

EQUILIBRIUM VERSUS KINETICS IN CO₂ DOMINATED HYDROTHERMAL ALTERATION

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SUMMARY - Compositional differences between unaltered protoliths and altered rocks from mineral water wells can be related to the compositional variations between groundwater and highly concentrated bicarbonate waters in order to reveal the alteration reactions. One basic process is sufficient to explain the range of bicarbonate waters occurring in the Rhenish Massif: Carbonic acid, produced by the dissolution of magmatic CO₂ in groundwater, gradually dissolves unstable primary minerals of the wallrock, exposed on fresh fracture surfaces along the flow path, while the successive formation of stable aluminosilicates and carbonates precipitates the surplus of dissolved species. Thermodynamic reaction progress simulations including irreversible and equilibrium steps are suitable to quantify water rock ratios as well as the amounts of reaction products.

1. INTRODUCTION

The understanding of hydrothermal alteration reactions at temperatures below 100°C is made difficult, because of slow reaction velocities. Alteration reactions, especially those involving complex silicate minerals often do not reach thermodynamic equilibria with the surrounding fluids. Protolith minerals formed at higher temperatures may remain unaffected in metastable states of stability even for long periods of time. Thus, calculations of fluid compositions and secondary phase assemblages, based on thermodynamic equilibrium assumptions, often fail to reproduce the observations. Chemical equilibrium considerations between rock and water, useful in metamorphic or high temperature geothermal systems, do not apply to cool hydrothermal alteration reactions. Mineral waters from the Rhenish Massif do not plot along the solid line in Fig. 1, that marks the composition of waters in equilibrium with average crustal rocks (Giggenbach 1988).

To overcome the difficulties of slow reaction kinetics it is necessary to identify and to separate the equilibrium reactions from those alteration steps which are limited by reaction velocities. The consideration of both reaction types in a reaction progress concept allows to calculate the compositions of the altered rocks and those of the associated mineral waters as well. One single reaction progress model is sufficient to explain different degrees of hydrothermal alteration and the occurrence of various mineral water types. This will be demonstrated for the kaolinisation of silicate rocks by cool CO₂ rich waters.

CO₂ rich waters often occur in regions of Quaternary volcanic activity. They are frequently found in areas of continental rifting, associated with alkalibasaltic

volcanism. In areas with subduction volcanism they also occur in hydrothermal systems related to degassing magmas in subvolcanic intrusions.

2. STUDY AREA

The Rhenish Massif is part of a larger region characterized by carbonic springs, recent crustal extension, uplift, rifting, alkalibasaltic volcanism and high fluxes of mantle helium, that extends from the French Massif Central to the Bohemian Massif. Its geodynamic features and the relation between mineral waters and mantle processes have been discussed by May (1994a) and May et al. (in press). The predominant rock types in the massif are Palaeozoic shales, greywackes and sandstones, that form the fractured aquifers for the mineral waters. Within the massif, HCO₃ waters discharge from numerous small springs or wells, with frequency maxima in the Quaternary Eifel volcanic fields. In mineral waters from the margins of the massif, Cl⁻ is the dominant anion.

The CO₂-rich waters reach well-head temperatures of up to 73 °C, while most of the spring waters are only slightly warmer than the mean annual air temperature of 10 °C. Thermal waters discharge in the major valleys and along the margins of the massif from topography driven flow systems. Since many springs are used for drinking and health purposes, they are analysed frequently and a representative set of almost 800 mainly published water analyses has been available for this study. The siliciclastic rocks of the massif are often bleached and kaolinised. This alteration is partly the result of weathering under subtropical conditions in the Mesozoic and in the Early Tertiary. The recent hydrothermal alteration by CO₂-rich groundwaters also

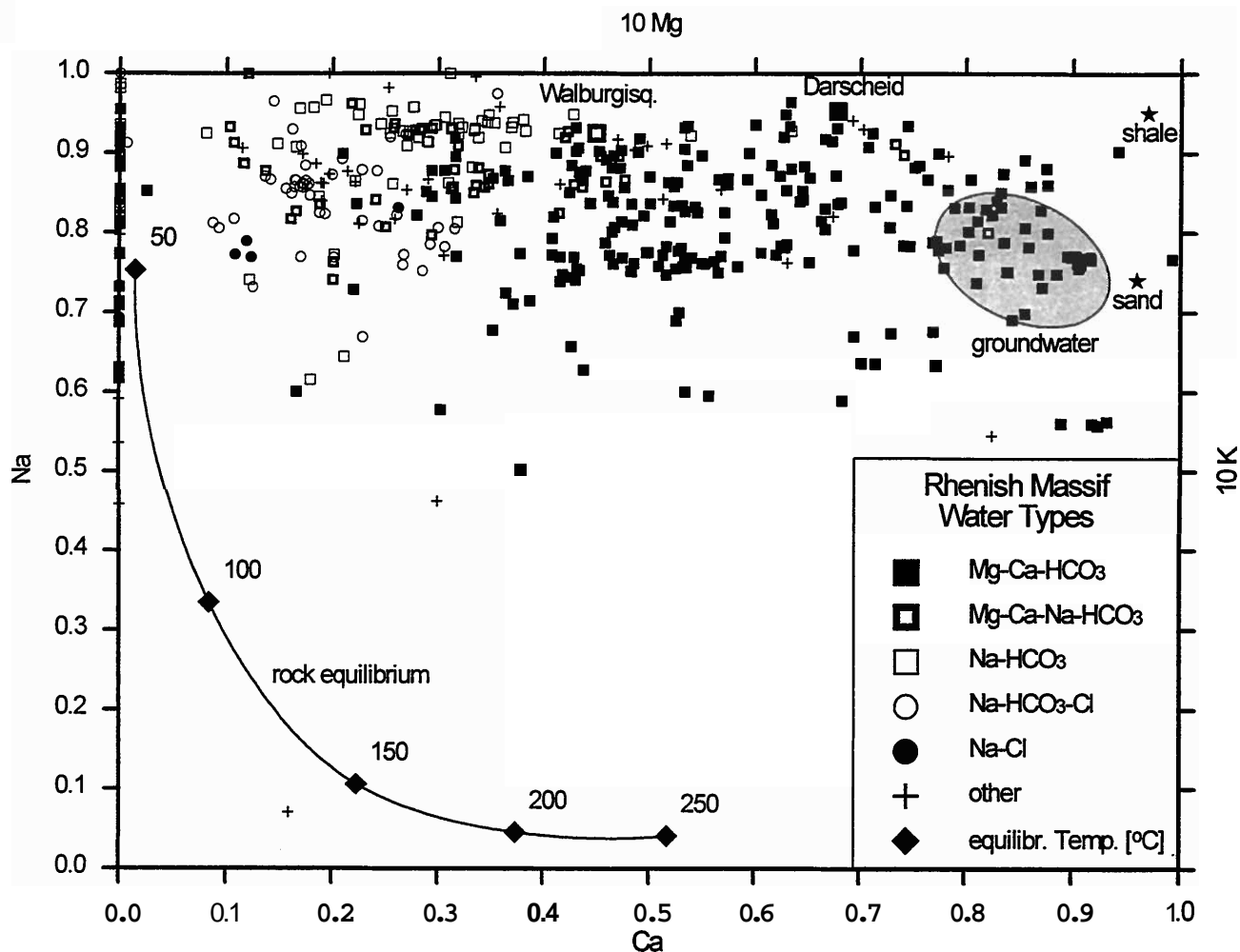
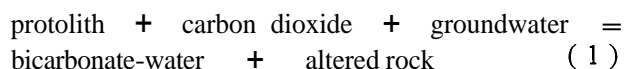


Fig. 1. Mass ratios of alkali and alkaline earth element concentrations in mineral waters from the Rhenish Massif

results in kaolinisation of wallrocks. Iron minerals and the topographical position of the altered rocks allow a distinction between both types of alteration (May 1994b). In the altered rocks encountered in mineral water wells chlorite has been replaced by kaolinite. Their albite contents are lower than in the protoliths. Dolomite/ankerite and (Mg-) siderite are common secondary phases in the altered rocks. Alunite and smectite occur occasionally but barite, cristobalite and halloysite rarely exceed the XRD detection limits. Abundant quartz veins with euhedral crystals indicate that silica precipitates during alteration too. The degree of alteration varies within individual wells, according to the structure of the fractured aquifers. Significant trends with depth (temperature) are the exception in the sampled wells, which are 100 to 600 m deep. Further properties of the secondary phases are given by May et al. (in press).

Matching rock and water analyses from these wells provides the opportunity to test possible alteration reactions using both, the solid reaction products that remain in the aquifer and the dissolved reaction products that emerge in the mineral springs. Suitable reactions have to fulfil mass balances for the changes in

composition of rocks and water, resulting from the alteration reactions:



3. ANALYTICAL RESULTS

Dissolved $\text{CO}_2(\text{aq})$, H_2CO_3 and HCO_3^- are the main carbon species in the slightly acidic waters. The dissociation of H_2CO_3 provides H_3O^+ for the dissolution of the primary minerals. The conversion of H_2CO_3 to HCO_3^- proceeds continuously with progressive rock alteration. Thus, the HCO_3^- concentrations reflect the amount of rock altered by the mineral waters, while CO_2 and H_2CO_3 remaining in the water represent the potential for further rock alteration.

Relative HCO_3^- concentrations in mineral waters from the Rhenish Massif vary from 1 to 95 mol % of total C, indicating quite different degrees of reaction progress and neutralisation of carbonic acid. The cation concentrations provide information on the minerals participating in the alteration reactions. Variograms of the major cations against HCO_3^- concentrations of Ca-

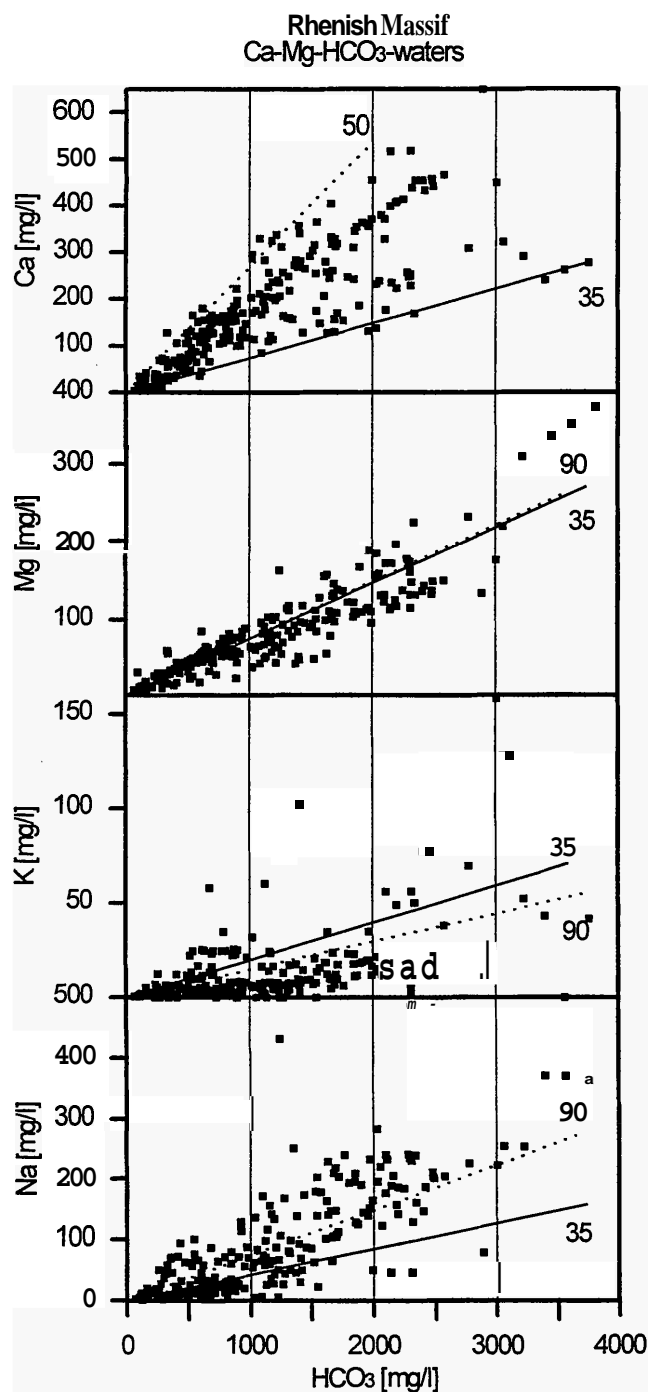


Fig. 2. Variation of major cation concentrations with bicarbonate concentrations in Ca-Mg-Na-HCO₃ waters.

Mg-Na-HCO₃ waters exhibit nearly linear trends with positive slopes, indicating that the acid neutralization is proportional to whole rock dissolution. The Ca, Mg and Na concentrations are in the range expected for the dissolution of average shale or sandstone wallrocks. The dissolution of primary quartz is negligible in the mineral waters, which are usually supersaturated with respect to this mineral. The K contents however, are considerably lower, indicating that illite, the main K phase is stable and only K-feldspar contributes to the K content. Since

the mineral waters are mostly undersaturated with respect to illite, its dissolution reaction appears to be slow. The lines in Fig. 2 have been calculated for complete leaching of all the Ca, Mg and Na of average unaltered sandstones (dotted) and siltstones (solid) from the Palaeozoic basement, and for the dissolution of 5 wt.-% of their K, according to their illite and K-feldspar contents. An equivalent amount of HCO₃⁻ is added to maintain the solutions charge-balance. The main cation contents in one kg of the most highly concentrated waters are equal to their amounts contained in the soluble minerals of 35 g shale or 90 g sandstone.

The congruent dissolution of chlorite should liberate substantial amounts of Fe, Al and Si too. These elements usually have low concentrations in mineral waters, and they do not correlate with the HCO₃⁻ concentrations, as the major cations do, but they are constituents of the secondary phases kaolinite, siderite and (vein-)quartz. The unstable primary minerals chlorite, albite, K-feldspar and calcite dissolve in proportion to their abundance in the wallrocks. The Fe, Al and Si phases precipitate in fast reactions, approaching to thermodynamic equilibrium. The dissolution reactions of the soluble primary minerals do not reach equilibrium instead, as indicated by the excess of aggressive H₂CO₃ still present in the mineral waters. The dissolution of wallrock in CO₂ charged water and the state of reaction progress are limited by the amount of fresh wallrock available along the waters flow path.

4. NUMERICAL RESULTS

The combination of irreversible and equilibrium reactions in reaction progress simulations is a suitable way to quantify the water compositions as well as the associated degrees of wallrock alteration. The computer code PHREEQC of Parkhurst (1995), which is based on an ion association concept, has been used for the numerical models.

The total C (initial CO₂) contents of the Rhenish HCO₃⁻ waters reach 160 mmol/kg. The first equilibrium step in the simulation shown in Fig. 3, is the dissolution of CO₂ at a partial pressure of 0.2 Mpa in pure water, at 20 °C, at pH 6, resulting in a carbonic acid solution of pH 3.8. The lower Devonian siliciclastic wallrocks are represented by silty shales, 100 g containing 8.5 g chlorite (thuringite - ripidolite), 27.5 g illite, 0.35 g kaolinite, 58.5 g quartz, 4 g albite, 0.3 g K-feldspar, and 0.6 g carbonate. The 'soluble' minerals chlorite, feldspar and carbonate comprise 13.8 % b.w. of the rock. S has been added as FeSO₄ without further assumptions about actual redox reactions, which involve Fe and organic C species too. The elements produced by the dissolution of unstable primary minerals are added stepwise to the carbonated water, up to 100 g whole rock. The precipitation of secondary phases and the species distribution in the resulting solution are calculated for equilibrium conditions again.

At first, the element concentrations increase linearly with progressive rock alteration (see Fig. 3). Carbonic acid dissociates to bicarbonate and hydronium ions are consumed in the silicate hydrolysis. After the alteration of about 0.3 g rock by one kg of carbonated water, the solution becomes saturated with silica and chalcedony (to allow for some supersaturation of the solution with respect to quartz) starts to precipitate. Further on the Si content of the water remains almost constant at about 6.9 ppm. Alunite follows at 0.4 g and halloysite (a metastable kaolinite precursor) precipitates beyond 0.5 g whole rock alteration. The predominant supply of SiO_2 from silicate dissolution is sufficient to maintain an excess of silica to precipitate, even during halloysite precipitation, so that the SiO_2 concentration remains at the level of chalcedony saturation. The next mineral to precipitate is siderite at 3 g of rock alteration. At this stage only 390 mg of primary minerals have been dissolved yet and the maximum iron content of 76 ppm is reached. Between siderite and dolomite saturation, a quasi-steady state of reaction progress is attained. The amount of secondary phases produced is proportional to the amount of dissolved rock. Most of the Mg-Ca- HCO_3 waters are within this range of steady state alteration progress, which explains the linear trends in Fig. 2. The alkali and alkaline earth element concentrations continue to increase linearly, until 50 g of rock have reacted with the water and the saturation of dolomite is reached. Now Ca and Mg begin to precipitate, the Mg/Ca ratio increases and the solution evolves forward to become a Na- HCO_3 water.

Higher CO_2 pressures which can occur at depth will not change the general pattern of reaction progress, but they will increase the amounts of dissolved elements forming bicarbonate complexes, and the precipitation of siderite and dolomite will start at higher degrees of rock alteration. At a CO_2 partial pressure of 20 Mpa 3 kg whole rock can react until the solution becomes saturated with respect to chlorite. The high CO_2 content will prevent the precipitation of other secondary silicates and increase the stability field of alunite. Thus, the principal reaction is the same, if we assume dilution of CO_2 -saturated water before - or after reaction with the wall rocks.

The reaction temperature influences the order in which the saturation of the secondary minerals is reached during progressive rock alteration, but not the relative amounts that precipitate. At a temperature of 40 °C, the solubility of CO_2 is lower and the carbonates precipitate earlier than at a reaction temperature of 20 °C. At 40 °C, carbonic acid will be used up earlier and halloysite as well as alunite will finally dissolve in the alkaline carbonate solution.

At initial stages of the alteration reactions (low rock-water ratios), the cation concentrations of the CO_2 -rich but HCO_3^- -poor solutions are close to the composition of the local groundwaters (see Fig. 1).

Variations in the composition of clastic rocks will affect the alteration reactions to a lesser extent, e.g. increased SO_4^{2-} concentrations can result from S-rich shales. Locally pyroclastic rocks and carbonates form parts of the aquifers and modify the alteration reactions and the resulting solutions. In case of the irreversible alteration of West-Eifel foidites, goethite, montmorillonite and other sheet silicates will precipitate. The general pattern of alteration progress is maintained however, since chalcedony, halloysite, siderite and dolomite remain major secondary phases.

Montmorillonite and illite may be secondary phases produced by alteration of the siliciclastic rocks too. They will not replace kaolinite as the predominant clay mineral, but they can replace alunite, at low CO_2 pressures or at higher temperatures, and they can limit the K concentrations.

5. DISCUSSION

The calculated alteration reactions, as described above, confirm the reaction progress concept derived from the considerations of mass balances. The amounts of primary mineral dissolution and the precipitation of secondary phases are in accordance with the modal compositions of rocks from the sampled wells.

The calculated water compositions are similar to those observed in the Rhenish Massif. The analytical element concentrations plot on the calculated reaction progress curves within a narrow range of rock alteration, as shown for two examples: the low-concentrated Fe-Mg- HCO_3 water from Darscheid and the more highly concentrated Na-Mg-Ca- HCO_3 water from the well Walburgisquelle in Bad Neuenahr (see Fig. 3). Low degrees of wallrock alteration produce the Fe rich bicarbonate waters, typical of cool, free discharging springs. No dissolution of iron sulfides, as often stated, is required for low-concentration Fe- HCO_3 waters. The non-monotonous evolution of the Si, Al and Fe concentrations explains their bad correlations with the other elements, which significantly correlate with each other. The precipitation of siderite does not cause kinks in the linear Ca/ HCO_3 and Mg/ HCO_3 trends (see Fig. 2), because it occurs early in the alteration process at very low total contents of dissolved solids (400 ppm), whereas most of the analysed waters have higher concentrations.

Compositional differences among waters at one location, or even within one well, can be explained by different 'access' to fresh wall rocks and various degrees of reaction progress, without the need of hydraulic isolation of different aquifer domains. These differences correspond to varying degrees of alteration within wells, reflecting the nature of the fractured aquifers. 'Access' is used as a bulk term integrating the volumes of water, the rock surface area, the contact time and diffusion through secondary phases on fracture surfaces. The generation of

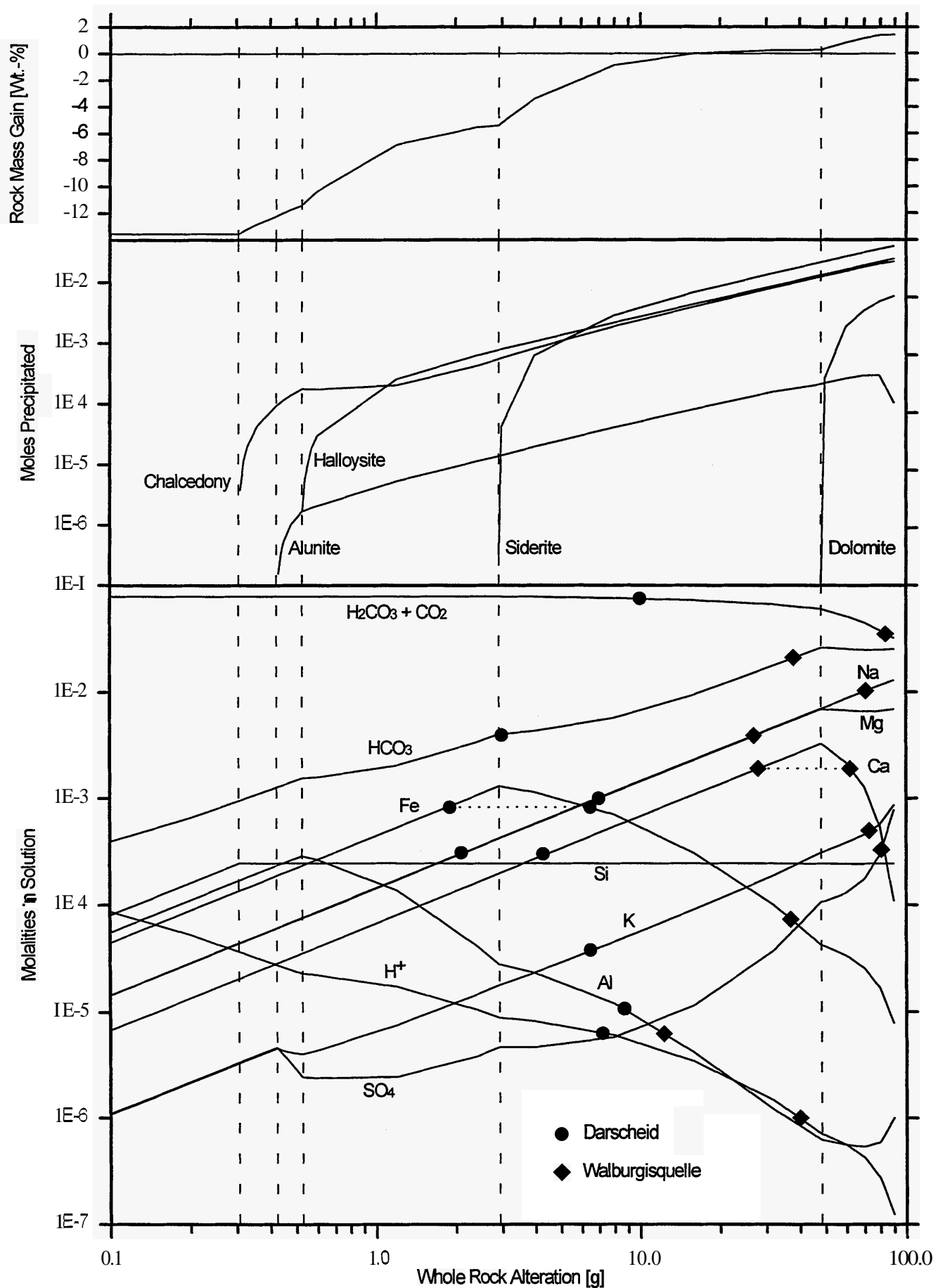


Fig. 3. Progressive alteration of average Siegen/Ems siltstones: rock mass balance (top), secondary phase assemblage (center), element and species concentrations in solution (bottom).

Na-HCO₃ waters is favoured on active faults along the Middle Rhine area, which continuously create new porosity and fresh fracture surfaces.

While the reaction progress simulations show that Na-HCO₃ waters result from advanced wallrock alteration, they are usually seen as products of ion exchange reactions, an explanation made popular by Schwillie (1955). Though Plum (1989) recognized that silicate alteration and carbonate precipitation can produce Na-HCO₃ waters, he did not believe that they could form by these reactions alone and stressed the importance of ion exchange. In none of the papers suggesting ion exchange for Rhenish HCO₃ waters, have the exchange reactions been quantified. Their authors did not demonstrate the effects of ion exchange on specific exchange phases in the wallrocks either.

When dolomite saturation is exceeded, the mineral mass balance becomes positive. The mass of minerals precipitated exceeds the mass of dissolved minerals. (Volume balances depend on the actual mineral densities, but they are similar to the mass changes.) At this stage the alteration process may come to an end by self-sealing of the pore and fracture space. This can be the reason why no further evolved alkaline Na-CO₃ waters, which are expected at further alteration progress, occur in the Rhenish Massif, despite of the remaining alteration potential in the Na-HCO₃ waters.

The reaction progress simulations allow to determine ranges where the cation ratios depend on the amount of wall rock alteration, limiting the applicability of certain geothermometers. While the silica geothermometer is only affected at very low concentrations, thermometers using Ca and Mg are limited to less than ~50 g whole rock alteration per kg water. The simulations provide a way to obtain water/rock ratios from actual water compositions and to test the sensitivity of values obtained for different elements to changes in reaction progress.

The numerical results show the possibility of illite and montmorillonite precipitation. Unknown reaction kinetics, variable mineral compositions and uncertainties of thermodynamical data are reasons not to draw conclusions about their actual formation, based on numerical simulations alone. The detection of low amounts of montmorillonite and secondary illite, among abundant primary illite, by conventional XRD is difficult too. Thus, more detailed clay mineralogical studies are required to reveal the role of illite and montmorillonite in the alteration reactions. The validity of the equilibrium assumptions, for their formation at the time scales of deep groundwater flow, should be tested by hydrothermal experiments.

6. CONCLUSIONS

One single genetic model is sufficient to explain many features of wall rock alteration and the range of different HCO₃ waters found in the Rhenish massif. The variety of individual processes proposed by previous workers to explain the compositions of different water types or the abundance of individual elements can be restricted. Local peculiarities modify the reactions, but they do not alter the general principle of progressive wallrock alteration. Numerical simulations help to check the general probability of possible reactions and they allow to quantify the water chemistry and the wallrock composition as a function of water-rock ratios and physical aquifer conditions. A prerequisite for successful numerical simulations is the identification of irreversible and equilibrium reactions.

7. ACKNOWLEDGEMENTS

The results presented here were obtained during a post-doctoral visit at IGNS, Lower Hutt, sponsored by the Deutsche Forschungsgemeinschaft.

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