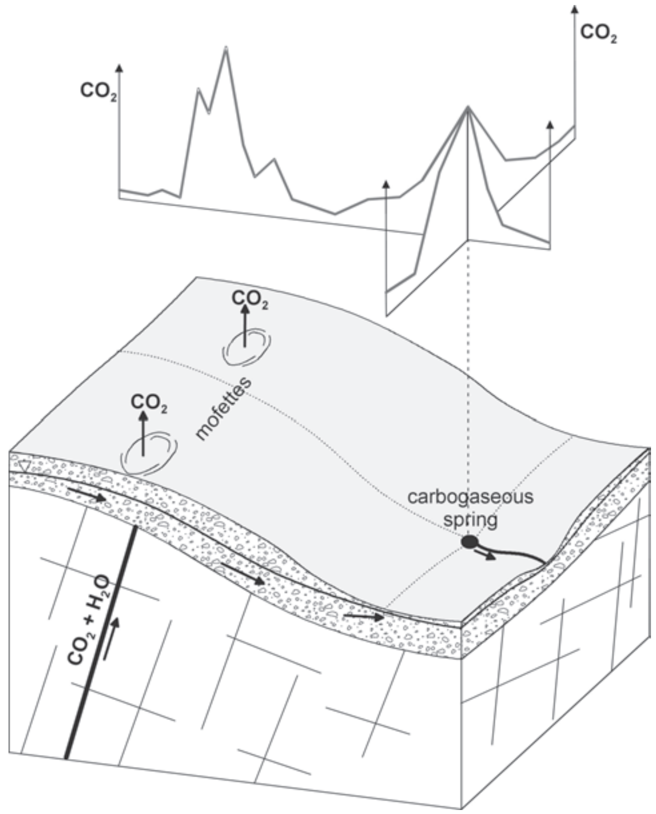

Fig. 10. Schematic illustration of the relation between dry CO_2 exhalations and carbogaseous springs.

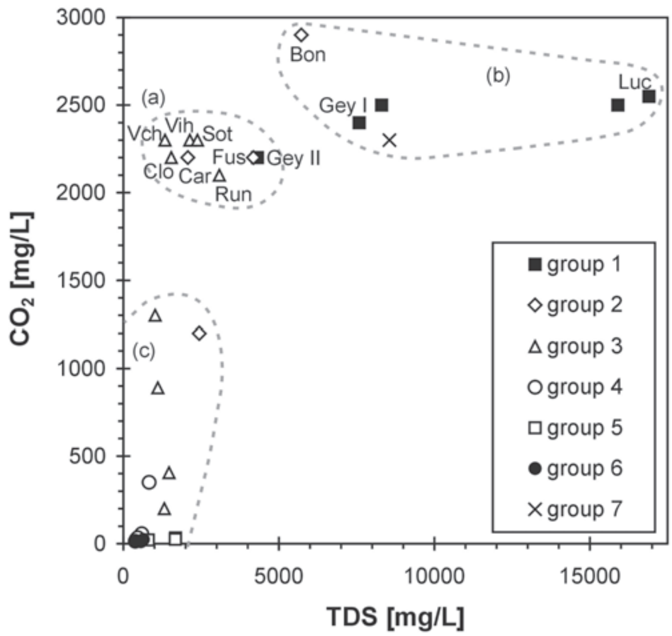

Fig. 11. According to their CO_2 concentration and mineralisation (TDS), the springs in the region of Scuol-Tarasp can be classified into three groups: (a) high CO_2 and low to medium TDS, (b) high CO_2 and high TDS, (c) low to medium CO_2 and low TDS.

alised waters of group 2 (Bonifazius, Fuschana) can be considered as mixtures of components 1 and 2; the Carola spring additionally includes a significant contribution of fresh groundwater.

The low spring temperatures seem to contradict a deep origin of the carbogaseous mineral water. However, the discharge rates of the mineral springs are very low (Tab. 2). Due to the low flow rates and velocities, the hot mineral waters rising from depth have enough time and contact with the rock mass to cool.

6.2 Hydrochemical criteria to localise a new geyser drilling

The abovementioned coldwater geyser in Andernach yielded 60-m-high eruptions from a 350-m-deep borehole. The fact that the geysers near Scuol-Tarasp produced 10-m-high fountains, although the boreholes were only 100 m deep, suggests that there is potential for higher fountains if a deeper borehole was drilled at the right place. The observations described in this paper indicate that Geyser II is still active, although its functioning is strongly reduced as the borehole is partly filled with sediments and blocked at 14 m depth.

The short-term functioning of a coldwater geyser depends on two major aspects: inflow of groundwater from a sufficiently transmissive aquifer, and inflow of CO_2 from depth. However, high CO_2 content often coincide with high mineralisation, and the mineral precipitation from the fluid phase is likely to clog the borehole. The long-term functioning thus additionally requires a relatively low mineralisation. Fig. 11 presents the CO_2 concentration and total mineralisation of all spring and geyser waters in the region of Scuol-Tarasp. Ideal conditions to drill a new coldwater geyser should be present when the water is rich in CO_2 while mineralisation is low, i.e. within group (a).

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