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Alteration of Wall Rocks by CO₂-Rich Water Ascending in Fault Zones:

Natural Analogues for Reactions Induced by CO₂ Migrating along Faults in Siliciclastic Reservoir and Cap Rocks

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Résumé — Altération des roches, dans des zones de failles, par des eaux ascendantes riches en CO₂ : analogues naturels pour les réactions provoquées par la migration du CO₂ le long des failles, dans les réservoirs silici-clastiques et dans les couvertures — L'activité tectonique récente dans le massif Rhénan est accompagnée de la migration d'eaux riches en CO₂, d'origine mantellique. Lors de son ascension, le CO₂ se dissout dans les eaux interstitielles des roches sédimentaires fracturées du substratum varisque. Les réactions d'altération sont connues à partir des analyses pétrologiques des roches exposées dans les parois de faille, de la composition chimique des fluides et de la modélisation thermodynamique. La réaction principale est l'altération de la chlorite et du feldspath en kaolinite, carbonate de fer, quartz et eau bicarbonatée. Les vitesses d'écoulement, les températures, les profondeurs, les temps de résidence des eaux souterraines, les types de roche et le produit des réactions diffèrent selon les systèmes naturels étudiés. Les conditions de réaction peuvent être contraintes en comparant les variations naturelles des paramètres et la progression des réactions dans les simulations thermodynamiques. Selon le degré d'avancement des réactions, une augmentation de la porosité induite par la dissolution des minéraux primaires, ou au contraire une réduction de la porosité pouvant atteindre la cicatrization complète des fractures, peuvent se développer dans la même roche.

Abstract — Alteration of Wall Rocks by CO₂-Rich Water Ascending in Fault Zones: Natural Analogues for Reactions Induced by CO₂ Migrating along Faults in Siliciclastic Reservoir and Cap Rocks — The recent tectonic activity of the Rhenish Massif is associated with the discharge of CO₂-rich fluids of mantle origin. Ascending CO₂ dissolves in groundwater of the fractured sedimentary rocks of the Variscan basement. Alteration reactions have been derived from petrological analyses of wall rocks, fluid chemistry, and thermodynamic modelling. The principle reaction is the alteration of chlorite and feldspar to kaolinite, Fe-carbonate, quartz, and bicarbonate water. Fluid flow rates, temperatures, depths, groundwater residence times, rock types, and reaction products vary among the natural systems studied. Reaction conditions can be constrained by comparison of natural parameter variations with thermodynamic reaction progress simulations. Depending on the degree of reaction progress, either porosity enhancement due to dissolution of primary minerals or porosity reduction, and eventually even self-sealing of fractures can occur within the same rock.

INTRODUCTION

Natural reaction times and dimensions of flow systems exceed the dimensions of laboratory experiments by several orders of magnitude, making upscaling and predictions from lab experiments difficult for slow reactions. CO₂-rich mineral waters emerge in the Rhenish Massif from fractured Variscan basement rocks consisting of sandstones, greywacke, shale, minor carbonates, and superficial volcanics. The ground-water flow systems discharging at these springs provide an excellent opportunity to study water-CO₂-rock interaction processes. Solid, liquid, and gaseous educts and products of alteration reactions can be sampled from mineral water wells. The temporal evolution of slow silicate alteration reactions can be derived from geochemical evolution trends that can be correlated to the geomorphology of various flow systems. Systematic variations of the waters' composition along flowpaths between recharge and discharge areas represent different degrees of reaction progress. Possible geochemical consequences for the injection of CO₂ into siliciclastic reservoir rocks can be derived from the understanding of these reactions.

1 ORIGIN OF CO₂ AND FAULTS IN THE RHENISH MASSIF

The Rhenish Massif, similar to the French Massif Central, is an area of young tectonic activity: Cenozoic alkali basaltic volcanism, uplift, rifting, and CO₂ emissions. CO₂ emissions are concentrated in the volcanic fields; however, they are not restricted to these areas. Their distribution rather coincides with a wider area of anomalously low seismic velocities in the upper mantle that underlies much of the massif (*Fig. 1*). Uplift of the Rhenish Massif began in the late Tertiary, contemporaneous with subsidence along the Rhine Rift, and accelerated about 700 ka ago, contemporaneous with the onset of Quaternary volcanic activity. Along the margins and outside of the massif, mineral waters contain little CO₂ and mantle helium: $R/Ra < 1$ (R/Ra is the ³He/⁴He isotope ratio in a sample (R) normalised to the atmospheric value (Ra)). A mantle origin of the carbon dioxide is indicated by trace gas concentrations that plot on linear mixing trends between a mantle component and atmospheric air; and furthermore by carbon isotopes and helium isotope ratios of up to 4 R/Ra , measured in samples from the Eifel volcanic fields (Griesshaber *et al.*, 1992).

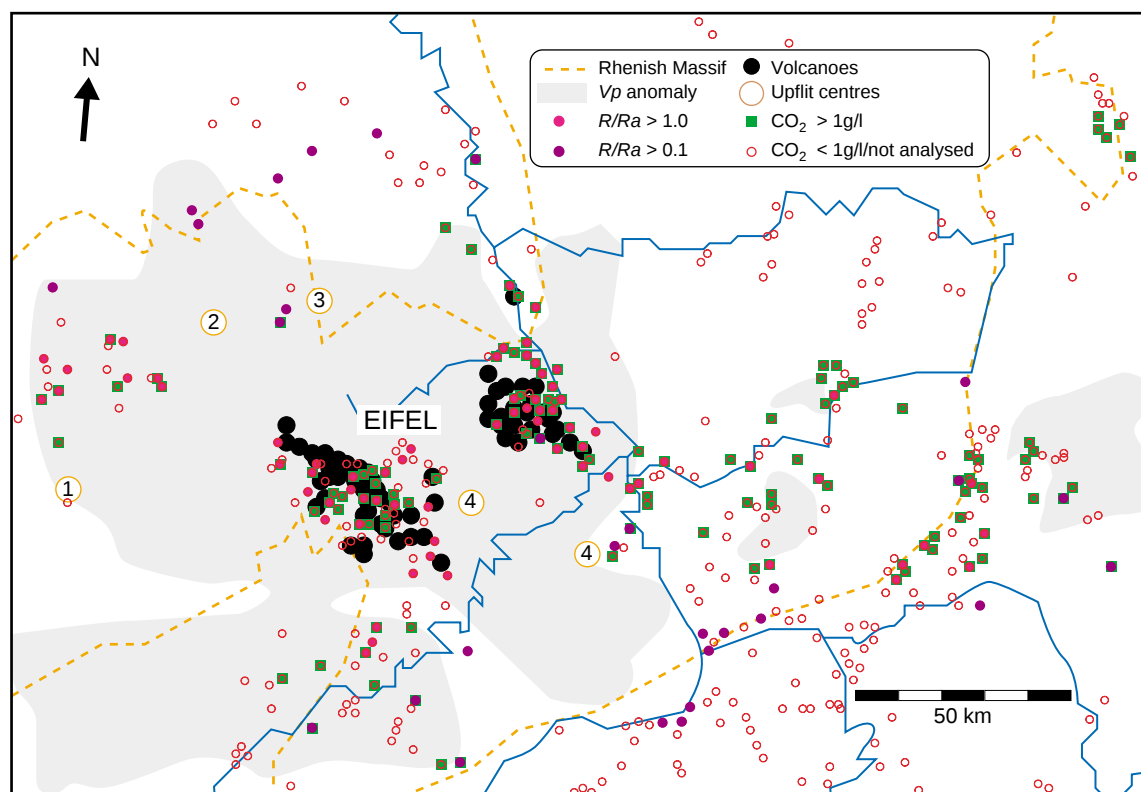


Figure 1

Geodynamic features of the Rhenish Massif: upper mantle velocity anomaly, Quaternary volcanic fields in the Eifel, CO₂-bearing mineral springs, and uplift centres in the Rhenish Massif. Helium isotopy after Griesshaber *et al.*, 1992, p -wave anomaly after Raikes and Bonjer (1983), centres of uplift: (1) after Berners (1983), (2) after Müller (1983), (3) after Mälzer *et al.* (1983), and (4) after Meyer and Stets (1998).

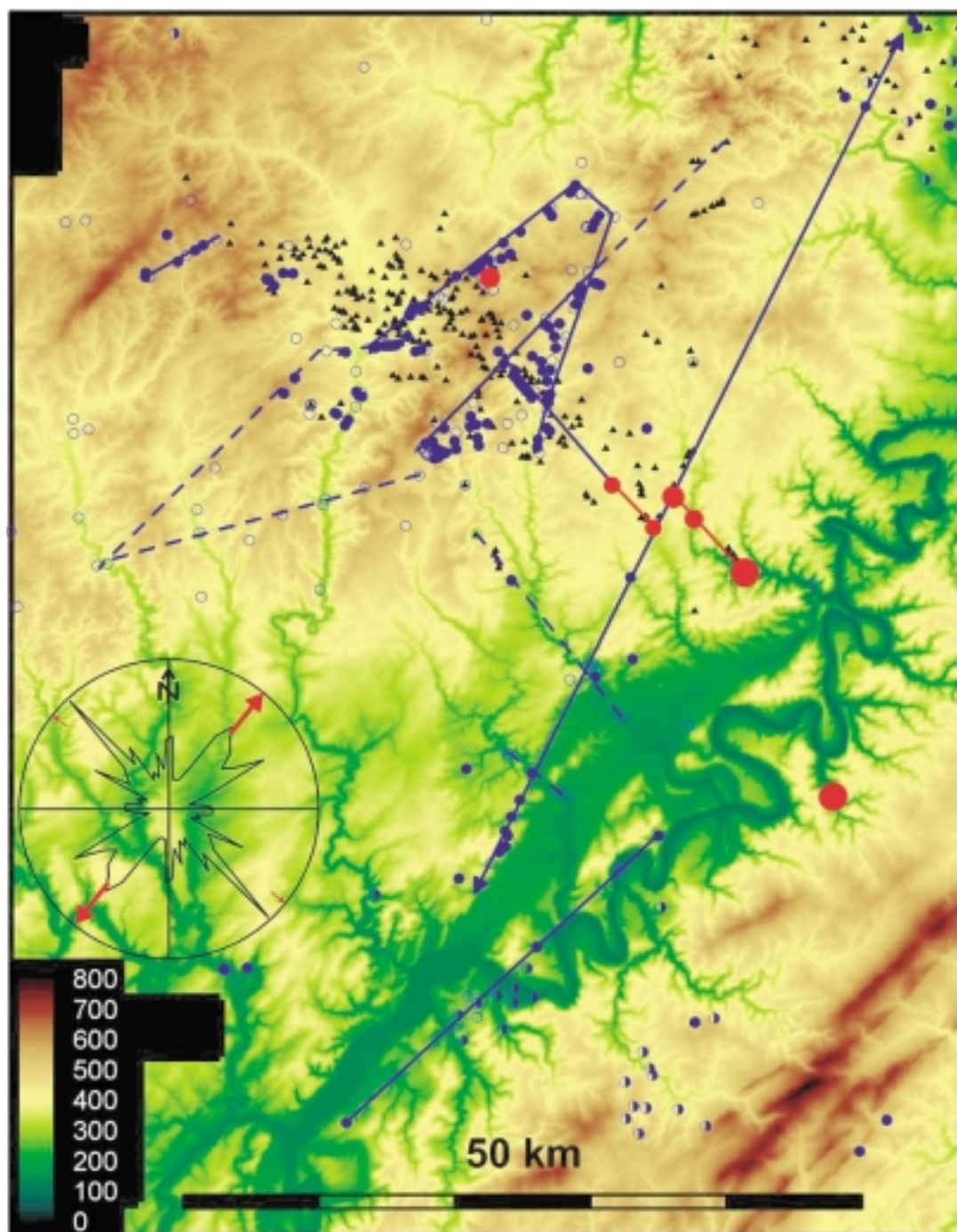


Figure 2

The alignment of CO₂-bearing mineral springs (blue) in the Westeifel volcanic field indicates CO₂ ascent along linear basement sutures (a selection of major ones is indicated, according to May, 2002). Thermal waters (red), Quaternary volcanoes (black); rose diagram shows lineament directions and recent horizontal stress measured *in situ* (arrows).

Along the margins of the massif chloride-rich mineral waters with low CO₂ contents and crustal helium dominate. These waters probably contain altered fossil seawater that penetrated deep into the basement fractures during Mesozoic and Cenozoic inundations of the massif and is still draining from deep topography driven flow systems created by the Quaternary uplift of the massif (May *et al.*, 1996).

According to the conceptual model of May (2002), CO₂ is set free from upper mantle rocks during melting processes in the region of low seismic velocity (Eifel-Plume), which is probably a region of elevated temperature and is partially molten (Ritter *et al.*, 2001). Deep reaching basement sutures could facilitate the direct ascent of CO₂ to the Earth's surface. Some of these faults delineate geological or geomorphological units. In the volcanic fields rising alkali basaltic magma can transport additional CO₂ into the lower crust, from where it ascends upon cooling of intrusions through the brittle upper crust on abundant faults. Within the monotonous lower Devonian sedimentary sequence faults seldom can be mapped directly, but often the course of valleys and alignments of volcanic eruption centres and mineral springs indicate their presence (Fig. 2).

In the Westeifel volcanic field alone, CO₂ reaches the surface at about 200 different locations. These sites range from gas dominated springs with little water discharge (mofettes) to groundwater dominated springs containing little dissolved CO₂. The carbon flux of these springs is similarly highly variable, covering a range of 9.6×10^{-4} mmol/s in a unobtrusive, barely visible roadside seep of CO₂ bearing groundwater to 760 mmol/s in a mineral water production well.

In only 30 of the 200 springs gaseous CO₂ is the dominant C species. In most springs dissolved C species dominate the total carbon flux. Geochemical modelling is used to estimate the fraction of CO₂ that has been converted to carbonate during water rock interaction. In some wells, probably fed by deep reaching flow systems that facilitate extensive wall rock alteration along the water's flow path, solid carbonate may take up most of the CO₂ flux entering the groundwater. The proportion of solid carbonates (*Fck*, expressed in mol·s⁻¹) has been calculated assuming congruent dissolution of average source rock and precipitation of divalent cations, according to Equation (1):

$$Fck = S \cdot \sum_{i=1}^3 \left\{ \left[\left(\frac{cNa}{mNa} - 0.86 \frac{cCl}{mCl} \right) \cdot \frac{cMe_{iEms}}{cNa_{Ems}} \cdot \frac{mNa}{mMe_i} \right] \right. \\ \left. - \left(\frac{cMe_i}{mMe_i} - \frac{cMe_{iGw}}{mMe_i} \right) \right\} \quad (1)$$

In this equation, *S* is the flow rate of a spring (l_{solution}·s⁻¹), *cMe_i* (g·l⁻¹) are the concentrations of dissolved Mg, Ca, and Fe in the mineral water, *cMe_{iEms}* are the concentrations of these elements in average Emsian rock, and *cMe_{iGw}* are the

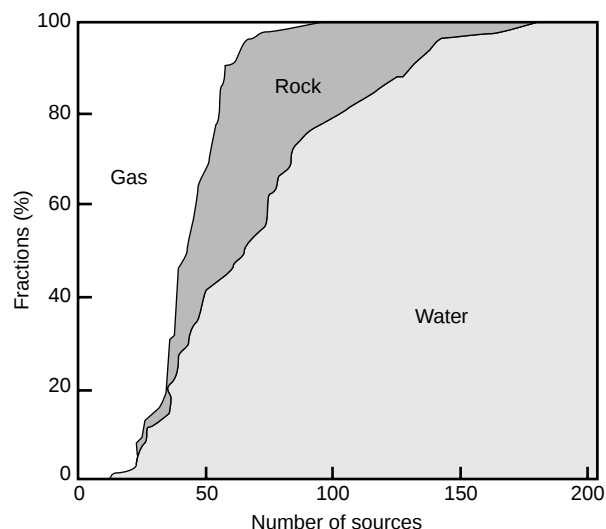


Figure 3

Relative portions of the C-flux to mineral water flow systems in the Süd- and Westeifel: gaseous CO₂, dissolved carbon species emerging in springs, and carbonate precipitated during wall rock alteration within the aquifers.

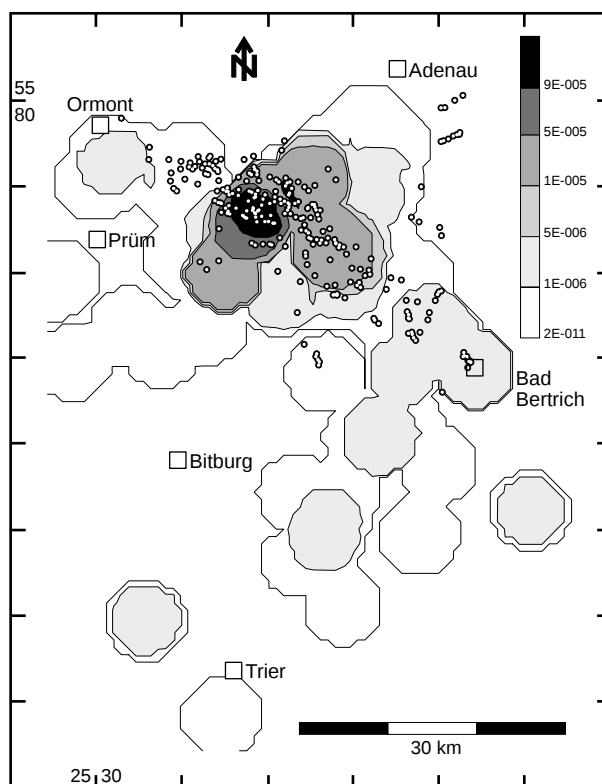


Figure 4

Flux density of mantle carbon (mmol/m²s) in the Süd- and Westeifel. Circles mark eruption centres of Quaternary volcanoes, after Büchel (1982). The scaling of the flux density classes is: 90, 50, 10, 5, 1, and 0% of the maximum value.

average concentrations of these elements in regional CO₂ free groundwater from lower Devonian aquifers. Molar masses of the respective elements are indicated as m_i (cMe_i/m_i is the molarity, expressed in $\text{mol}\cdot\text{l}^{-1}_{\text{solution}}$). The amount of rock dissolved in water is proportional to its Na content, since Na is not precipitated in secondary carbonates. The Na content of groundwater recharge and possible admixture of NaCl rich basement brines ($c\text{Cl}/c\text{Na} = 0.86$) is subtracted from the mineral water's total Na concentration in this calculation. In Equation (1), the first term in the sum is the molar concentration of Me_i that comes from the congruent dissolution of the rock; the second term is the molar concentration of Me_i that is present in excess in the CO₂-rich water, compared to the CO₂-free one. Accordingly, in only about one half of the springs investigated, CO₂ is visible as free gas (Fig. 3). However, gaseous CO₂ contributes about one half to the total C flux in the volcanic field, dissolved species about one third, and precipitated carbonates only 13.6 mol%. The total CO₂ flux (gas, dissolved, carbonates precipitated) is estimated to be 0.5 kg/s, with an annual areal average of about 150 000 kg/km² per year in the centre of the field (Fig. 4).

2 PRODUCTS OF GAS-WATER-ROCK INTERACTION

Geochemical, mineralogical, and isotopic analyses have been performed on rock samples and on the associated gas and

water produced from about a dozen wells. Based on the comparison of fresh water and mineralised waters, and fresh and altered rocks, geochemical reactions have been formulated.

CO₂-rich mineral waters exhibit systematic compositional trends ranging from low concentrated acidic waters, rich in dissolved CO₂, to mineralised neutral bicarbonate waters that usually contain less dissolved CO₂. This progressive water evolution can be observed in general compilations of regional water analyses (Fig. 5) and also in some flow systems with several mineral water discharges along the water's flow path from the elevated watershed towards the main discharge in the lower valley (Fig. 6). The water analyses plot along a trend between regional fresh groundwaters reflecting the source rock compositions (shale, sandstone and minor volcanics) and low temperature water rock equilibrium. Concentrations of dissolved solids generally increase in this direction. The analyses do not plot along Giggenbach's (1988) "full water-rock equilibrium line" however.

The mineral water compositional trends reflect CO₂ consumption by progressive alteration of silicate minerals along the flow paths. Corresponding trends can be seen in geochemical and mineralogical analyses of wall rock samples from mineral water wells. Depending on their tectonic setting, the wall rocks show different degrees of alteration. A comparison of two wells with little and strongly altered rocks is shown in Figure 7. The well Fachingen S22 has been drilled in the surroundings of natural mineral water

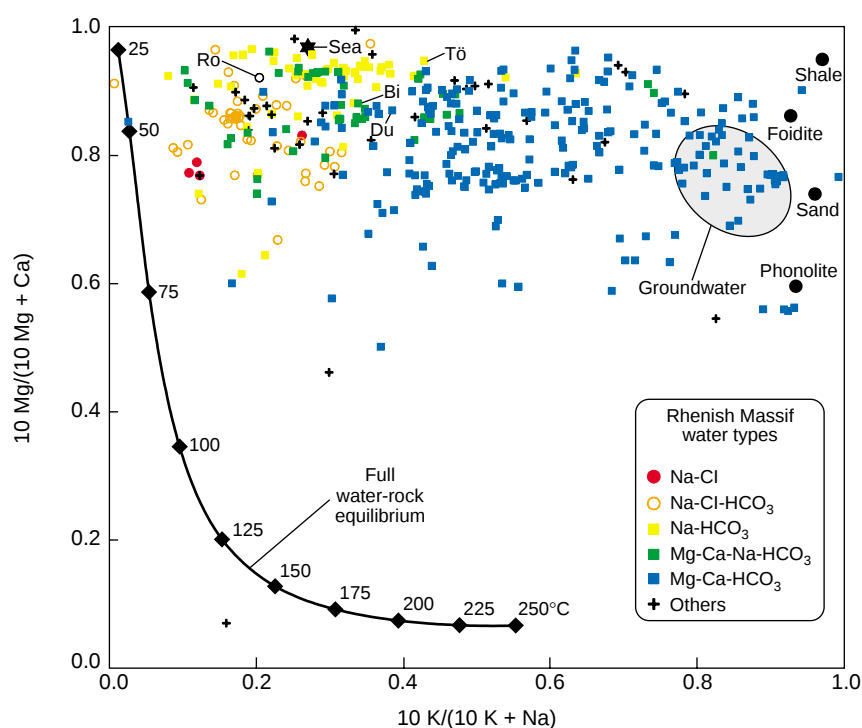


Figure 5

Relative concentration of the major cations in mineral waters in the Rhenish Massif; Mg, Ca, Na, K denote respective element concentrations in mg/l. Water analyses are mainly from the compilations of Langguth and Plum (1984) and Carlé (1975). Representative compositions of groundwaters from the Westeifel are taken from Köppen (1987). The geothermometers have been calculated according to Giggenbach (1988). Marked waters are from Birresborn (Bi), Duppach (Du), Tönisstein (Tö), and Roisdorf (Ro).

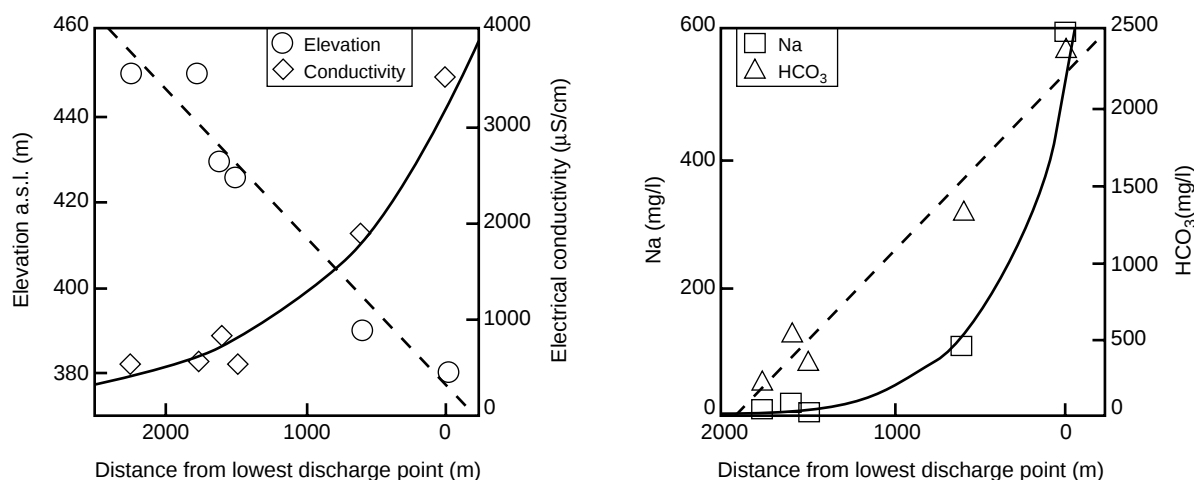


Figure 6

The systematic variation of mineral water composition within a single flow system in the Westeifel indicates progressive wall rock alteration and mixing with saline basement brines along the flow path.

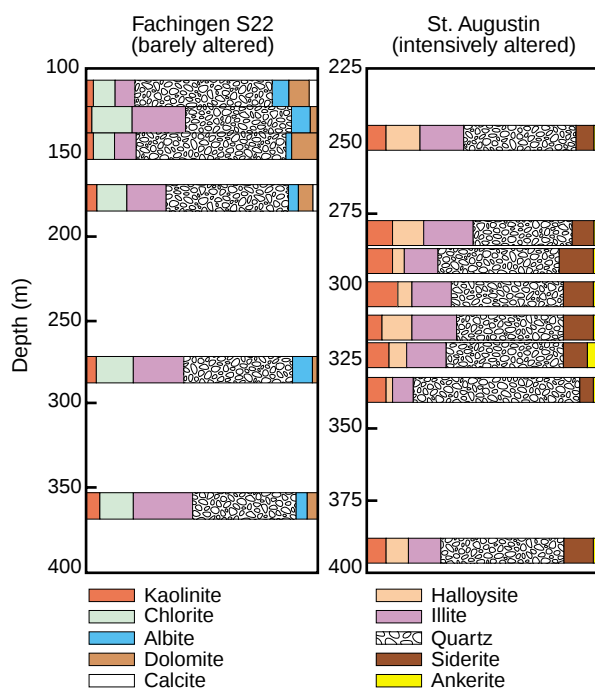


Figure 7

Contrasting degrees of hydrothermal wall rock alteration, visible in samples from two mineral water wells of the Rhenish Massif. Coloured bars show relative amounts of normative minerals of samples from different depths.

St. Augustin tapped a mineral water flow system, in one of the major graben boundary faults at the southern margin of the Niederrheinische Bucht. Chlorite and albite are present in all samples from Fachingen, but missing in the samples from St. Augustin. On the other hand the Fachingen samples contain little kaolinite/halloysite and carbonates in contrast to the strongly altered samples from St. Augustin. No siderite is observed in the Fachingen samples. A range of various degrees of wall rock alteration can also be observed among samples from different depths of individual wells, some from mineral water bearing fissures and others from more coherent rocks less affected by carbonic acid. However, no systematic variation of rock composition with depth has been observed within the sampled intervals within the two flow systems' zones of fluid ascent and discharge.

Chlorite thermometry according to the method of Kranidiotis and MacLean (1987), based on normative compositions, indicates temperatures of 230 to 260°C. These temperatures confirm a primary origin of chlorite. They correspond to anchimetamorphic conditions in the Rhenish Trough during the Variscan orogeny. In contrast siderite, the main Fe-phase in the altered rocks, indicates low temperatures present in the recent hydrothermal systems. Stable carbon and oxygen isotopes show that it is in isotopic equilibrium with the recent bicarbonate waters and that it is distinct from diagenetically formed siderite nodules within the lower Devonian sediments (Fig. 8). Siderite is the most abundant carbonate mineral in the altered rocks. However, dolomite-ankerite and calcite also occur in altered rocks and as precipitates in mineral water producing wells.

The modal composition of Fe-Mg-Ca carbonates correlates to the relative cation concentrations of the waters and

springs. However, it did not encounter mineral water of sufficient quantity and quality. Only peripheral parts of the mineral water flow systems have been struck and thus the rocks are little affected by alteration. In contrast, the well

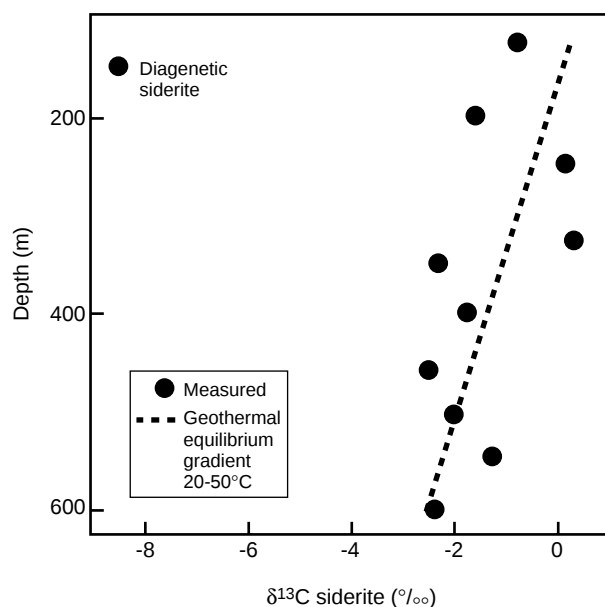


Figure 8

Stable isotopes of siderite from a mineral water well in Wehr indicate precipitation of siderite in equilibrium with the discharging mineral water. Carbon isotopes indicate an elevated thermal gradient, probably caused by rising mineral water.

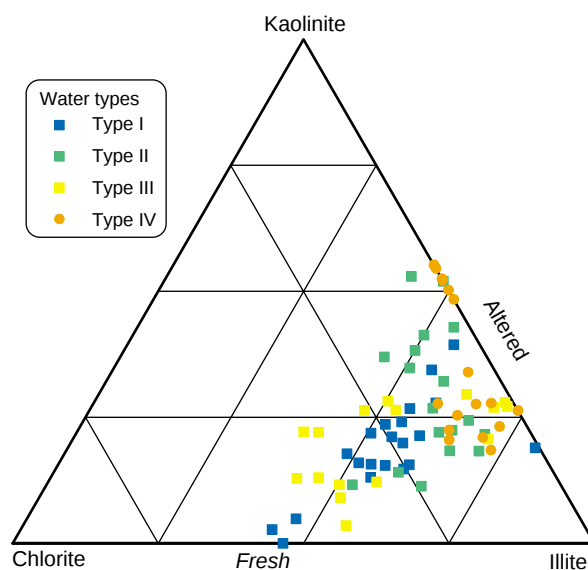


Figure 9

Clay mineral fractions in rocks from mineral water wells in the Rhenish Massif, affected by various degrees of alteration. Classification of mineral water types according to May (1992).

the presence of carbonate rocks in the aquifer systems. Numerical simulations indicate that the carbonate composition further depends on the degree of wall rock alteration (bulk water/rock ratio). However, no systematic study has been performed on carbonates in the altered rocks yet, that would allow predictions about the solid solution composition of carbonates, based on water analyses and physical reaction conditions.

The main reaction is the alteration of chlorite and albite to quartz, kaolinite, and iron-rich carbonates. Illite is not significantly altered by these reactions. Clay minerals show a contiguous compositional trend between fresh and altered rock (Fig. 9). This trend is paralleled by the contiguous non-equilibrium trend in water compositions (Fig. 5). These trends infer that the bulk reaction is slow, that usually does not reach equilibrium within the natural flow systems. Since CO₂ reaches the Earth's surface, it is not completely used up by alteration reactions. Decomposition of chlorite is probably the rate limiting reaction step. The reactions may also be retarded by altered mineral assemblages lining the surface of mineral water conducting fractures.

Besides bicarbonate, chloride is a major cation, especially in "mature" mineral waters of type IV. Its origin is believed to be fossil sea water. While HCO₃⁻ concentrations follow a linear trend along the water evolution path in Figure 6, Na concentrations increase exponentially. This trend is explained by progressive reaction of CO₂ bearing groundwater with

wall rocks and mixing with saline waters in the deep parts of the flow system.

3 GEOCHEMICAL MODELLING OF REACTIONS

Thermodynamic simulations have been used to quantify the mass transfer between fluid and solid phases. The principal reactions have been modelled by a mass transfer approach for a closed system, simulating progressive wall rock alteration.

The average compositions of lower Devonian siliciclastic rocks (Schulz-Dobrick and Wedepohl, 1983) is used as an approximation for the Emsian aquifer rocks, since compositional differences of the clastic rocks ranging from shales to quartzites are levelled out by the alternation of different lithologies along flow paths. Average amounts of quartz and illite (Flehmig, 1983) are subtracted from the rock analysis. For this purpose, an average Al-celadonite content within the illite phase of 20 mol% has been assumed, according to the analyses by May *et al.* (1996). For the remaining amounts of element oxides hydrolysis reactions have been formulated. The products of these reactions have been added incrementally to the solution, that was allowed to equilibrate with the secondary mineral phases (Fig. 10). The reaction temperatures listed in Table 1 were held constant. The CO₂ partial pressures dropped from initial values of up to a few bars, according to the amount of CO₂ transformed to dissolved and solid carbon species. The PHREEQC program

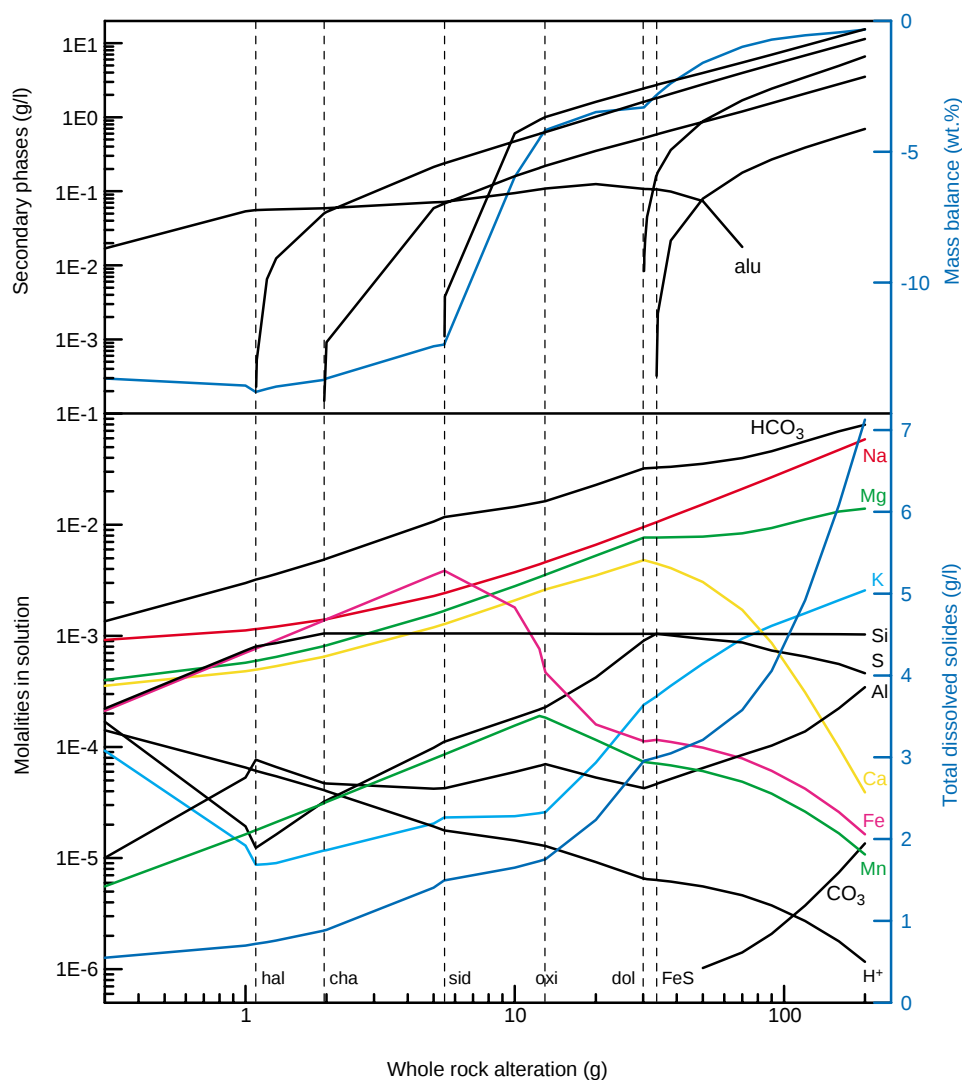


Figure 10

Progressive alteration of average Emsian rocks. Initial solution: 99.85 vol.% groundwater mixed with sea water and equilibrated with CO_2 at 85°C and $3.2\text{ MPa } p\text{CO}_2$. The vertical dashed lines indicate the beginning of precipitation of secondary phases: alunite (alu), halloysite (hal), chalcedony (cha), siderite (sid), dolomite (dol), and precipitated iron sulphide (FeS), and the transition from oxidising to reducing Redox conditions (oxi). The upper part of the diagram shows the masses of precipitated secondary minerals. Minor phases like barite, F-apatite, iron sulphide and rhodochrosite are not shown. The mass balance of the solid phases and the total amount of dissolved solids are shown as blue curves.

(Parkhurst, 1995) in combination with the WATEQ4F database (Ball and Nordstrom, 1991) has been used for the numerical reaction progress simulations. A detailed description of the modelling procedure and assumptions is given in May (1998b).

The alteration of little rock is needed to achieve equilibrium with secondary silica (simulated as chalcedony) and kaolinite. The main secondary phase is siderite however. Dolomite will only precipitate at high rock/water ratios. Most of the Rhenish carbonaceous mineral waters do not reach dolomite (or calcite) saturation though.

In Figure 10 the compositional variation of CO_2 bearing ground water due to progressive alteration (rock/water ratios) of average lower Devonian rocks is shown. Initially the element concentrations are similar to the original groundwater composition. Fe and Si increase linearly with the amount of altered rock, since they were not detected in the groundwater. Al and K decrease due to the precipitation of alunite, which commenced at 0.02 g of whole rock alteration (mass including quartz and illite) per litre of water. Carbonic acid dissociates to HCO_3^- and H_3O^+ ions. The latter are consumed in the silicate hydrolysis. With increasing

concentrations of dissolved elements, the solution becomes saturated with respect to secondary phases. At about 1 g halloysite starts to precipitate, followed by chalcedony at 2 g. They limit the concentrations of the respective dissolved elements. When the precipitation of siderite commences, only 1 g of the primary minerals have been altered yet, to produce a Fe-HCO₃ dominated water. A quasi-steady state of reaction progress is attained between siderite and dolomite saturation, when the mass of secondary phases produced is proportional to the amount of dissolved primary minerals. Na-Mg-Ca-HCO₃ waters are produced within this range of water-rock ratios.

At about 30 g rock alteration the Ca and Mg concentrations start to decrease, due to dolomite precipitation, while Na concentrations continue to increase. The beginning of dolomite precipitation marks the shift in water composition towards Na-HCO₃ waters. The simulations demonstrate that these waters result from advanced wall rock alteration, rather than by ion exchange reactions, an explanation made popular by Schwille (1955). Ion exchange reactions have not been quantified, and the effects of ion exchange on specific exchange phases in the wall rocks of Rhenish mineral waters have not been demonstrated yet. In the South and Westeifel most mineral water compositions are consistent with the progressive alteration concept. Only few waters have cation ratios that indicate a relative Na enrichment by additional processes, which may include ion exchange (May, 2002).

At low degrees of reaction progress the volume of primary minerals dissolved exceeds the volume of secondary minerals precipitated and thus porosity increases. With the precipitation of dolomite the mass of secondary minerals becomes about equal to the mass of dissolved primary minerals (Fig. 10). Positive mass balances were obtained by other simulations. Reaction progress could lead to self-sealing of fractures in cap rocks of CO₂ storage. Self-sealing could also limit the degree of reaction progress attainable and thus the amount of *in situ* mineralization of CO₂ in fractured reservoir rocks.

The major cation concentrations and ratios depend on the degree of alteration achieved. Thus, cation geothermometers generally do not indicate reliable temperatures for the cool CO₂-rich hydrothermal systems in the Rhenish Massif. Only silica thermometers appear to be applicable to these systems, since primary silicates are abundant in fresh and altered rocks and equilibrium with secondary silica phases will be achieved at low rock/water ratios already (May, 1998a).

A comparison of measured and simulated element concentrations for different mineral water types is shown in Figure 11. Minor components in solution and in the aquifer rocks, like pyrite or alunite, allow the simulation of various mineral water compositions and reaction conditions. However, trace element concentrations can not always be modelled satisfactory, since they may be in equilibrium with minor phases not detected in the bulk rock XRD patterns, or they occur as trace elements in major phases only. A detailed

discussion is given in May (1998b). Simulated reaction conditions for the four water types (Fig. 11) and a low mineralised CO₂-rich groundwater (Type 0) are given in Table 1; representative mineral water analyses for the different water types are given in Table 2.

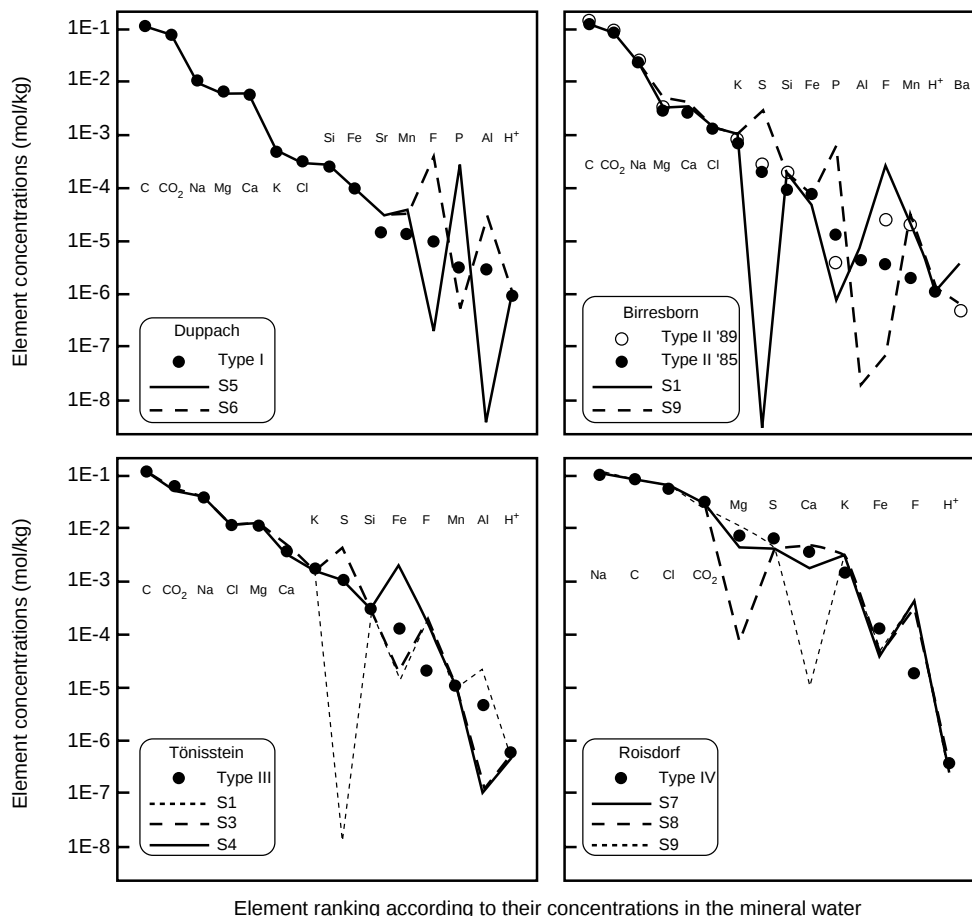
The numerical simulations for average lower Devonian rocks have been used to construct a diagram that facilitates estimates of two main reaction parameters: temperature (depths) and bulk rock/water ratio (May, 1998b). Estimated depths of the mineral water formation, (within deep parts of the fractured aquifer, prior to the fast ascent in fault zones) are typically between 1 and 3 km. One litre of carbonated water has altered 1-400 g of rock (most of it transformed into secondary phases, and some as dissolved species). Systematic variations in water composition from Type 0 to Type IV result from increasing depth and extent of flow systems. Groundwater flow models indicate that deep reaching regional flow systems in the Rhenish Massif are overlain by small, shallow, local flow systems (May *et al.*, 1996). Water flowing in deep, extensive systems is more likely to encounter and mix with saline basement water, CO₂, and fresh wall rocks than fresh groundwater circulating in small, shallow systems. Long residence times in deep flow systems promote advanced wall rock alteration, "mineralization" of CO₂, and the generation of mature mineral waters. Different stages of alteration illustrated by the examples of the flow systems shown in Figure 11 and Table 1 represent a general trend of progressive wall rock alteration and mineral water evolution (Fig. 12)—the neutralisation reaction of acid carbonic waters by basic wall rock.

TABLE 1
Simulated reaction conditions and reaction products

Water Type	0	I	II	III	IV
Total dissolved solids (g/l)	0.275	2.740	2.800	5.400	8.350
Saline water fraction (wt.%)	0	0.03	0.2	2	5.5
Reaction temperature (°C)	12	25	45	60	75
Initial CO ₂ (g/l)	2.5	5.7	8.0	8.3	12
Rock altered (g/l)	1.8	33	75	100	220
SiO ₂ precipitated (g/l)	0.1	0.6	1.3	1.8	3.9
Kaolinite precipitated (g/l)	0	1.9	4.3	5.7	13
Siderite precipitated (g/l)	0	2.8	6.1	7.3	17
Dolomite/ankerite prec. (g/l)	0	0	1.7	2.9	8.3

4 DISCUSSION

The reactions observed in natural flow systems of the Rhenish Massif may serve as analogues for reactions in siliciclastic cap rocks and in fractured reservoirs with rather low matrix porosity. Water circulation through deep parts of



Element ranking according to their concentrations in the mineral water

Figure 11

Comparison of measured and simulated concentrations, for 4 mineral waters representative of different mineral water groups (classification of types after May *et al.*, 1992). The selected simulations (curves S1-S9) demonstrate the sensitivity of some element concentrations to variations of the input parameters.

TABLE 2

Mineral water analyses according to Langguth and Plum (1984); concentrations in mg/l, temperature in °C

Name	Dreis, Alte Nürburgquelle	Duppacher Drees	Birresborn Adonisquelle	Tönisstein Birkenquelle	Roisdorf, Brunnen 5
Type	0	I	II	III	IV
Temperature	10.7	8.9	11.1	11.9	15.3
pH	5.2	6.1	6	6.3	5.8
Li	0	0.2	0.5	0.7	0.6
Na	8.4	219	531	868	944
K	5.2	13.7	28.3	65	31.1
Mg	18.2	160.5	71.7	263.8	87.5
Ca	30.1	238.5	104.2	144.3	126.3
Fe	0.1	5.5	4.3	6.9	4.4
Cl	8.8	11.2	46.1	390	929
HCO ₃	159	2050	1979	3532	1438
SO ₄	17.9	0	19	97	359
NO ₃	12	0.2	2.1	0.6	0.3
SiO ₂	14	32	12	37	10
CO ₂	2466	3551	3972	2602	2383

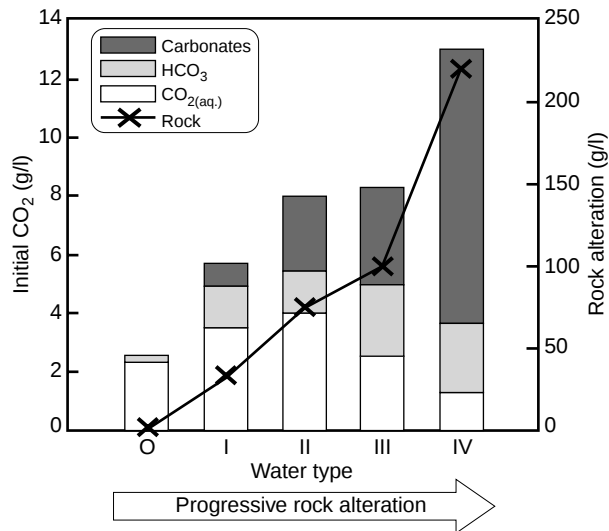


Figure 12

Simulated evolution of HCO₃ waters with progressive wall rock alteration (rock/water ratio), illustrated for five examples representing different water types. Columns indicate fractions of initial CO₂ that have been transformed to solid carbonate, dissolved bicarbonate, and remaining as dissolved gas (aq.) after alteration reactions.

these fractured systems is caused by topography-driven flow. Water discharging below river valleys originates from elevated recharge areas typically in a distance of about 20 km. Fluid and heat transport in a typical flow system within the Rhenish Massif including a fault perpendicular to the course of a river valley and some tributaries has been simulated with the SHEMAT programme (Clauser, 1988; Fig. 13). According to the length of the flow paths, waters have time to react and have access to unaltered wall rock. Hence, they reach different degrees of progressive evolution (Figs. 6 and 12). Shallow flow systems discharging at local streams overly and shield the deep regional groundwater flow. They allow shorter residence times only and hence their waters have less chance and time to react with fresh wall rocks and therefore these waters are only low concentrated. The chemistry of waters evolving from rock dominated cation ratios towards equilibrium (Fig. 5) thus reflects the length and depth of fault dominated flow systems as well as their underground residence time.

Groundwater flow in deep sedimentary basins suited for CO₂ storage may be controlled by topography related hydraulic head gradients, but also by gradients caused by the dewatering of under-compacted sediments, density differences of saline formation waters, and most likely by

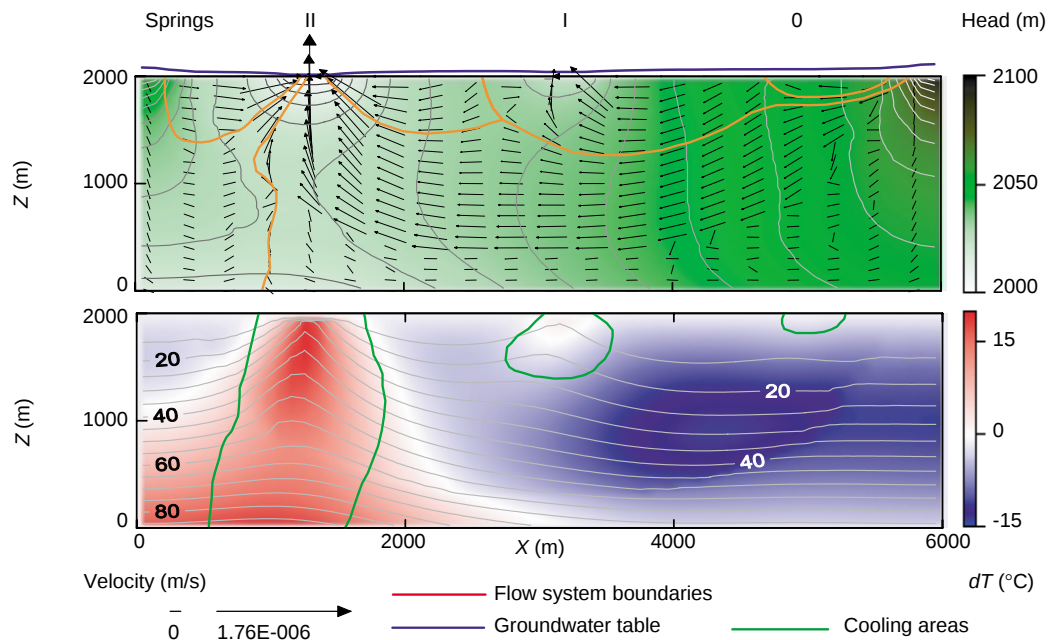


Figure 13

Groundwater flow model for typical topographic situations in the Rhenish Massif. Profiles are plotted in the plane of a fault zone of 5 m width, perpendicular to a river valley and two smaller tributaries. Top: hydraulic heads and Darcy velocity vectors; orange lines separate shallow and deep catchment areas of springs 0 to II. Bottom: temperature contours and thermal anomalies caused by advective heat transport. Areas outlined in green mark cooling in the direction of groundwater flow. Further details about model assumptions can be found in May *et al.* (1996).

pressure build-up due to the injection of CO_2 . Apart from the reservoir and the immediate cap rocks, these pressure differences are probably low, so that the expected flow velocities are low also. At higher temperatures and longer residence times (compared to rather fast topography induced flow) high integral rock/water ratios can be expected. Despite probably higher CO_2 partial pressures in CO_2 stores—compared to Rhenish mineral water flow systems—principal reactions will probably be comparable, leading to the formation of kaolinite, carbonates and silica, on the expense of chlorite and albite (Fig. 14). In case of the topography driven flow systems, along most of the length of the deep flow paths, temperatures increase. Cooling of ascending water is limited to rather restricted areas below groundwater discharge areas in the valley floors. In these parts of the flow systems the precipitation of silica and other minerals with temperature-proportional solubility can be expected, eventually causing self sealing of permeable fault zones.

In the larger part of the deep system (Fig. 13) groundwater velocities are low and temperatures increase along the flow path. In these areas silicate alteration reactions can take place, access to fresh wall rock provided. The reaction progress simulations indicate that porosity enhancement and self-sealing can occur in the same natural flow system. Dissolution should be dominant early, in the recharge area, creating secondary porosity (Fig. 10). Further downstream much of the dissolved CO_2 has been consumed by silicate alteration reactions, the water's content of dissolved solids has increased, and progressive amounts of carbonates

precipitate, so that the cumulative mass of dissolved and precipitated phases becomes balanced or even positive. Self-sealing of fractures due to carbonate precipitation becomes more likely with progressive rock alteration, either due to long contact times at low flow velocities at the margins of intact CO_2 reservoirs, or in downstream areas in case of advective flow of CO_2 -bearing ground water through rocks containing reactive aluminosilicates.

Reaction progress simulations indicate the precipitation of siderite and later that of dolomite (Fig. 10). Saturation indices for most of the CO_2 -rich mineral waters in the Rheinland indicate equilibrium with siderite, while only few reach dolomite saturation. Accordingly, the carbonates analysed from rocks recovered from mineral water wells are iron rich solid solutions: (Mg)-siderite and ankerite-dolomite, however also rarely calcite was observed. The activity ratios of Fe, Ca, and Mg in the mineral waters follow a trend calculated for progressive alteration of average Emsian aquifer rocks (Fig. 15). According to the equilibrium diagram of Woods and Garrels (1992), most mineral waters plot in the dolomite-ankerite stability field. These waters have lost much of their iron already due to siderite precipitation. The mineral water compositions indicate that the precipitation of pure dolomite (simulation I) is not likely. The reaction progress model explains the occurrence of siderite, ankerite and dolomite (solid solutions) within one aquifer. However, no systematic variation of bivalent cation ratios for different water types is evident from Figure 15. Reasons are likely the local wall rock variability, reaction temperatures, initial dissolved carbon contents, and initial groundwater compositions that may explain very low Fe/Ca activity ratios in the case of low concentrated waters. Thus, the mineral water composition and ideal equilibrium diagrams alone are not suitable to predict the amount, number, and composition of carbonate phases precipitating.

In the case of CO_2 storage, the recharge area would be the aquifer surrounding an injection well, while the discharge area would be equivalent to the propagating injection front. Both, dissolution and precipitation may cause geotechnical problems like destabilising the well or reducing injectivity. On the other hand, such siliciclastic rocks may provide an internal geochemical barrier that could, in the long-term, facilitate the in situ mineralisation of parts of the injected CO_2 . For real fractured aquifers reaction kinetics coupled to transient flow conditions has to be considered in order to quantitatively predict mass transfer in space and time. This complex interaction between fluid flow and geochemical reactions is also reflected by the irregular variation of alteration with depth within the sampled wells (up to 600 m depth). And moreover, even within single rocks from fault zones of hand specimen size, both corroded and euhedral quartz crystals occur in veins, demonstrating intricate geochemical variability and probably temporal variability, within the generally strongly altered sample. Thus, geochemical modelling is seen as a tool for the

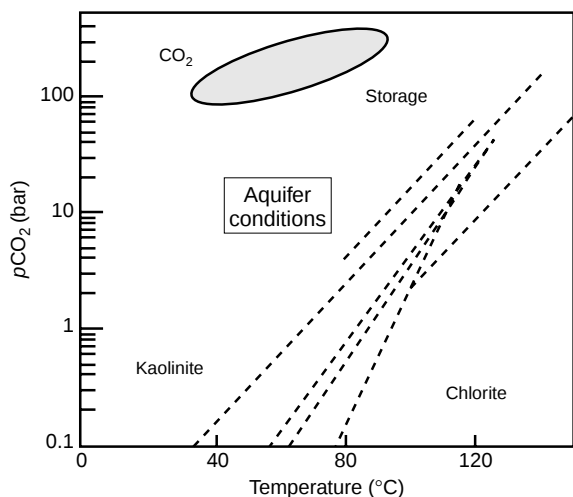


Figure 14

Predominance fields of chlorite and kaolinite for mineral assemblages of albite, chlorite, kaolinite, siderite, and chalcedony in equilibrium with Rhenish mineral waters of type I to IV (Wehr, Neuenahr, Birresborn, and Tönisstein), calculated for various CO_2 partial pressures and temperatures using the thermodynamic simulation software PHREEQE (Parkhurst, 1995).

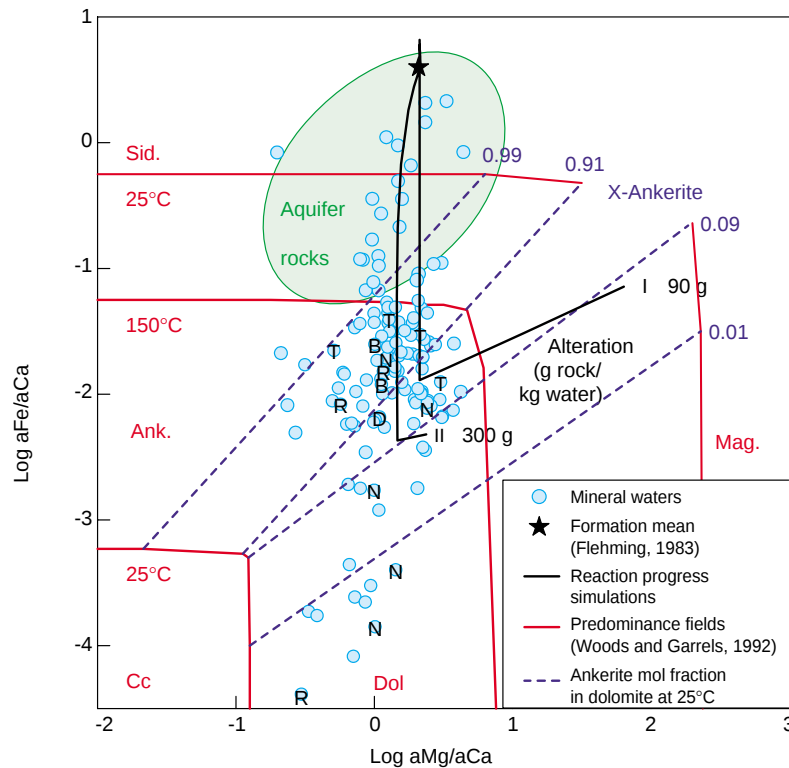


Figure 15

Activity ratios for divalent cations from carbonic mineral springs in the western Rhenish Massif, plotted into the predominance diagram of Woods and Garrels (1992) for carbonates in equilibrium with aqueous fluids. Element concentrations in rocks from mineral water wells are shown for comparison. Two simulated reaction paths are shown:

- I $p\text{CO}_2 = 0.2 \text{ MPa}$, temperature = 20°C , carbonates are pure siderite and dolomite;
 - II $p\text{CO}_2 = 20 \text{ MPa}$, temperature = 70°C , carbonates are ideal solid solutions of $(\text{Fe}_{0.9}\text{Mg}_{0.1})\text{CO}_3$ and $(\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Ca})(\text{CO}_3)_2$.
- Letters indicate mineral waters from Nürburgquelle Dreis (N), Duppach (D), Birresborn (B), Tönisstein (T), and Roisdorf (compare Table 2).

evaluation of the possibility of reactions that are likely to occur, rather than a tool that allows predicting the impact of alteration reactions at specific locations of an aquifer during or after CO₂ injection.

Unfortunately, timing of the alteration reactions described is difficult, or has not been attempted yet. Therefore no reliable reaction kinetic data (for bulk reactions) can be derived directly from the natural analogues described above. However, the variability of alteration degrees within single wells and even samples indicates that results of reactive transport simulations using poorly justified rate constants (for natural impure nonideal solid solutions of sheet- or network silicates) and a simplified structure and geometry (for natural 3D heterogeneous and fractured aquifers hosting transient flow systems) have to be interpreted with caution. Geochemical simulations seem to be more appropriate to aid understanding of alteration processes than to make quantitative predictions about those. The various degrees of alteration found in the rock samples from individual wells document disequilibrium and progressive water evolution. Coupled kinetic reactive transport models might help to constrain the transit time for the water within a flow system and the age of the flow system, *i.e.*, the exposure time of rocks to the carbonated water, within the uncertainties implied by the kinetic constants.

Alteration reactions can "capture" CO₂ leaking from a reservoir. Therefore leakage may not be detectable by geochemical monitoring of free and dissolved gas in shallow

aquifers or at the Earth's surface. The cation composition of deep groundwater may indicate such hidden leakage however. Unfortunately many deep groundwaters are saline brines. Changes due to water-rock interactions may be comparatively small. Thus, in order to detect such changes, the chemical composition of formation waters above storage formations and their variability has to be analysed prior to storage projects. In shallow freshwater aquifers, reactions caused by CO₂ or mixing with ascending saline formation waters will cause more dramatic changes of the water composition that will be easier to detect. However, it is principally desirable to detect leakage as early as possible in order to take actions against it. Otherwise, geochemical monitoring may come into the situation that it has to restrict to the mapping of the extent of damage rather than preventing damage. As a consequence, geochemical monitoring devices for deep well conditions should be developed. Changes of pH should be detectable, before significant changes of major ions occur. Impurities in CO₂ resulting from flue gas or from chemicals used in the separation or transport process which are otherwise absent in deep groundwater are also potentially valuable for leak detection.

CONCLUSION

Natural analogues are valuable to understand slow reactions taking place under *in situ* conditions in a range of non-

stationary flow systems. These reaction conditions cannot nearly be verified in lab experiments. Natural analogues offer a wide range of alteration phenomena due to the “natural parameter variation”. These natural experiments may be used to calibrate geochemical simulation tools and data bases using real world conditions and reactant properties. Such models have to be calibrated at a range of different natural systems. Then they can be used to make predictions about which reactions can be expected in comparable aquifers. Though quantitative predictions for siliciclastic rocks are unrealistic, tendencies about the range of reaction progress and the amount of reaction products in central and distal positions within a storage aquifer can be derived from numerical simulations. Such information may help to design injection strategies taking into account the effects of alteration reactions including measures to mitigate unwanted effects.

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