Origin of salinity of deep groundwater in crystalline rocks

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ABSTRACT

Deep groundwater in fractured crystalline basement has been reported from deep mines and from scientific deep wells. Highly saline brines have been described from several km depth in the continental basement of the Canadian, Fennoscandian and Ukrainian shields and elsewhere in the world. The origin of salinity is unknown and many different possibilities have been presented. We compare the compositional evolution of deep waters in the Black Forest basement, SW Germany, with those of other deep crystalline waters, and use halogen systematics (e.g. Cl/Br ratios) and other parameters of the waters to deduce the origin of their salinity. In the Black Forest the composition of deep thermal waters results from chemical interaction of surface water with the rock matrix (mainly weathering of plagioclase and mica) and from mixing of the reacted water with stagnant saline deep water. Here we show by Na/TDS-and Cl/TDS-investigations, by molality-ratios of the Na and Cl concentrations, and by Cl/Br systematics that these deep saline waters have a marine origin. The Cl/Br ratios in deep crystalline waters are very close to normal marine ratios (Cl/Br = 288 ppm basis). In contrast, Cl/Br ratios of other possible sources of salinity show distinctly different Cl/Br ratios: water derived from dissolved Tertiary halite deposits of the rift valley is in the order of Cl/Br = 2400 and water from dissolved Muschelkalk halite deposits has values of about Cl/Br = 9900. Leaching experiments on crystalline rocks, on the other hand, show that the average Cl/Br ratio of crystalline rocks is far below Cl/Br = 100.

Terra Nova, 11, 181–185, 1999

Introduction

Continental crust consists predominantly of granitoids and quartzo-feldspathic gneisses. The rocks are typically fractured to various degrees and the fracture system contains water of widely varying composition. The fracture system represents the water reservoir of the continental crust and furthermore the flow system, in short the continental crust acts as an aquifer. Deep groundwater in fractured crystalline basement has been reported from deep mines and from scientific deep wells. Highly saline brines have been described from several km depth in the continental basement of the Canadian, Fennoscandian and Ukrainian shields and elsewhere in the world (Kozlovsky, 1984; Stober, 1986; Frape and Fritz, 1987; Kanz, 1987; Edmunds and Savage, 1991; Pauwels *et al.*, 1993; Emmermann *et al.*, 1995; Banks *et al.*, 1996; Fritz, 1997). Our study area is the Black Forest region in SW Germany, where continental basement is exposed and water data are available from a large number of wells in crystalline rocks.

Regional geology

Geologically, the Black Forest area represents an erosional window through the post-Variscan cover to the Central European continental crystalline basement. The exposed basement rocks stretch N–S about 130 km and with a W–E extension of *c.*50 km. The basement is composed predominantly of granitic and mafic gneisses that are migmatized locally and of post-deformational granite plutons. The uplift and exhumation history of the basement is related to the formation of the Upper Rhine rift system in the Tertiary. The local uplift of the graben shoulders started in the Oligocene and the general regional updoming of the Black Forest area lasted from the Miocene until present time. The uplift exposed the Black Forest to erosion that stripped away the post-Variscan cover and exposed the basement of the European continental crust. Post-Variscan sediments are still present in the Rhine valley as a succession of sedimentary and volcanic rocks, several km thick. The youngest marine sediments in the Rhine valley date back to the Middle Oligocene. Sedimentation in the valley was in fresh water beginning in the Upper Oligocene and in the Miocene. The last contact with marine water was about 24 Ma, and the topography of the Upper Rhine valley gulf periodically favoured evaporation and ultimately led to halite and sylvite deposits in the Lower Oligocene. The last possibility of sea water infiltration of the crystalline basement ended in the northern parts of the Black Forest in the Upper Oligocene and in the south in the Lower Miocene. In the middle to late Miocene (15–10 Ma) the first locally derived crystalline pebbles appear in the conglomerates, indicating that the basement was exposed to the erosion surface from that time on (Stober and Bucher, 1999a; Thury *et al.*, 1994).

Regional hydrogeology

Groundwater composition in the crystalline basement of the Black Forest is quite variable. There are at least three different groundwater types: Cl-rich thermal water, CO_2-rich mineral water and weakly mineralized surface-related water. The chemical characteristics of the two chemically very distinct types of groundwater – CO_2-rich mineral waters and Cl-rich thermal waters – are shown on the Schoeller diagram (Fig. 1).

Thermal water has a higher degree of mineralization in general compared with the CO_2-rich mineral water. Thermal water springs are typically found in granite; mineral water springs are located predominantly in gneiss. In the mineral waters the total dissolved solids (TDS) reach values of 3000–4000 mg kg^{-1}. Detailed information concerning major elements of the water analyses is given in Stober and Bucher (1999a). The source and reservoir regions of the mineral waters are relatively shallow. However, CO_2 probably has a deep-seated source. In contrast, thermal waters with well-head temperatures of up to 65 °C originate typically some thousands of metres below surface, as shown by the geothermo-

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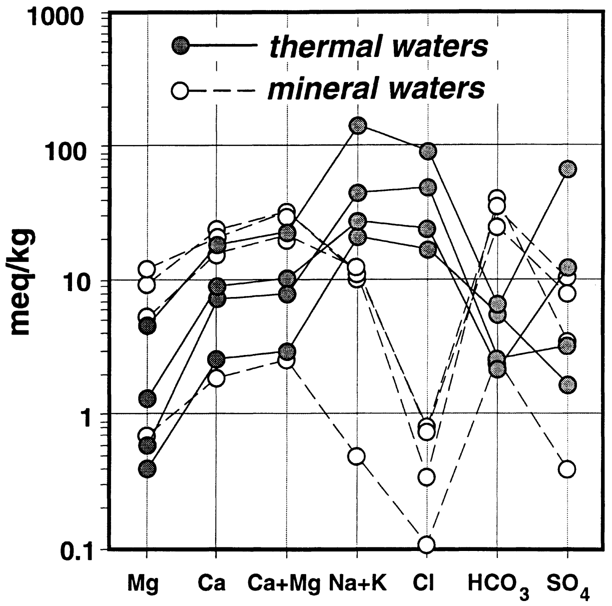

Fig. 1 Logarithmic concentration plot (Schöller diagram) of major ions in thermal and mineral waters of the Black Forest showing the striking chemical differences between the two types of groundwater.

metric calculations of Stober (1995). Well-head temperatures of CO_2-rich mineral waters are typically in the range of 10–15 °C. Bottom hole temperatures of both types of waters are mostly 1–3 °C higher than well-head temperatures since water is pumped out of the wells continuously.

Chemically the thermal waters are NaCl-dominated and TDS ranges from 600 to 10,000 mg kg^{-1}. At a depth below 2–3 km groundwater in the Black Forest generally is of Na–Cl-type and has a TDS of more than 5 g kg^{-1}. Upwelling thermal waters are therefore usually Cl-rich. There are a lot of famous, traditional spas in the region, some known since Roman times, e.g. Baden-Baden, Badenweiler and many others (Stober, 1995; Stober and Bucher, 1999a).

Worldwide, deep waters in the crystalline basement rocks have TDS up to some 100 g kg^{-12} and the water types vary mainly between Na–Cl and Ca–Na–Cl waters.

Geneses of water-composition in crystalline basement rocks

The interesting question is, where does the salinity come from? While there is an abundance of saline water on Earth, chloride is not a common major component of granite. There are many theories to explain the chemical composition of these deep Na–Cl-or Ca–Na–Cl-rich crystalline waters (Thury *et al.*, 1994).

Weathering reactions

In the Black Forest the composition of deep thermal waters results from chemical interaction between surface water and rock matrix, and from mixing of the reacted water with stagnant saline deep water of marine origin. The chemical composition of crystalline water is therefore depth dependent. For short-lived processes the chemical composition of crystalline water is a result of the weathering mainly of plagioclase resulting in two major components: anorthite and albite. If there is enough CO_2 in the water then TDS can increase to high values. Weathering of plagioclase leads to an increase of the Ca, Na, HCO_3 and SiO_2 content in groundwater. Kaolinite is the major residual mineral that forms from feldspar weathering. If calcite saturation is reached then plagioclase weathering produces secondary calcite that precipitates in the fractures and cavities and may be the source of Ca-HCO_3 waters for a new generation of waters. The shallow circulating CO_2-rich mineral waters are a good example of the result of this kind of weathering reaction. Water in a plagioclase environment could develop – depending on the composition of plagioclase – until water is saturated with respect to laumontite and albite, the end-point of a possible evolution of water in a plagioclase surrounding. Nevertheless, weathering of plagioclase continues until all plagioclase is consumed; since weathering reactions of magmatic rocks consume water, TDS in the remaining fluid increases.

Salinity in crystalline waters

With increasing depth, weathering reactions of minerals with lower abundance or small solubility rates, e.g. K-feldspar, biotite or amphibole, become more and more important because of longer residence and reaction time. With increasing depth, the water composition changes to a water-type where Na, SO_4 and Cl will get more and more important. The increase of Cl with depth may not only be the result of weathering of biotite or amphibole with release of Cl out of the crystal-lattice, but could also be the result of halite solution of cracked fluid inclusions and of halite present on mineral grain-surfaces. Halite between mineral grains is reported by several authors (Trommsdorff *et al.*, 1985; Althaus and Bauer, 1987; Markl and Bucher, 1998). Some genetic hints are discussed by Kullerud (1996). At greater depth, where recharge is negligible, important additional processes are water-consuming reactions, e.g. weathering, leading to an increase in TDS. Relicts of fossil seawater may be important for the water chemistry, especially for chlorine.

TDS in crystalline waters increases with depth, temperature, reaction time and flowpath. Only in thermal waters do the Na and Cl contents follow the seawater-dilution line (Figs 2, 3). The Na and Cl concentration in the Cl-poor mineral waters or other near-surface waters increase with TDS too, but their Na and Cl contents are, compared with TDS, much lower than that of diluted seawater (cf. seawater-dilution line on Figs 2, 3). In the Cl-rich thermal waters the molality of Cl is about the same as that of Na (Na/Cl = 1.2). In the CO_2-rich mineral waters the molal ratio is about Na/Cl = 10.0. Both results indicate different origins of salinity in thermal and mineral waters of crystalline basement rocks. Seawater is known to have a molal Na/Cl ratio of about 0.86. The molal-ratios indicate a predominantly marine origin for the salinity in thermal waters, whereas the Na and Cl content of the CO_2-rich mineral waters has its origin in intensive weathering processes.

Halogens

The halogen contents of crystalline water and their host rock matrix, as well as in other rocks, were investigated. Of special interest are chloride and bromide, because they behave rather like conservative tracers in water. Chloride and bromide are the most frequent halogens in sedimentary formation waters. Saline waters could be observed within all kind of formations regardless of the proximity of evaporitic halite deposits. Both chlorine and bromine are important trace elements of magmatic and metamorphic rocks. They can be found in the crystal lattice of minerals, in fluid inclusions of minerals and along grain boundaries of minerals. After initiation of weathering, halogens along grain boundaries are removed most easily compared to halogens bound in the mineral lattice, which are removed only after heavy alteration of the rock matrix.

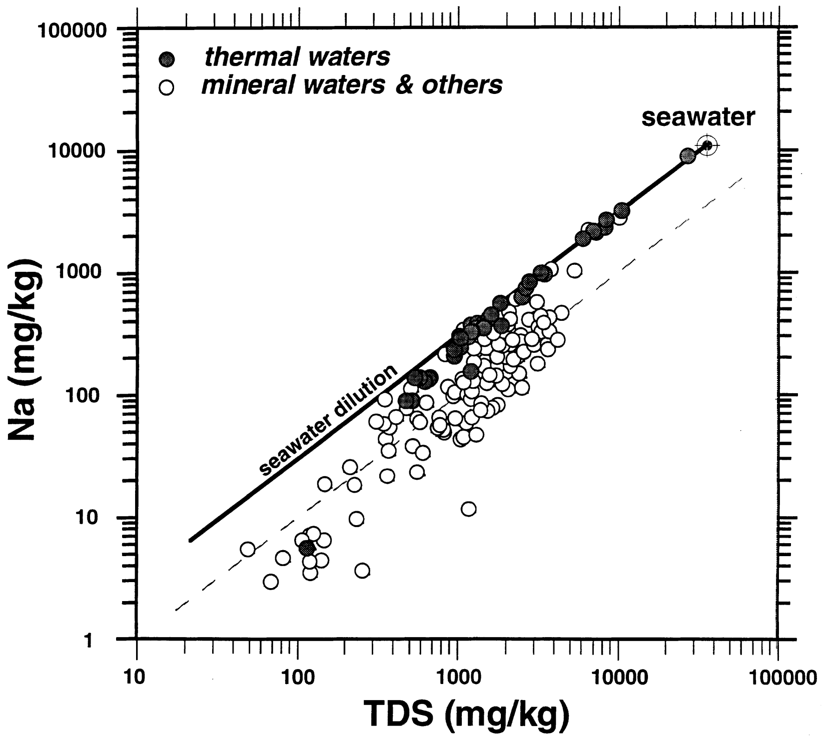

Fig. 2 Na vs. TDS; circles. Thermal water falls close to the seawater dilution line, mineral water define a scattered trend that parallels the seawater dilution line at lower level.

Cl/Br ratios in rocks, fluid inclusions, halite and seawater

The Cl concentration in magmatic rocks is typically some 100 ppm In biotite, amphibole or apatite (hydroxyl minerals) the chlorine-contents can reach values of some 1000 or 10 000 ppm. Magmatic rocks contain in contrast to seawater quite a lot of bromine. Data in the literature show that the Cl/Br ratio in these rocks is typically about Cl/Br = 100 or less (Behne, 1953; Correns, 1956).

The Cl/Br ratio of seawater is constant and has a value of Cl/Br = 288. All Cl/Br ratios given in the text are weight ratios.

Data from fluid inclusions, on the other hand, show very different Cl/Br ratios: during cooling of the rock matrix the colder younger fluid inclusions contain much higher concentrated saline fluids (Mullis, 1987; Yardley and Banks, 1995), probably with lower Cl/Br ratios (« 288) than the warmer, older ones which have higher Cl/Br ratios (» 288), indicating that magmatic rocks could take up much more Br leading to a lower Cl/Br ratio (« 288) in the remaining fluid.

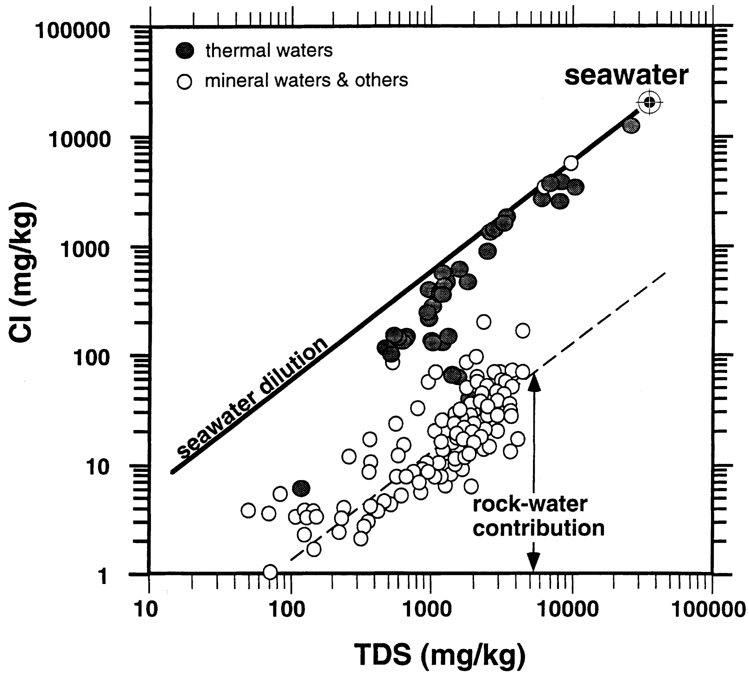

Fig. 3 Cl vs. TDS. The overall pattern is similar to the Na vs. TDS diagram (Fig. 2). Thermal waters with high TDS fall close to the seawater-dilution line, all other waters define a scattered trend that parallels the seawater-dilution line at a lower level. Since Cl in mineral water results from rock–water reactions, the displacement of the Cl-trend is a measure of the rock–water contribution in thermal waters. This contribution is low compared to the contribution from mixing with fossil seawater.

If seawater is diluted with meteoric water the ratio in the diluted seawater will remain the same since seawater-concentration is very high. When seawater is evaporating, then the Cl and Br concentrations increase, but the Cl/Br ratio remains constant, until a TDS-value of about 100 g kg^{-1} is reached. Then halite crystals (NaCl) will begin to grow, containing very little bromine. During further evaporation of seawater, bromide will be enriched in the remaining fluid leading to a decrease of the Cl/Br ratio in the fluid. With ongoing evaporation and after halite formation then sylvite and other salts will grow with a somewhat higher Br content (Braitsch and Herrmann, 1963).

Cl/Br investigations

Figure 4 shows that the Cl/Br-data of the thermal waters in the crystalline basement rocks of the Black Forest follow the seawater-dilution line. The Cl/Br systematics suggest a marine origin of salinity: the Cl/Br ratios on a ppm basis are very close to normal marine ratios (Cl/Br = 288).

In contrast, Cl/Br ratios of other possible sources of salinity show distinctly different Cl/Br ratios. We measured Cl/Br ratios of halite in formations situated nearby, proposed to be responsible for the high salinity in the crystalline waters. We measured the Cl/Br concentrations in dissolved halite solutions originating from different halite depositions in the Rhine graben and in the south of the Black Forest. Water derived from dissolved Tertiary halite deposits of the Rhine rift valley in the west is on the order of Cl/Br = 2400 and water from dissolved Muschelkalk halite deposits in the south of the Black Forest has values of about Cl/Br = 9900 (Fig. 4). Therefore, the origin of the salinity in deep waters of the Black Forest is clearly not derived from solution of evaporitic halite deposits nearby situated.

Our leaching experiments on crystalline rocks, granites and gneisses of the Black Forest, revealed Cl/Br ratios of about 100 and 80, respectively (Fig. 4) These values are significantly lower than seawater. From our experiments we could conclude that biotites in the Black Forest should have Cl/Br ratios of about 42. The Cl/Br ratios differ significantly depending on experimental conditions: experiments without CO_2 input resulted in higher Cl/Br ratios compared with experiments with CO_2 streaming, which implies that we cracked the lattices of the minerals. In the experiments without CO_2 the main input of Cl and Br is from fluid inclusions and from halite along grain boundaries of the minerals. We used powder fractions of about 5 μm, so we are sure that we opened the fluid inclusions, which typically have larger diameters. Therefore, we conclude that there must be relatively – with regard to the Cl/Br ratio – much more bromine in the lattice of relevant hydrate minerals than elsewhere. In the CO_2-saturated experiments there is a contribution mainly from the hydrate mineral biotite to the Cl and Br budget of the solution (Liegl *et al.*, 1999; Stober and Bucher, 1999b).

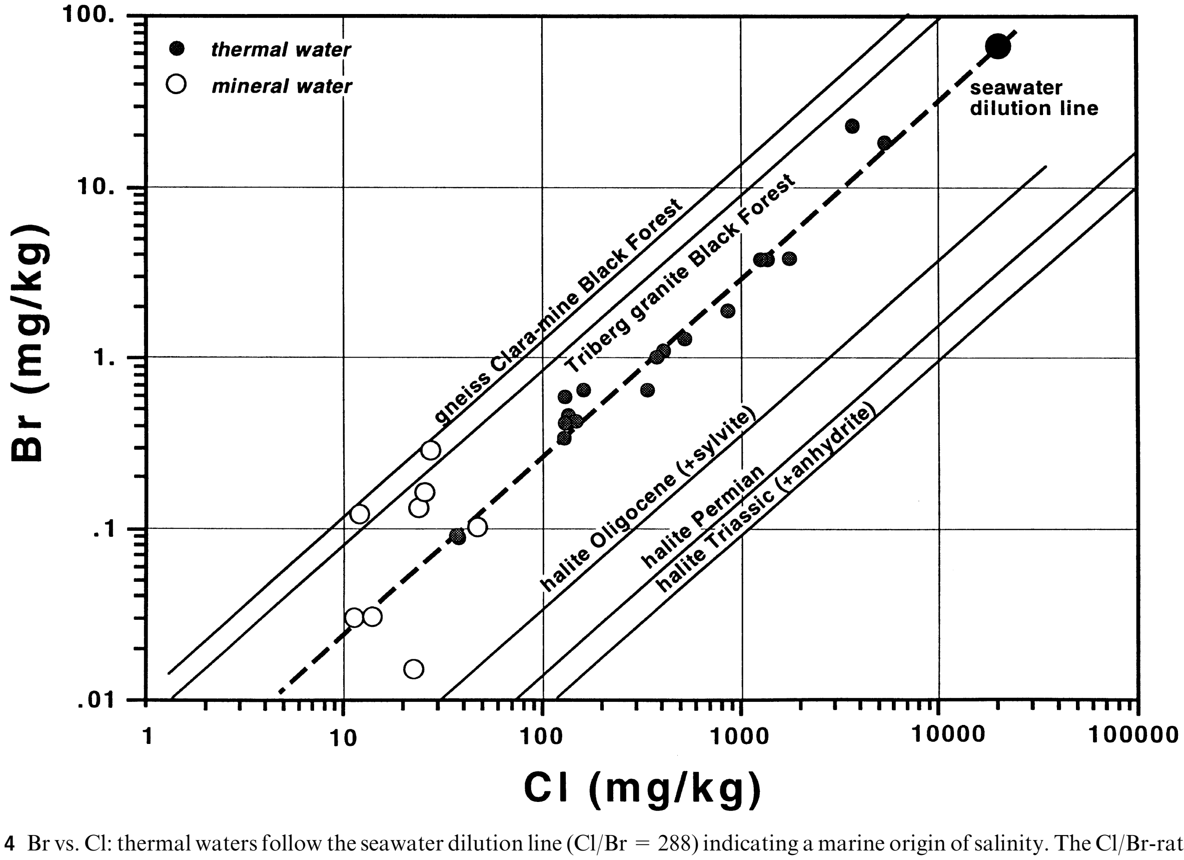

Fig. 4 Br vs. Cl: thermal waters follow the seawater dilution line (Cl/Br = 288) indicating a marine origin of salinity. The Cl/Br-ratio in halite-diluted waters is much higher (Cl/Br = 2400÷9900) and in waters from leaching experiments in magmatic or metamorphic rocks (powderfraction) much lower (Cl/Br « 100)

Conclusions

Our data from waters and different salt samples and experiments with dilution of magmatic rocks clearly show that the deep waters in the crystalline basement of the Black Forest with a mean Cl/Br ratio of 295 must have a predominantly marine origin. The youngest possible age of this water could be Oligocene. The CO_2-rich mineral waters of the Black Forest, which have no deep-seated origin, have low salinities. Their Cl/Br-values are much lower than those of the thermal waters which occur at greater depths and show the influence of the CO_2-induced intensive water–rock interaction. In contrast, deep groundwater from Precambrian shield areas has significantly lower Cl/Br ratios than water from the Black Forest. These waters have had a much longer reaction history and consequently contain a much higher water–rock interaction component. Their Cl/Br values evolved due to halite precipitation in brines oversaturated with respect to NaCl due to water-consuming processes and from prolonged reaction with crystalline rocks.

Acknowledgements

Financial support from the DFG (German research community) is gratefully acknowledged. The authors would also like to thank two anonymous reviewers.

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Received 22 June 1999; revised version accepted 12 October 1999