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TECHNISCHER BERICHT 85-05

SONDIERBOHRUNG BÖTTSTEIN – RESULTS OF HYDROCHEMICAL INVESTIGATIONS: ANALYSIS AND INTERPRETATION

F. J. PEARSON

JANUARY 1985

INTERA TECHNOLOGIES, INC., HOUSTON, USA

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ABSTRACT

During drilling and testing at Boettstein, samples were collected for geochemical and isotopic analysis. The sampling and analytical procedures, and chemical and isotopic results are described in detail in other Nagra Technische Berichte. This report reviews the procedures and analyses and provides a geochemical interpretation of the results.

Two sedimentary horizons were sampled: the upper Muschelkalk and the Buntsandstein/weathered crystalline zone. Four sets of samples for geochemical analyses and five for isotope analyses were taken from the crystalline section above 1,000 m. They represented the three zones of highest hydraulic conductivity in that interval. The zones of highest conductivity below 1,000 m were also sampled but yielded so little water that only mixtures of formation water and borehole fluid could be collected.

Samples were collected by pumping or from artesian outflow at the surface, and by using pressure vessels at depth. The crystalline section was drilled with deionized water and (or) formation water which contained uranine and MTFMBA tracers. The residual drilling fluid present in samples could thus be monitored precisely.

The sedimentary section was drilled with mud which contained no tracer. Environmental tritium was used as a tracer for samples from both sedimentary and crystalline zones.

The amount of drilling fluid present in the Muschelkalk and upper crystalline samples was negligible for geochemical interpretation. The samples from the Buntsandstein/weathered crystalline zone also contained very little drilling fluid, but, because the interval had been drilled with brine, the sample was not suitable for geochemical interpretation.

The zone of highest hydraulic conductivity in the lower crystalline section was sampled several times. No sample contained less than 40 percent drilling fluid, but the tracer in the drilling fluid made it possible to calculate back to the composition of formation water and so make some geochemical conclusions.

The analyses were examined for charge balance, concordance between measured and calculated total dissolved solids content, and for consistency between duplicate

samples or analyses. All showed excellent internal consistency and agreement among duplicates. The results were also examined for their geochemical consistency using the geochemical computer program PHREEQE.

Calculations using measured pH values resulted in dissolved CO_2 concentrations below those measured, and indicated that all samples are oversaturated with respect to calcite. From this it seems all the measured pH values are too high, probably as a result of CO_2 gas loss during sampling or analysis.

The pH of Muschelkalk formation water was calculated using its analyzed dissolved CO_2 content. At this pH, Muschelkalk water is at equilibrium with both calcite and dolomite.

There is isotopic and petrographic evidence that calcite is precipitating from water now present in some fractures in the upper crystalline section. pH values for the samples from this section were calculated assuming the formation water is saturated with respect to calcite.

All samples were affected by the iron packers, tubing and newly-installed casing in the borehole. Iron and hydrogen were added to the samples by corrosion of this iron. Dissolved iron values representative of the formation waters were estimated from analyses from older wells sampled during the Regional Program. Oxidation potentials calculated from the H_2/H^+ couple are more reducing than those from any other indicator and are not representative of the formation waters.

Small concentrations of dissolved oxygen were reported in almost all samples. The oxygen was most probably introduced during sampling and was not present in the formation water.

Oxidation potential values were derived from measured platinum electrode potentials, calculations using analyzed concentrations of members of redox couples, and calculations based on mineral-water and mineral-mineral reactions. The waters appear to be responding to a range of oxidation potentials. The magnetite/hematite mineral pair and the redox pairs comprising the dissolved species NH_4^+/N_2 and CH_4/CO_2 give similar values and define the most reducing conditions to which the waters respond. The potential at which the uranium dissolved in the waters would be in equilibrium with uraninite is more positive and represents the most oxidizing conditions to which the waters respond.

The potentials measured with the platinum electrode were not consistent with any other single indicator of oxidation potential. The measured potentials of some samples corresponded to values calculated from the H_2O/O_2 couple using Sato's (1960) relationship between dissolved oxygen and oxidation potential. Potentials measured in other samples were similar to values calculated from the dissolved uranium concentrations.

Aluminum and silica concentrations of waters from the upper crystalline were calculated assuming saturation with respect to kaolinite and chalcedony. The calculated aluminum concentrations agreed with those measured within the analytical precision reported. Two dissolved silica analyses agree with the calculated values but two are significantly higher. It is possible that the high-silica samples were not filtered before silica analysis.

Calculations suggest that all samples are at equilibrium with fluorite. However, no fluorite was observed in the core.

Water in the Muschelkalk is saturated with respect to calcite, dolomite and gypsum. Its chemistry is interpreted as evolving through a process of dedolomitization driven by gypsum dissolution. The stable carbon isotopic composition of the water agrees with the values calculated from a model of this dedolomitization process and thus supports it. With the model, the ^{14}C content can be used to estimate a water residence time of $17,000 \pm 6,000$ years.

Samples for geochemical and isotopic analyses were taken from zones in the upper crystalline centered on depths of 399, 621, 619 and 792 m. The 399 and 621 m samples were taken during drilling, while the 619 and 792 and a sample from 649 m for isotopes alone were collected during the testing phase, after the completion of drilling.

The chemistry of water in the upper crystalline section is virtually identical in all samples. It is a sodium-bicarbonate water with pH of about 8 and a total dissolved solids content of 1,000 to 1,110 mg/l. It appears to be responding to oxidation potentials in the range of -0.1 to -0.3 volts.

Samples from the Buntsandstein/weathered crystalline and those taken during drilling have decreasing ^{14}C contents with depth. The ^{14}C from the Buntsandstein/

weathered crystalline at about 316 m was 12 to 14 percent modern carbon (pmc), at 399 m it was 8 pmc and at 621 m it was <1.3 pmc.

Two later samples were taken from the same water-bearing zone as the 621 m sample. The 619 m sample, taken about 200 days later had about 8 pmc and the sample from 649 m taken about 260 days after the 621 m sample had about 14 pmc.

This behavior suggests that the water-bearing zones of the upper crystalline are well connected. While under natural conditions, deeper waters at Boettstein have lower ^{14}C contents and so longer residence times, the flow in the system induced by the borehole was enough to bring water from the Buntsandstein/weathered crystalline to below 620 m in no more than 250 days.

It is clear from these results that future sampling in boreholes of this type must be done as soon after drilling as possible.

The deep crystalline section is represented by a series of samples from an interval centered on 1,326 m. These samples are of mixtures of formation water with traced, de-ionized drilling fluid. The composition of formation water was estimated by extrapolating the compositions of the mixtures to a tracer concentration of zero.

Water from the deep crystalline is a sodium-chloride water with a total dissolved solids content of over 13,000 mg/l. The origin and evolution of this water cannot be evaluated without further study, but it is likely that it has a very high residence time in the crystalline rock and may have its origin in, or be influenced by, water in the Permo-Carboniferous trough.

ZUSAMMENFASSUNG

Während der Bohr- und Testphase wurden in Böttstein Proben für geochemische und isotopenhydrologische Analysen entnommen. Die Methoden der Probenahme und Analyse sowie die Ergebnisse der Untersuchungen werden in anderen Technischen Berichten der Nagra eingehend beschrieben; der vorliegende Bericht dagegen gibt einen Ueberblick über die Verfahren und befasst sich vorwiegend mit der geochemischen Interpretation der Resultate.

Beprobt wurden u.a. zwei Aquifere im Sedimentgestein: der obere Muschelkalk (Trigonodus-Dolomit bis Dolomit der Anhydrit-Gruppe) und der Buntsandstein mit den obersten Metern des (verwitterten) Kristallins. Aus den drei Zonen höchster hydraulischer Leitfähigkeit im Kristallin oberhalb von 1000 m wurden für geochemische Analysen vier, für Isotopenuntersuchungen fünf Probensätze genommen. Die durchlässigste Zone unterhalb 1000 m wurde ebenfalls beprobt, ergab jedoch nur so wenig Wasser, dass lediglich mit Deionatspülung vermischte Grundwasserproben gezogen werden konnten.

Gewonnen wurden die Proben entweder durch Pumpen, aus artesischem Auslauf an der Oberfläche oder durch den Einsatz von Druckgefässen im Bohrloch. Im kristallinen Bereich wurde mit deionisiertem Wasser und/oder Formationswasser gebohrt, das mit Natriumfluorescein- und MTFMBA-Tracer markiert war; dadurch konnte der Anteil von verbleibender Bohrspülung in den Proben genau kontrolliert werden. Der sedimentäre Bereich wurde mit Tonspülung (ohne Tracer) erbohrt. "Natürliches" Tritium wurde als Tracer in Sediment- und Kristallingrundwässern interpretiert.

Weder im Muschelkalk noch im Kristallin wurden die geochemischen Untersuchungen durch die geringen Mengen von Bohrspülung beeinträchtigt. Auch die Probe aus dem Buntsandstein und verwitterten Kristallin enthält sehr wenig Spülflüssigkeit; da aber dieses Intervall mit Tonsalz-Spülung erbohrt wurde, sind die Proben für eine geochemische Interpretation ungeeignet.

Die Zone der höchsten Permeabilität im tieferen Kristallin wurde mehrfach beprobt: Keine Probe enthielt weniger als 40 % Spülflüssigkeit; dennoch war es möglich, aus dem Tracergehalt den Anteil an Formationswasser zu errechnen und einige geochemische Schlussfolgerungen zu ziehen.

Die Analysen wurden auf Ionenbilanz, Uebereinstimmung zwischen gemessener und berechneter Gesamtmineralisierung und auf Unterschiede zwischen Paralleluntersuchungen geprüft; alle Analysen zeigten dabei eine ausgezeichnete interne Konsistenz bzw. Uebereinstimmung. Ausserdem wurden die Resultate mit dem Computerprogramm PHREEQE auf ihre geochemische Plausibilität überprüft.

Berechnungen auf der Basis gemessener pH-Werte ergaben niedrigere CO_2 -Konzentrationen als bei der Analyse, was eine Uebersättigung der Proben in Bezug auf Calcit bedeuten würde. Es scheinen also alle gemessenen pH-Werte zu hoch zu sein, was auf einen Verlust von CO_2 bei der Probenahme oder Analyse zurückgeführt werden dürfte.

Der pH-Wert des Muschelkalkwassers wurde anhand des gemessenen Gehalts an gelöstem CO_2 berechnet; dieses Wasser befindet sich damit bezüglich des Calcits und Dolomits im Gleichgewicht.

Isotopenuntersuchungen und petrographische Befunden zeigen, dass in den Wässern einiger Klüfte im oberen Bereich des Kristallins Calcit ausfällt; entsprechend wurden die pH-Werte dieser Proben unter der Annahme einer Calcit-Sättigung berechnet.

Alle Proben unterliegen dem Einfluss der Eisenteile an den Packern, der Steigleitung und der Verrohrung des Bohrlochs: Durch die Korrosion gelangen Eisen und Wasserstoff in die Proben, sodass die Werte für gelöstes Eisen in den Formationswässern aus Analysen von Proben früherer Bohrungen des hydrogeologischen Regionalprogramms geschätzt wurden.

Die Redoxpotentiale, die aus dem H_2/H^+ -Paar errechnet wurden, sind negativer als jene, die sich aus anderen Indikatoren ableiten lassen und sind wegen der oben erwähnten Korrosionsprozesse nicht repräsentativ für die Grundwässer.

Gelöster Sauerstoff, der in fast allen Proben in geringen Mengen enthalten ist, muss wahrscheinlich auf die Probenahme zurückgeführt werden; er ist ursprünglich nicht im Grundwasser vorhanden.

Die Redoxpotentiale wurden abgeleitet von den an Platinelektroden gemessenen Potentialen, von Berechnungen aus Analysenwerten der Komponenten entsprechender Redoxpaare sowie der Reaktionen zwischen Wasser- und Mineralphasen.

Es scheint, als reagierten die Wässer innerhalb eines engen Bereichs von Redoxpotentialen. Dabei ergeben sich ähnliche Werte für das mineralische Magnetit/Hämatit-Verhältnis und für die Redoxpaare mit den gelösten Spezies NH_2^+ und N_2 bzw. CH_4 und CO_2 . Die Paare bestimmen die niedrigsten Potentiale (untere Grenzwerte), auf die die Wässer reagieren. Hingegen werden die am stärksten oxidierenden Bedingungen (obere Grenzwerte) durch das Potential bestimmt, das sich aus dem Gleichgewicht zwischen gelöstem Uran und Uraninit ergibt.

Die mit der Platinelektrode gemessenen Potentiale sind mit keinem anderen einzelnen Redoxindikator konsistent. Die gemessenen Potentiale einiger Proben entsprechen jenen Werten, die über das H_2O/O_2 -Paar unter Verwendung von SATO's (1960) Beziehung zwischen gelöstem Sauerstoff und Redoxpotential berechnet wurden. An anderen Proben gemessene Potentiale wiederum ähnelten den aus Konzentrationen gelösten Urans errechneten Werten.

Die Konzentrationen von Aluminium und Silizium in Wässern aus dem oberen Kristallin wurden unter Annahme einer Kaolinit- bzw. Chalzedonsättigung errechnet. Der Aluminiumgehalt stimmt mit den gemessenen Werten innerhalb der Analysengenauigkeit überein. Zwei Analysen der gelösten Kieselsäure entsprechen den berechneten Werten, zwei jedoch ergaben beträchtlich höhere Konzentrationen. Möglicherweise waren die Proben mit hohem Silizium-Gehalt vor der Analyse nicht gefiltert worden.

Ogleich im Bohrkern kein Fluorit beobachtet wurde, ergaben die Berechnungen doch, dass sich alle Proben im Gleichgewicht mit Fluorit befanden.

Das Wasser des oberen Muschelkalks ist gesättigt in Bezug auf Calcit, Dolomit und Gips. Bei der Interpretation wurde davon ausgegangen, dass der Wasserchemismus auf Entdolomitierungsvorgänge infolge von Gipslösung zurückgeführt werden kann. Dabei stimmt der Gehalt an stabilen Kohlenstoffisotopen überein mit den Werten, die mit Hilfe eines Entdolomitierungsmodells errechnet wurden. Dies ist eine gute Bestätigung des Modells. Aus dem ^{14}C -Wert errechnet sich damit ein Modellalter von $17'000 \pm 6000$ Jahren für das Muschelkalkwasser.

Geochemische und Isotopenanalysen im oberen Kristallin wurden an Proben aus 399, 621, 619 und 792 m Tiefe durchgeführt; die 399 m und 621 m-Proben stammen aus der Bohrphase, während die 619 m und 792 m-Proben sowie eine ausschliesslich für Isotopenuntersuchungen aus 649 m Tiefe während der Testphase, also nach Abschluss der Bohrung, gezogen wurden.

Die chemische Zusammensetzung des Wassers im Bereich des oberen Kristallins ist in allen Proben praktisch gleich: es handelt sich um ein Natrium-Bicarbonat-Wasser mit einem pH-Wert von etwa 8 und einem Gehalt an gelösten Feststoffen von 1000 bis 1110 mg/l. Das Redoxpotential liegt wahrscheinlich zwischen -0.1 und -0.3 V.

In den Proben aus Buntsandstein und verwittertem Kristallin sowie in jenen aus der Bohrphase im Kristallin nimmt der ^{14}C -Gehalt mit der Tiefe ab. Die ^{14}C -Konzentration im Buntsandstein-Wasser aus 316 m Tiefe war 12 - 14 % modern; bei 399 m ergaben sich 8 % modern und bei 621 m weniger als 1.3 % modern.

Zu einem späteren Zeitpunkt wurden aus der wasserführenden Zone zwischen 600 und 650 m noch einmal 2 Proben gezogen: die 619 m-Probe mit ca. 8 % Kohlenstoff-14 modern wurde etwa 200 Tage, die mit 14 % modern aus 649 m Tiefe ca. 260 Tage später entnommen als die aus der Bohrphase bei 621 m.

Die Befunde weisen auf einen engen hydraulischen Zusammenhang zwischen den wasserführenden Zonen des oberen Kristallins: Während die tieferen Wässer in Böttstein unter natürlichen Bedingungen einen niedrigeren ^{14}C -Gehalt d.h. eine längere Verweilzeit aufweisen, genügte der durch die Bohrung induzierte artesische Abfluss bereits, um Wasser aus der Zone von Buntsandstein und verwittertem Kristallin in nur 250 Tagen etwa 300 m tiefer zu leiten.

Dieser Sachverhalt bedeutet aber auch, dass in Zukunft Proben aus Bohrungen dieser Art so schnell wie möglich nach Erbohren der wasserführenden Zone genommen werden sollten.

Das tiefere Kristallin wird durch eine Reihe von Proben aus dem Bereich von 1326 m repräsentiert, die eine Mischung von Formationswasser mit markiertem deionisiertem Wasser enthalten. Die Zusammensetzung der Mischung wurde auf eine Tracerkonzentration von null extrapoliert und somit der Grundwasser-Chemismus errechnet.

Das Wasser des tieferen Kristallins ist ein Natrium-Chlorid-Wasser mit einem Gehalt an gelösten Feststoffen von mehr als 13'000 mg/l. Die Herkunft und Entwicklung dieses Wassertyps bedarf noch genauer Abklärung, doch scheint eine hohe Verweilzeit im Kristallingestein wahrscheinlich; möglicherweise entstammt er dem Permokarbon-Trog oder ist zumindest von ihm beeinflusst.

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1. INTRODUCTION

During the drilling and testing phases of the Boettstein borehole, a number of water samples were collected for chemical and isotopic analyses. The sampling and analyses followed the program of work given in NTB 82-09 and are described in NTB 85-01, Chapter 8.

This report examines the sampling and analytical results and provides a geochemical interpretation of them. An overview of the samples taken is given in the remainder of this chapter. Chapters 2 and 3 describe the sample collection procedures and the selection of samples for detailed interpretation. Chapter 4 discusses in some detail the methods used to critically evaluate the samples themselves and the principles underlying the geochemical interpretations made. The geochemistry of the sedimentary formation waters is given in Chapter 5, and of the upper and lower crystalline sections in Chapters 6 and 7. Chapter 8 provides a summary of the conclusions of the previous chapters.

1.1 Sedimentary Sequence

Water samples were taken from two sedimentary horizons at Boettstein. A pumping test of the water-bearing upper Muschelkalk from 123.2 to 202.3 m (meters) depth was conducted beginning on 29-October-1982 (NTB 85-01). A water sample was taken at the conclusion of this test.

The second sedimentary formation of interest was the Buntsandstein. At Boettstein, the top of the Buntsandstein is at 307.12 m, and it directly overlies strongly weathered crystalline rock at 315.30 m. Several samples were taken from intervals including the Buntsandstein and adjacent upper weathered crystalline rock both during drilling in November, 1982 and later after the conclusion of borehole testing in January, 1984 through casing perforations made for this purpose (NTB 85-01).

The Muschelkalk was drilled using fresh-water mud and heavily pumped before the water samples were taken. Although no tracer was used in the drilling fluid for the sedimentary sequence at Boettstein, the tritium content of the sample suggested that it contained no more than 1% drilling fluid and, thus, it well

represents the formation fluid itself. The Buntsandstein/weathered crystalline zone was drilled with salt-water mud, however, and yielded much less water than did the Muschelkalk. Thus, it is less certain that the several Buntsandstein/weathered crystalline samples do not still reflect the presence of residual drilling fluid in spite of the attempts made during their collection to minimize this potential problem.

1.2 Crystalline Rock

Figure 1.1 shows the distribution of hydraulic conductivities in the crystalline rock of the Boettstein borehole as given in NTB 85-08. It is apparent that the hydrologic regime at depths below about 1,000 m is quite different from that at shallower depths. Below 1,000 m, only the zone from about 1,320 to 1,340 m has a hydraulic conductivity above 10^{-10} m/s (meters per second). In the upper part of the crystalline section however, three zones are present with conductivities above 10^{-7} m/s - from about 340 to 410 m, 610 to 650 m and 785 to 805 m.

This difference above and below about 1,000 m is also evident in the chemistry and mineralogy of the core material as described in the Boettstein Borehole Geology Report (NTB 85-02). For example, as the 1:1,000 profile in that report shows, ferric iron minerals are common in fractures above about 950 m, but occur only infrequently between 950 and 1,050 m and are entirely absent below about 1,050 m. This pattern is also evident in the figure of that report which displays the ratio of ferric (Fe^{+3}) to total iron (oxidation grade) in the core. In fresh or only weakly altered rock at all depths, this ratio is less than about 0.3. Above 950 to 1,000 m, however, the ratio in fracture material and in strongly altered crystalline rock approaches 0.9. The pattern of greater alteration, increasing oxidation state and the presence of several zones of relatively high hydraulic conductivity suggests that the region above 1,000 m is one of active water circulation. The character of the lower zone on the other hand suggests that little or no active circulation is occurring.

The zones from which complete water samples were taken are also shown in Figure 1.1. The collection procedures and results of analyses of these samples are described in detail in Chapters 2 - 7. A summary here, though, is an important part of this introduction.

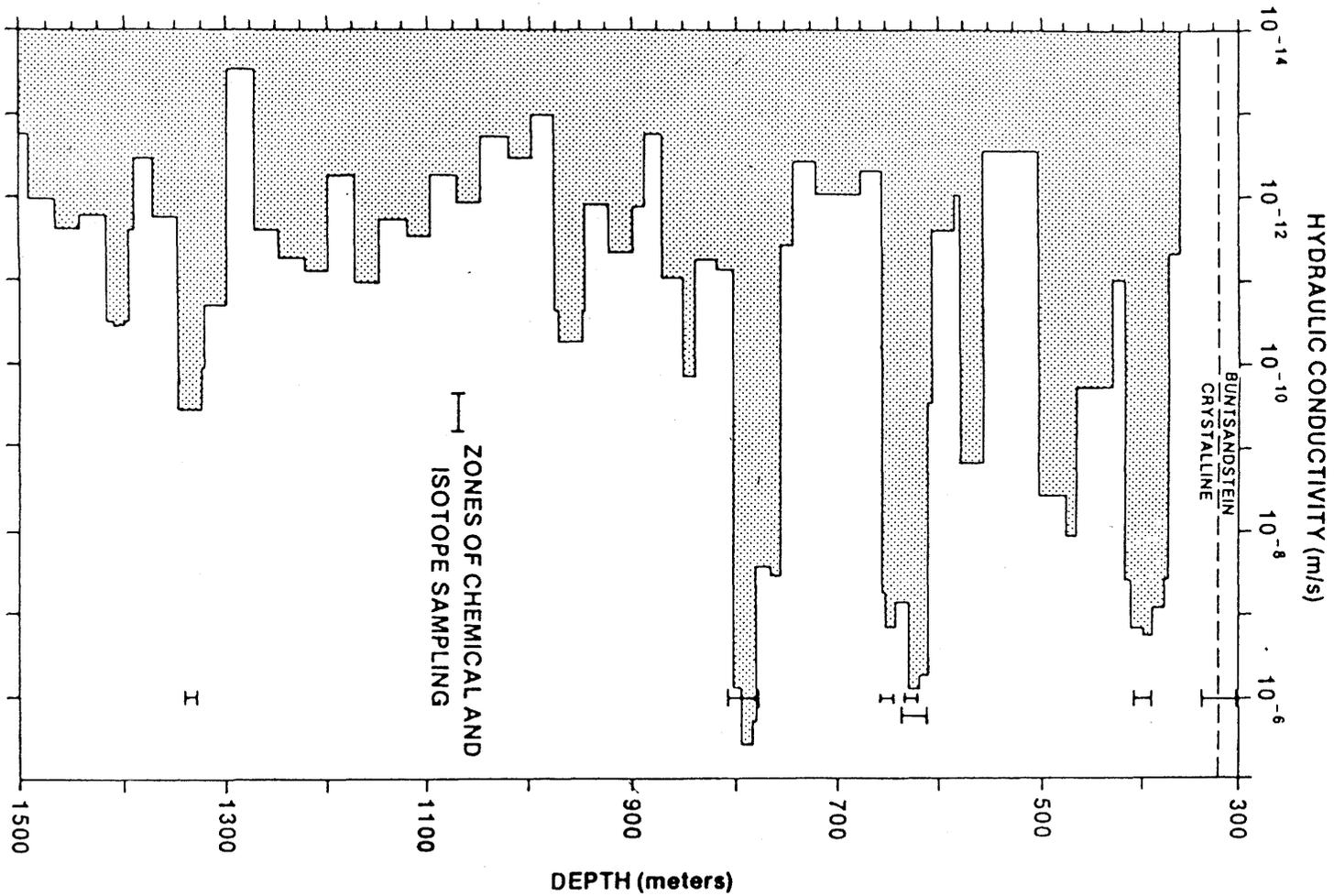


Figure 1.1: Hydraulic conductivity profile in the crystalline rock of Boettstein borehole (from NTB 85-08) showing intervals from which water samples were taken.

The samples from zones centered at 399 and 621 m depths were collected during the drilling phase. The hydraulic head in both zones was above the elevation of the drilling platform and the samples were taken using the natural artesian flow. These two samples are judged to be fully representative of formation water naturally present at the depths sampled.

The 619 m (a resampling of the 621 m zone) and the 792 m samples were taken during the test phase using a submersible pump. Field observations during sampling indicate that these samples are not entirely of formation water at the depths given, but contain water from shallower zones as well. Nonetheless, with the two earlier samples, they demonstrate that the chemistry of water in the three highly conductive zones above 1,000 m is virtually identical.

Only isotope analyses were made on samples pumped from the zone centered on 649 m. The results are included here because they are important to understanding the chemical results from other zones.

The zone centered on 1,326 m was also sampled during the test phase. The head in this zone is also above the drilling platform elevation, and so it flowed into the packer and tubing string. The interval yielded such a low volume of water however, that in the time available for sampling, only the packer interval and lower most part of the tubing were filled. A series of bailer samples of differing mixtures of borehole fluid and formation water was taken from close to the tubing bottom. From these mixtures the composition of the deep formation water itself could be calculated. It has a markedly higher dissolved solids content (ca. 13,400 mg/l (milligrams per liter)) than water from the shallower zones (ca. 1,100 mg/l) and is distinctive in other ways as well.

Several attempts were made to sample other intervals below 1,000 m, but because of low water yields in this region of low hydraulic conductivities, none was successful. The core and physical hydrology studies suggest that the system below about 1,000 m is quite different from that above. The single sample from 1,326 m shows a different type of water than is present above 1,000 m and suggests this conclusion.

Although this report is directed at the Boettstein borehole, it is important also to include some discussion of samples collected as part of the Regional Program from the thermal borings at Zurzach. Samples were collected from the Zurzach boreholes and analyzed by the same organizations using the same techniques as employed for the Boettstein samples. The overall

chemistry of the Zurzach samples is virtually identical to those from the shallow depths at Boettstein. The several consistent differences are related to the fact that the Boettstein samples were taken through newly installed packers and tubing which are likely to have reacted with certain components in the formation water. The Zurzach wells, on the other hand, have been flowing for a considerable length of time and these transient effects have passed so the samples from them better represent formation water. By noting the differences between the Boettstein and Zurzach results, one can estimate the influence of equipment in the borehole on the Boettstein samples and correct for them in order to arrive at a better estimate of the true chemistry of formation water in the Boettstein area.

2. DATA COLLECTION

2.1 Techniques of Sample Collection

The sample collection procedures adopted were intended to make available for field or laboratory analyses samples of formation fluid which were as little changed from in situ conditions as possible. In traveling from the formation conditions to the ground surface and on to the laboratory, water undergoes changes in temperature and pressure. It may also be exposed to new materials, such as iron in the sampling equipment in the borehole or rock flour or fluid from the drilling, which has the potential to mix or react with the formation water.

Experience shows that it is impractical to try to collect a single sample on which all desired analyses can be made. Instead it is expedient to collect several samples using different techniques, each tailored to the type of analysis to be performed on it. For example, the concentrations of such common cations and anions as sulfate, chloride and sodium are not affected by pressure release or exposure to the atmosphere, but important errors could result from even small admixtures of non-formation water. Thus the concern in collecting this type of sample is not whether it is exposed to the atmosphere, but that it contains a minimal amount of drilling fluid. A sample for the analysis of dissolved gasses however, is very sensitive to pressure release and can stand no exposure to the atmosphere. Thus such samples must be collected in closed systems at the surface or, preferably, within the borehole at as close to formation pressure as possible.

Samples of geochemical utility from the Buntsandstein and crystalline section were obtained through tubing which ran from the drill platform to packers in the borehole which isolated the zone of interest. Most of the samples were collected at the surface and were of water which was either flowing under its own head (artesian) or from a submersible pump installed inside the tubing. The surface samples from the 399 and 621 m zones were collected using their own flow, while those from the 619 and 792 m zones were pumped as described in NTB 85-07.

Samples from the Muschelkalk were not taken through tubing, but by means of a submersible pump installed in the casing itself. The interval sampled was that between the casing shoe and the bottom of the borehole.

Surface samples collected for gas and radioisotope analyses had to be protected against exposure to the atmosphere. A sampling head was installed at the top of the tubing or on top of the pump discharge pipe through which airtight connections to the gas and isotope sampling equipment could be made. This equipment, which is described in NTB 85-01, Section 8.4 and NTB 85-07, also permitted connection to a flow-through cell for measurement of pH, platinum electrode potential and dissolved oxygen.

Samples were also taken at depth within the tubing using two types of equipment. The first system, the GTC-sampler, was designed to collect samples for the analysis of gas and other sensitive substances at close-to-formation pressure with a minimum of sample disturbance. The system was designed to be used within the 2 7/8" tubing initially available in the NAGRA drilling program. It permitted flushing of the sample vessels and generated no pressure release on the sample at time of final filling. The apparatus is described in NTB 85-01, Section 8.2 and in NTB 85-07. It was used successfully for sampling in the 399, 619 and 621 m zones and apparently met its objectives.

The second down-hole system was supplied by Preussag and is also described in NTB 85-01, Section 8.2 and NTB 85-07. Although this system can be operated somewhat more rapidly than the GTC sampler and in smaller tubing, it has disadvantages with respect to the GTC sampler in that it cannot be flushed with formation water and it sharply reduces the pressure on the sample when filling. A Preussag sampler was used for the samples from the 1,326 m zone where the requirement was for precise and repetitive sampling from great depths in tubing with a relatively small inside diameter.

The actual analyses were performed and(or) coordinated by Institut Fresenius, Taunusstein, BRD, the Swiss Federal Institute for Reactor Safety (EIR), and the Low-Level Counting Laboratory (LLC), at the University of Bern. Representatives of each group were present at the borehole to collect samples and to perform field analyses and extractions as required for their specific needs. These procedures are described in NTB 85-01, Section 8, NTB 85-04 and NTB 85-07. In general, they do not influence the geochemical interpretation, and are not repeated here. Gas sampling and electrode potential measurement which do affect the geochemical interpretations are discussed below.

2.2 Criteria Guiding Data Collection

Water samples were collected to define the aqueous geochemistry at depth at the Boettstein site. Thus it was important to:

Maintain a balanced distribution of samples with depth so that all important water-bearing zones were sampled, while also attempting to sample zones of poor water yield as required for depth distribution;

Assure that samples were representative of formation water from the interval of interest and, if they were mixed, that the degree of mixing be known as well as possible; and

Without sacrificing any scientific data, select the lowest cost procedure, if several were available.

Three practices were followed during drilling of the crystalline section to assure the collection of representative samples. First, the quality of the drilling fluid was carefully controlled so that it would have a minimal effect on analytical results and that its presence, if any, in a sample could be corrected for. Thus drilling in the crystalline section began with de-ionized water, and in later stages of testing, the borehole was flushed with de-ionized water just prior to sampling. Because of the flow of formation water into the borehole, de-ionized water could not be maintained as the drilling fluid throughout the entire drilling phase. However, the chemistry of the formation water which was present in the borehole was by then well defined.

Second, known concentrations of tracers were maintained in the borehole fluid. Thus, as water was removed from an interval in preparation for sampling, the decline of the concentration of these tracers could be used as an indication of the flushing of borehole fluid from the interval and tubing and the approach to unmixed formation water. The tracer and borehole fluid program are described in NTB 85-01, Section 8 and in NTB 85-07.

Third, the longer an interval is open to the borehole, the greater is the chance that its chemistry may be changed by flow into or out of the borehole. Sampling during drilling is more expensive than sampling during the testing phase following completion of the borehole. Thus for cost reasons, the sampling of certain intervals was deferred to the testing phase.

Samples taken from the crystalline section of the Boettstein borehole do meet these criteria and, retrospectively, support them. The three zones sampled above 1,000 m are the most conductive in the section and sampling all three was in accordance with the first criterion. Even though extraordinary efforts were required to sample and interpret the results of the analyses from the 1,326 m zones, the efforts were required in order to obtain at least one sample from the lower 700 m of the borehole.

The presence of traced de-ionized water in the borehole prior to sampling the 1,326 m zone made it possible to calculate its formation water chemistry in spite of the fact that none of the samples collected from it contained more than 60 to 65 percent formation water.

The 399 and 621 m samples were obtained during drilling and are unquestionably more representative of their respective intervals than any of the other crystalline Boettstein samples. The 619 and 792 m samples were collected during the testing phase some six months after the intervals were first drilled. As discussed in detail in Section 6.6 below, the 619, 621 and 649 m samples are of the same water-bearing zone, yet had quite different ^{14}C contents. The first sample (621 m) had <1.3 percent modern carbon (pmc), the second (619 m) sample taken some 200 days later had 7.9 pmc, and the third (649 m) taken about 60 days after the second had 14 pmc. These later, high ^{14}C results are probably related to the facts that much time had elapsed between the time of drilling and sampling and that much water had flowed from the zones sampled into the borehole. This result strongly argues that every effort should be made to sample zones of potential interest during drilling rather than later in the program when changes in formation water chemistry related to prolonged flow may have occurred.

3.0 SAMPLE SELECTION

During drilling and testing of the Boettstein borehole, a variety of samples were collected. Most were analyzed in the field for one or two constituents and the results used for operating decisions about the drilling itself. Some were intended for geochemical interpretation. These were collected using special techniques and were analyzed for many dissolved constituents and isotopes. The results of the analyses on samples of this type are given in NTB 85-01, Beilagen 8.20, and 8.32.

Not all of the samples collected are tabulated in NTB 85-01 nor were they given a detailed geochemical interpretation. This chapter describes the criteria used to choose among the available data sets and briefly discusses how the criteria were applied to the samples chosen.

3.1 Criteria for selecting samples for detailed interpretation

To be suitable for a geochemical interpretation, a sample should have the following attributes:

It should have been collected from a relatively short interval of the borehole so that its characteristics can be associated with a specific rock unit or feature of hydrologic significance;

It should be as pure a sample of formation fluid as possible. If there is a possibility that it contains some contamination, from drilling fluid for example, some means for correcting for that contamination must be available; and

The analyses on the sample must be complete enough that their internal consistency can be checked and that their interpretation will provide useful geochemical and(or) hydrological information.

3.2 Samples Selected

Results of the analyses of samples potentially suitable for geochemical interpretation are given in NTB 85-01, Beilagen 8.20 and 8.32. In NTB 85-01, the results are listed in the report in the order of their date of

collection, but in the following section they are discussed in order of their depth in the borehole.

Each sample collected is discussed here in light of the criteria given above. A description is given of why each was or was not selected for detailed interpretation. The sample numbers and dates collected are as given in Beilagen 8.20 and 8.32 of NTB 85-01.

Upper Muschelkalk - 163 m - Sample 2, 1.11.82

This sample was pumped from an interval of borehole open between the bottom of the casing at 123.2 m and the hole bottom at 202.3 m. It was collected at the surface from pump discharge at the end of an extended pump test. No tracer was used in the drilling fluid when this interval was drilled so it was not possible to test the potential contamination of this sample in the field. Later laboratory analysis of its tritium content showed that it contained less than 1 TU (Tritium unit). The tritium content of the drilling fluid was of the order of 110 TU (see Table 7.5). Thus the sample apparently contained less than 1 percent drilling fluid and was chosen for the geochemical interpretation given in Section 5.1.

Buntsandstein - 313 m - Sample 27, 20.01.84

This sample was taken through perforations in the casing and cement at 315 m. The perforations were made at the end of the test phase. This interval was drilled with a brine mud which contained no tracer. The tritium content of this sample is below detection which shows that it contains less than 1 percent drilling fluid. As discussed in Section 5.2, the presence of even this small amount of drilling fluid could have profoundly influenced the sample's observed chemistry.

Buntsandstein/Weathered Crystalline - 316 m -
Samples 5, 16.11.82 and 6, 16.11.82

This section of the borehole was drilled with brine mud containing no tracer. The interval between a packer at 305.58 m and the hole bottom at 327.55 m was tested. A sample taken on 13.11.82 had a conductivity of over 20 mS/cm (milliSiemens per centimeter) and a tritium content of 6.2 ± 2.3 TU. Even before the tritium information was available however, it was clear that

this sample contained considerable drilling fluid. Two later samples from the same interval had lower conductivities - 3.5 and 3.0 mS/cm, respectively. The last sample, sample 5, was treated as one of potential geochemical importance. It was collected from the artesian flow of the borehole at the surface and was followed by sample 6 which was taken from the same interval using a drill-stem test tool. The tritium content of sample 5 was less than 1 TU and that of sample 6 was also below detection. These two samples are consistent internally, and with each other, and are discussed in Section 5.2. The concentration of salt in the drilling fluid for this section was so high that contamination with even the small amount permitted by the tritium concentrations would have significantly changed the chemistry of the formation water itself.

Upper Crystalline - 399 m - Samples 8, 14.12.82
and 9, 15.12.82

The drilling fluid used in the crystalline section of the Boettstein borehole contained two tracers. It was therefore possible to judge the extent of contamination of samples in the field. An interval between a packer at 393.9 m and the hole bottom at 405.1 m was tested. Sample 8 was taken at the surface from artesian flow while sample 9 was taken via pressure sampler at depth following the collection of the surface sample. The tracer concentration in sample 8 shows that it contained less than 0.6 percent drilling fluid. This is supported by its tritium concentration of less than 1 TU. Both samples 8 and 9 were selected for detailed geochemical interpretation, and are discussed in Section 6.1.

Upper Crystalline - additional samples

Several additional samples were collected at the surface from the artesian outflow of the borehole during the course of certain hydraulic tests. The tracer concentration of one sample showed that it contained 1 percent or less drilling fluid. Neither sample was analyzed for tritium, however, nor selected for detailed geochemical interpretation because each represents a considerable depth of borehole - over 49 m for one and 237 m for the other. These depths were too great for either sample to have been of use in delineating the chemical character of a specific borehole interval.

Upper Crystalline - 621 m Zone - Samples 12 and 13,
22.01.83

An interval between a packer at 618.5 m and the hole bottom at 624.1 m was tested. Sample 12 was collected at the surface from artesian outflow. Sample 13 was collected at depth with the pressure vessel sampler following the collection of sample 12. Tracer analyses showed that these samples contained about 2.5 percent of drilling fluid. Both of these samples were selected for detailed geochemical interpretation and are discussed in more detail in Section 6.2.

Upper Crystalline - 619 m Zone - Samples 16 and 17,
9.08.83

During the test phase following completion of drilling, an interval between packers at 609.0 m and 629.7 m, including the interval described above, was sampled. This interval was pumped and sample 16 was collected at the surface from the pump outflow. Sample 17 was collected at depth with the pressure vessel sampler. The tracer concentrations of these samples showed that they contained less than a few tenths of a percent drilling fluid. Both samples were selected for detailed geochemical interpretation and are discussed in Section 6.3. It should be noted that the ^{14}C content of sample 16 is considerably higher than that of sample 12 collected earlier from the same water-bearing zone. The changing ^{14}C content is discussed in Section 6.6.

Upper Crystalline - 649 m Zone - Samples of 17.10 and
3/5.11.83

During the test phase, isotope samples were taken from an interval between packers at 640.8 m and 657.2 m. The zone was pumped and the samples were collected at the surface from the pump discharge. The tracer concentration of the sample taken on 17.10 showed that it contained less than a few tenths of a percent of drilling fluid. However, its tritium concentration, 3.2 ± 0.7 TU, suggested that the sample may have contained as much as a few percent drilling fluid. Two samples were collected during a single period of pumping from 3.11 to 5.11. The earlier sample had a tracer concentration corresponding to a drilling fluid content of no more than a few tenths of a percent and had a commensurate tritium concentration of 1.2 ± 0.7 TU.

The later sample had a tracer concentration corresponding to nearly 5 percent drilling fluid and a tritium concentration of 3.2 ± 0.7 TU. Chemical analyses of samples from this interval are not available. The isotopes results are important however, and are discussed in Section 6.6.

Upper Crystalline - 792 m Zone - Sample 18, 16.08.83

Chemical and isotope samples were taken during the test phase from an interval between packers at 782.0 m and 802.7 m. The zone was pumped and the sample collected from the pump discharge at the surface. Its tracer concentration indicates that this sample contained less than one-half percent drilling fluid. It was selected for detailed geochemical interpretation and is discussed in Section 6.4.

Lower Crystalline - 1326 m Zone - Samples 19, 30.09.83, 20, 7.10.83, 21, and 22, 10.10.83

The zone of highest permeability in the lower part of the hole was isolated with packers at 1320.9 m and 1331.3 m. Samples from this interval were collected by a pressure sampler from within the tubing. None contained less than 40 percent drilling fluid, yet as a group they could be used to indicate the chemistry of the water in the formation of interest well enough that geochemical interpretation was possible. These samples are discussed in detail in Section 7.

4. METHODOLOGY

The previous chapters summarize the data collection and sample selection aspects of the Boettstein Borehole Geochemical Program. In this chapter, the chemical and isotopic analyses themselves are summarized along with the methods used for interpreting the analytical results. Analyses important to determining the carbonate chemistry of waters, their gas contents, oxidation potentials, and iron and uranium chemistry are discussed. Certain apparent mineralogic controls on the chemistry of dissolved species are described as is the geochemical model used for interpreting the results.

4.1. Methods of Analysis and Interpretation

4.1.1. Chemical and Isotopic Analyses

The groups involved with the NAGRA analytical program and the contributions of each are as follows:

Motor Columbus Ingenieurunternehmung AG, Baden, was responsible for the tracer analyses and for certain field analyses including m- and p-titrations and flow-through cell measurements of pH, Eh and dissolved oxygen. The techniques used are described in Chapter 8 of NTB 85-01 and in NTB 85-07;

Institut Fresenius Chemische und Biologische Laboratorien GMBH, Taunusstein, BRD, performed laboratory analyses of dissolved constituents. These included major and trace inorganic and organic species and the concentrations of major dissolved gases. They also performed certain field determinations including m- and p-titrations, pH, Eh and dissolved oxygen. Brief descriptions of each of the Fresenius analytical methods are given in NTB 85-04;

Eidg. Institut fuer Reactorforschung (EIR), Wuerenlingen, measured the concentrations of total dissolved gases and uranium, as well as uranium isotope ratios. Methods used are described in NTB 85-04;

LLC, Low Level Counting Laboratory (LLC), University of Bern, is responsible for stable and radioisotope analyses. They performed tritium, ^{18}O ,

^{13}C , ^{85}Kr , ^{39}Ar , and ^{14}C analyses both by counting and by accelerator mass spectrometry. They were also responsible for the distribution of samples to, and the collation of results from, a number of other laboratories, including:

Institut für Radiohydrometrie, Neuherberg;
 ^3H , ^2H , ^{18}O .

AERE, Harwell;
 ^{14}C , ^{13}C , Uranium, Thorium and Radium Isotopes.

University of Bath;
Rare gas content of the samples and their
 $^{40}\text{Ar}/^{36}\text{Ar}$ and Ar/N_2 ratios.

University of Cambridge;
 $^3\text{He}/^4\text{He}$ ratios.

Université de Paris Sud, Orsay;
 ^{34}S , and ^{18}O in SO_4 .

Oak Ridge National Laboratory ;

Measurement of ^{81}Kr with RIS (Resonance Ionizations Mass Spectrometry) on Krypton samples extracted and separated in Bern.

The isotope analysis program is described in more detail in NTB 83-04, NTB 85-06, and in Chapter 8 of NTB 85-01.

Results of chemical and isotope analyses were compiled by the Geologisches Büro Dr. Heinrich Jaeckli, AG, Zurich, in a format similar to that used for the results of the Regional Program (NTB 84-21). The tables of analytical results in NTB 85-01 were selected from this compilation.

In preparing this report, data from the original reports of analyses supplied by the several laboratories were used to supplement the summaries given in NTB 85-01.

4.1.2. Interpretation Techniques

Two techniques were used in reviewing the analytical results. First, the analyses were examined for consistency among the results of several laboratories or on

duplicate samples, and tests of the internal consistency of individual analyses were made. Second, tests of geochemical consistency were made which required information on the chemistry and mineralogy of the water-bearing zones and the availability of a detailed geochemical solution model.

4.1.2.1 Concentration Units

The analytical results are reported in units of milligrams per liter of solution (mg/l) (NTB 85-01, Beilage 8.20). Chemical calculations are made in units of molality (m) which equals mols of constituent per kilogram of water. Conversions between mg/l and millimolality (mm = m x 10⁻³) are made using:

$$\text{mm} = \frac{\text{mg}}{\ell} \times \frac{1}{\text{FW}} \times \frac{1}{\rho_s - \Sigma (\text{mg}/\ell) \times 10^{-6}}$$

where:

FW = Formula weight in mg/mm
 $\Sigma (\text{mg}/\ell)$ = sum of analyzed concentrations of dissolved constituents in mg/l
 ρ_s = solution density in kg/l.

The last term in this equation is virtually equal to one except in relatively concentrated solutions. For water from the Boettstein Muschelkalk, for example, with $\rho = 1.0037$ and Σ dissolved solids = 6,169 mg/l, this term equals 1.0025, a factor which is smaller than the analytical accuracy for most constituents.

4.1.2.2 Intercomparison of Analyses

Several types of intercomparisons were used whenever possible to test reported results. The simplest type was among results from different laboratories when several analyzed for the same constituent. Several sets of uranium analyses are available, for example, as are several analyses for some dissolved gases. It was also generally the case that more than one sample was taken from the same interval - often one at the surface and one with a pressure sampler at depth. Analyses for a number of constituents were made on both samples and formed another basis for comparison.

The internal consistency of each set of analyses of inorganic constituents was also tested. From the principle of electroneutrality, the sum of cation and anion charges in any solution must be zero. Thus, if the

charge difference for an analytical set is not close to zero, it indicates that an error has been made in the determination of one or more of the dissolved constituents or that no analysis was made of an important species.

The total dissolved solids content of a sample is available from two sources - the reported residue on evaporation at 105 or 110 degrees celsius and the sum of the analyses of the individual dissolved species. These two values should also agree closely in an acceptable analysis.

Details of these comparisons are given in Chapters 5, 6 and 7 where results from the several intervals sampled are discussed. There is a high degree of consistency within the individual chemical analyses as demonstrated by the cation and anion sums and the comparisons between the total dissolved solids values. Furthermore, there is excellent agreement whenever more than one analysis is reported for the same constituent. Thus the chemical analytical results can on the whole be treated with confidence.

Ion balance and total dissolved solids comparisons are also given in Beilage 8.21 of NTB 85-01. The values there may not be exactly the same as those which appear in the tables in Chapters 5, 6, and 7 of this report. Those in NTB 85-01 are based on the raw analytical data while those in this report are based on analyses adjusted to better reflect the chemistry of the waters in their source formations.

Two samples for rare gas analyses were collected from most intervals tested. Rare gas samples are known to be difficult to collect and store and agreement between duplicates is important to assuring representative results. Both sets of analyses were reported.

Duplicate isotope analyses are available for a few constituents including uranium isotope ratios, and tritium. A number of duplicate results are available for tritium. One sample was analyzed rapidly as a test for significant drilling fluid contamination, and a second more slowly with greater precision. All such pairs of analyses were in agreement within their respective quoted errors.

Stable environmental isotopes of particular concern to this report include those of oxygen ($^{18}\text{O}/^{16}\text{O}$) in water and in SO_4^{-2} , hydrogen ($^2\text{H}/^1\text{H}$, also written D/H), carbon ($^{13}\text{C}/^{12}\text{C}$) in the total dissolved carbonate ($\text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{-2}$), and sulfur ($^{34}\text{S}/^{32}\text{S}$) in SO_4^{-2} .

Analyses of the carbon and oxygen isotope ratios of the carbonate minerals in water-bearing horizons were made to elucidate possible water-rock reactions. These analyses are discussed in NTB 85-06 but are mentioned only in passing in this report.

The stable isotope analyses were judged mainly by the internal consistency of results of all Boettstein analyses. No inconsistencies which could be attributed to analytical difficulties were noted.

The environmental radioisotope of particular interest, in addition to tritium, is ^{14}C . Again, the only test of these results is the internal consistency of the entire data set. Different ^{14}C contents were reported for samples taken at different times from the same water-bearing zones in the upper crystalline. As discussed in Section 6.6, this is more probably a result of changes in the hydrology of the system caused by drilling and pumping than a reflection of any difficulties with ^{14}C sampling or analysis.

4.1.2.3. Geochemical Consistency

Two types of tests for geochemical consistency were made: Tests of the internal consistency of the analytical data on a set of samples from the same interval; and, tests of the consistency of the observed water chemistry with minerals known or likely to be present in the rock of the zone sampled. Both types require the use of a geochemical model and a self-consistent thermodynamic data base. The model and data base used are described in the following section.

Tests for internal consistency were made among analyzed dissolved carbonate contents, measured pH and dissolved CO_2 values as described in Section 4.2.1. The consistency of various indicators of oxidation potential were also examined as described in Section 4.2.2.

The constraints on the water chemistry due to the demonstrated or likely presence of certain minerals in the formation were also examined as described in Section 4.2.4.

4.1.3 Geochemical Model

A geochemical model was used to evaluate the internal consistency of the water analyses and to examine the relationships between water chemistry and host rock

mineralogy. These relationships are important to understanding the evolution of the water. Geochemical models have three essential components: a theoretical and conceptual model framework; a computer code for solving the model equations; and a thermodynamic data base of the coefficients required to evaluate the model equations. These components are discussed in the following sections.

4.1.3.1 Conceptual Model

Raw chemical data consist of the analyzed concentrations of the chemical species in a water sample. The thermodynamic activities of dissolved substances are important in determining their geochemical behavior, rather than simply their concentrations. In an ideal solution, concentrations and activities are equal, but in real solutions the values of the two quantities differ because of the influence of the solvent itself and of other solutes on the behavior of each species. The difference between concentrations and activities generally increases with total solution concentration.

Thermodynamically correct evaluations of water chemistry are important because they permit addressing such questions as: Is water just saturated with respect to minerals present in the aquifer or is it dissolving or precipitating them; Does the analyzed, dissolved CO_2 content agree with that calculated from the analyzed pH and alkalinity values; and, Are the observed concentrations of the oxidized and reduced forms of various dissolved species consistent with each other.

To derive thermodynamic activities from measured concentrations requires a conceptual model of solution behavior. The model most commonly used to describe solute-solvent effects in dilute solutions results in the Debye-Hueckel equation. In an extended form this equation can be written:

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I$$

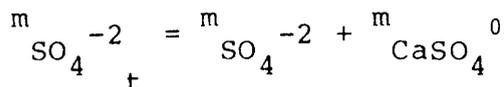
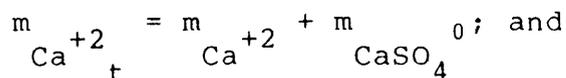
where: γ_i = Activity coefficient of species i ;
 A, B = Debye-Hueckel constants, functions of temperature and the dielectric constant of the solvent (Truesdell and Jones, 1974, p. 241). For water at 25° C; $A \approx 0.5$ and $B \approx 0.33$;
 z_i = Charge on ion i ; and
 I = Ionic strength of solution; $1/2 \sum m_i z_i^2$.

Several different sets of values are used for the coefficients a_i and b_i . In the original definition of this equation, a_i depends on the size of the ion i , and b_i is zero. The original definition of a_i is continued in most modern uses of the equation, but b_i is a deviation term to account for differences between observed and measured activity coefficients of salt solutions at moderate ionic strengths (Lewis and Randall, 1961; INTERA, 1983b).

In the WATEQ computer model (Truesdell and Jones, 1974), values for a_i and b_i for common dissolved ions are taken from fits of the above equation to mean salt activity coefficient data.

Another variant of the Debye-Hueckel equation, useful for species with poorly known solution properties is the Davies equation, in which the product $Ba_i = 1.0$ and $b_i = 0.3 A z_i^2$ (Stumm and Morgan, 1981).

As solute concentrations increase, reactions among dissolved ions begin to have a significant influence on solution behavior. These effects are described by the ion association model. This model assumes that in a CaSO_4 solution, for example, not only will Ca^{+2} and SO_4^{-2} ions be present, but also the dissolved complex ion or ion pair CaSO_4^0 . The analyzed concentrations of Ca and SO_4 will not be simply those of the free Ca^{+2} and SO_4^{-2} ions, but will include the CaSO_4^0 ion pair as well. Thus for each analyzed species there is a mass balance equation such as:



The formation of complex ions from their constituent free ions is described by mass action equations such as:

$$K_{\text{CaSO}_4^0} = \frac{a_{\text{Ca}^{+2}} a_{\text{SO}_4^{-2}}}{a_{\text{CaSO}_4^0}}$$

The activities (a) of the mass-action equations are related to the molal concentration units (m) of the mass balance equations by such equations as:

$$a_i = \gamma_i m_i$$

for each free and complex ion. The activity coefficients (γ) are calculated from Debye-Hueckel-type equations as described above.

For this simple example system, there are three known values: the analyzed $m_{\text{Ca}^{+2}}$ and $m_{\text{SO}_4^{-2}}$ concentrations and the equilibrium constant for $K_{\text{CaSO}_4^0}$. These are sufficient to solve the mass balance and mass action equations for the activities of the free Ca^{+2} and SO_4^{-2} ions and the CaSO_4^0 complex.

Other data and reaction types must be included to examine real solutions. The association of water is described by:

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}$$

K_w is part of the thermodynamic data base for the model and $a_{\text{H}_2\text{O}}$ is a known function of the total solute content of the solution. One additional piece of data is still required however, and this is usually the measured pH ($= -\log a_{\text{H}^+}$).

Oxidation-reduction (redox) reactions are discussed in detail in Section 4.2.2. They can be modeled in two ways. If analyses for both the oxidized and reduced members of a redox couple are available, for SO_4^{-2} and H_2S , or for N_2 and NH_4^+ , for example, the oxidation potential for that couple can be calculated. If, on the other hand, the concentration of only one member is known, an independent measure of the oxidation potential must be available.

The free ion activities determined using the model are required to calculate ion activity products of minerals or other solids of possible influence on the water. The mineral anhydrite (CaSO_4) would be of interest in the example, CaSO_4 solution. Its ion activity product

$$\text{IAP}_{\text{CaSO}_4} = a_{\text{Ca}^{+2}} a_{\text{SO}_4^{-2}}$$

is compared to its solubility product at the water temperature (KT) to calculate the mineral saturation index (SI):

$$\text{SI}_{\text{Anhydrite}} = \log (\text{IAP}/\text{KT}).$$

A negative saturation index indicates that the mineral is undersaturated and could dissolve in the solution, while a positive value means that the solution has the capacity to precipitate that mineral. Solution equilibrium with a mineral is indicated by a zero SI value. Analytical uncertainties lead to a precision of from ± 0.05 to ± 0.1 units in SI values.

4.1.3.2 Computer Code

The basic equations described above can be written in general forms.

The mass balance equation is:

$$m_{T,i} = m_i + \sum_{j=1}^J n_{ij} m_j, \quad i = 1, 2, \dots, I$$

where: m_i = concentration of free element of species i ;
 m_j = concentration of complex ion j containing n_{ij} moles of i (if the complex j does not include element i , n_{ij} is zero);
 $m_{T,i}$ = total (analyzed) concentration of i ;
 I = total number of elements for which analytical data are available or which are being considered; and
 J = total number of solution complexes.

The mass action equation is:

$$a_j = K_j \prod_{i=1}^I a_i^{n_{ij}}, \quad j = 1, 2, \dots, J$$

where: a_j = thermodynamic activity of solution complex j ;
 a_i = thermodynamic activity of free elements, i ;
 n_{ij} = stoichiometric coefficient of ion i in complex j (if the complex i does not include element i , n_{ij} is zero);
 K_j = equilibrium constant for formation of complex j ; and
 I and J are as for the mass balance equation.

Activity coefficients must also be calculated for each solution species i and j so that the molalities of the mass balance equations can be related to the activities of the mass action equations.

This set of equations is highly non-linear so its solution when 15 or 20 analyses of different elements (i) are available, and one hundred or more complex ions (j) are considered, requires the use of a computer and an efficiently designed program or code.

The program used for this work was the PHREEQE code. This was produced by the U.S. Geological Survey for general water equilibrium calculations (Parkhurst, and others, 1980) and adapted for nuclear waste isolation applications by INTERA (1983a).

The PHREEQE code calculates the set of equations by iteration. It uses a continued fraction approach for the mass balance equations and the Newton-Raphson technique to solve all other equations. The programming is general so that the species and complex ions considered are defined only by the thermodynamic data base input by the user.

The code is also capable of calculating mineral saturation indices, gas partial pressures, oxidation potentials and so on, as defined by the user in the data input. PHREEQE can also be used for solution mixing and for mineral-solution reaction calculations.

Equilibrium constants vary with temperature, as do the Debye-Hueckel constants A and B . PHREEQE includes several expressions for the temperature dependence of equilibrium constants, including an integrated form of the Van't Hoff equation, as used in WATEQ (Truesdell and Jones, 1974), and two types of power series in

temperature (INTERA, 1983a). The Van't Hoff equation requires a value for $\log K$ of the reaction at 25°C and for the enthalpy change (ΔH) of the reaction. The power series expressions require coefficient values. $\log K_{25}$ and ΔH values are most commonly available; therefore the Van't Hoff expression is used most.

Equilibrium constants are also dependent on pressure. This effect is relatively small over the range of pressures commonly encountered in aqueous geochemistry. Thus, equations describing pressure effects are not included in PHREEQE. Stumm and Morgan (1981, Section 2.12) discuss pressure effects and show that for pressures below 150 to 200 bars, differences of no more than 0.1 in $\log K$ values are to be expected. At Boettstein, the formation pressures of the fluids sampled were virtually hydrostatic and thus approximately equalled 1 bar per 10 m of depth. The maximum formation pressure would have been in the 1,326 m sample and, at less than 140 bars, is not likely to have significantly effected any of the geochemical calculations.

4.1.3.3 Thermodynamic Data Base

Required thermodynamic data include:

- Equilibrium constants for each of the solution complex ions considered;
- Equilibrium constants for each mineral or gas for which solution equilibria are to be examined;
- Equilibrium constants for each oxidation-reduction reaction to be included;
- Activity coefficient equation parameters for each ion included; and
- Reaction enthalpies or other coefficients for the variation with temperature of each of the equilibrium constants.

Data for the major ions and their complexes were taken from those used in the U.S. Geological Survey WATEQ series of models (Truesdell and Jones, 1974; Plummer and others, 1976; Ball and others, 1979, 1980). Some minor element data from these sources is also included. Additional data added by INTERA has been taken from such standard sources as Baes and Mesmer, (1976), Robie and others, (1979), and Wagman, and others, (1982). For consistency within the NAGRA program, iron and uranium data are those selected from a critical evaluation of the literature by Schweingruber (1983, 1984).

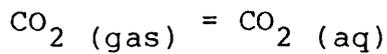
4.2 Results of Interpretations

Details of the sampling, and results and interpretations of the analyses themselves are given in Chapters 5, 6, and 7. Here these results are summarized and the background for the selection and application of interpretative techniques is given.

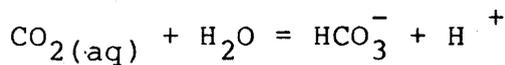
4.2.1 Carbonate System and Gas Analyses

4.2.1.1 Theory

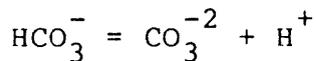
In a solution dilute enough that ion pair formation can be neglected, the carbonate system can be described by the following chemical reactions and equilibrium constant equations:



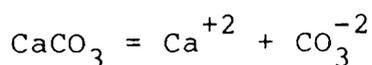
$$K_H = \frac{a_{\text{CO}_2(\text{aq})}}{P_{\text{CO}_2}} \quad (1)$$



$$K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2(\text{aq})} a_{\text{H}_2\text{O}}} \quad (2)$$



$$K_2 = \frac{a_{\text{CO}_3^{-2}} a_{\text{H}^+}}{a_{\text{HCO}_3^-}} \quad (3)$$



$$K_{\text{calcite}} = a_{\text{Ca}^{+2}} a_{\text{CO}_3^{-2}} \quad (4)$$

In these equations, K_H is the Henry's Law constant for CO_2 , and K_1 and K_2 are the first and second dissociation constants for carbonic acid ($\text{H}_2\text{CO}_3 = \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$). K_{calcite} is the solubility product of the mineral calcite.

The saturation index for calcite is:

$$\text{SI}_{\text{calcite}} = \log \frac{a_{\text{Ca}^{+2}} a_{\text{CO}_3^{-2}}}{K_{\text{calcite}}}$$

Given the normal uncertainties of geochemical analyses, $\text{SI}_{\text{calcite}}$ precision should be about ± 0.1 . For example, Pearson and Rettman (1976) found the mean $\text{SI}_{\text{calcite}}$ of 79 samples from a limestone aquifer to be -0.04 ± 0.09 . While it is not uncommon for ground waters to be undersaturated with respect to calcite ($\text{SI}_{\text{calcite}} < 0$), calculated calcite oversaturation ($\text{SI}_{\text{calcite}} > 0$) can often be shown to result from erroneous pH values.

Analyses relevant to the carbonate system include:

m- and p-values. These equal the number of milliequivalents (meq) of acid per liter of sample required to reach pH values of 4.3 (methyl-orange) and 8.2 (phenolphthalein), respectively. The dominant species contributing to the p-value is carbonate (CO_3^{-2}) while both bicarbonate (HCO_3^-) and carbonate contribute to the m-value. In North American practice, the m-value is referred to as the total alkalinity. Other species than bicarbonate and carbonate contribute to the m- and p-values, including hydroxyl and certain phosphoric, boric, and silicic acid species. Thus the total alkalinity (m-value) is usually slightly higher than the carbonate alkalinity (HCO_3^- (meq) + CO_3^{-2} (meq));

pH. In most ground waters, including those from the Boettstein borehole, the pH ($= -\log a_{\text{H}^+}$) is determined by the ratios of carbonate system species as shown in equations (2) and (3). pH is measured directly using a glass electrode;

$\text{CO}_2(\text{aq})$ or P_{CO_2} can be measured in two ways. The meq of strong base required to titrate to a pH of 8.2 (base capacity) equals the $\text{CO}_2(\text{aq})$ content. This procedure is not sensitive enough to measure the low $\text{CO}_2(\text{aq})$ amounts present in waters with pH values approaching 8 and above. CO_2 is also determined by gas chromatographic analysis of the total gas evolved from a water sample. This technique is much more sensitive;

Calcium. is required if $\text{SI}_{\text{calcite}}$ is to be determined; and

Other major dissolved species. must be known in order to calculate the activity coefficients (γ) required to convert measured concentrations to thermodynamic activities as required for the equilibrium calculations.

Measurements of m- and p-values, pH, and the base capacity were made in the field in water fresh from the borehole. In spite of all precautions, some CO_2 loss was likely to have occurred by the time a field pH measurement was made. This loss would have raised the pH according to reaction (2), and so increased the ratio of CO_3^{2-} to HCO_3^- in the solution and made the $\text{SI}_{\text{calcite}}$ calculated falsely positive.

Gas samples for chromatographic analyses were prepared by placing the water samples under vacuum and collecting the evolved gas. This technique yields good results for gases such as N_2 and Ar which do not react chemically with the solution. However, CO_2 from a solution under vacuum comes not only from $\text{CO}_2(\text{aq})$, but from disproportionation of HCO_3^- according to reaction (2). CO_2 contents so measured may be higher than the correct $\text{CO}_2(\text{aq})$ content of the water under formation conditions (NTB 85-04).

The set of equations (1), (2) and (3) can be solved if values for any two of the three quantities pH, m-value, or $\text{CO}_2(\text{aq})$ concentration are available. If the third was also measured, its value could be compared with that calculated from the other two. The comparison could be used to indicate the internal consistency of the set of measurements.

The calcite saturation index is also a useful indicator of potential analytical errors. Calculated oversaturation suggests that CO_2 outgassing may have occurred leading to an erroneously high pH value. Calculated calcite undersaturation, except in very young waters or

in calcite-free rock, is also unusual and may indicate an overestimate of the $\text{CO}_2(\text{aq})$ content.

4.2.1.2 Results and Conclusions

Calcite saturation indices were calculated using the analytical data in Beilage 8.20 of NTB 85-01 and field-measured alkalinity (m-) values. The reported pH values and alkalinities gave saturation indices ranging from saturation to considerably over-saturation ($\text{SI}_{\text{calcite}}$ from 0.0 to +0.2), and calculated dissolved CO_2 values well below those analyzed. Thus many of the reported pH values apparently are too high as a result of CO_2 loss before or during pH measurements.

Similar calculations were made using the reported dissolved CO_2 contents rather than pH values in the equations of the carbonate system. Those for the samples from the crystalline section gave $\text{SI}_{\text{calcite}}$ values indicative of strong undersaturation. As discussed below, this is inconsistent with the petrography of the system and indicates that the reported CO_2 values are too high.

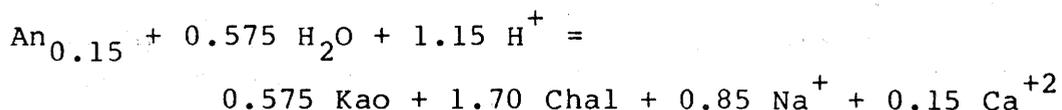
In the Muschelkalk, with $\text{pH} < 7$, $\text{CO}_2(\text{aq})$ was a significant part of the total dissolved carbonate and could be estimated from base capacity measurements. The measured pH led to a calculated $\text{CO}_2(\text{aq})$ concentration which was below that analyzed and to an $\text{SI}_{\text{calcite}}$ value of +0.2. Both suggested the measured pH was too high, so the calculations were done with lower pH values until both reasonable consistency between calculated and measured $\text{CO}_2(\text{aq})$ concentrations and an $\text{SI}_{\text{calcite}}$ value closer to zero were obtained. The details and results are given in Section 5.1.1.

Results of the petrographic studies on the Boettstein core (NTB 85-02) and of isotope analyses on water and mineral samples (NTB 85-06) are of assistance in reconstructing the chemistry of the crystalline formation waters. First, calcite is a ubiquitous fracture filling mineral, although it is virtually absent from the more highly porous zones, including those from which the water samples were taken. Second, the isotopic composition of the fracture filling calcite is in equilibrium with that of the carbonate dissolved in the waters sampled. The small amount of carbonate in the more porous fractures is not in equilibrium with the water. This suggests that while water in the zones of high yield is not calcite saturated, in less permeable fractures, water of virtually the same chemistry is precipitating calcite.

A hydrologic situation which would give rise to this chemical pattern is not hard to envision, and is consistent with the Boettstein system. In a given region of the upper crystalline section, spatial gradients of fluid potential will be the same regardless of variations of permeability or porosity within the region. Under the same gradient, fluid residence time varies inversely with hydraulic conductivity. Thus water in zones of low conductivity will have longer residence times during which fluid-mineral reactions can occur than will water in more conductive zones.

Important reactions between fluid and crystalline rock of the types found at Boettstein include feldspar hydrolysis and the production of secondary clay mineral and silica phases. These reactions tend to raise the pH of a solution and so increase its saturation state with respect to calcite.

As discussed in section 4.2.4, the measured aluminum and silica contents of the samples can be modeled by assuming equilibrium between the formation waters, the clay mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), and the silica (SiO_2) mineral chalcedony. If the feldspar being weathered is taken to be a plagioclase of 15 percent anorthite content ($\text{Na}_{0.85}\text{Ca}_{0.15}\text{Al}_{1.15}\text{Si}_{2.85}\text{O}_8$) (See NTB 85-02), the reaction can be written:



This reaction need not occur to any great extent to influence the saturation state of the water with respect to calcite. PHREEQE calculations show that if upper crystalline waters sampled from zones of high circulation were undersaturated by -0.02 SI units, only 0.006 to 0.007 millimols of plagioclase need dissolve to bring the water to calcite saturation. Likewise, if the waters were undersaturated by -0.05 SI units, only 0.02 millimols of reaction would be required.

These reaction amounts are too small to change the concentrations of any dissolved constituents by amounts large enough to be detected analytically. Thus the bulk chemistry of the water is likely to be measurably the same whether it is in the finer, calcite-bearing fractures or in the calcite-free zones of high water yield.

The pH values, if they could be precisely measured at formation conditions, would directly reflect this

difference in calcite saturation state. If the water sampled were undersaturated by -0.02 units, its pH would be 0.02 units lower than that of the same water at calcite saturation. Such pH differences are also not practically measurable, nor is the precise extent of calcite undersaturation known in the zones of high water yield. Thus in the reconciled analyses for the upper crystalline samples given in Chapter 6, calcite saturation of the samples has been assumed as reflective of the conditions throughout the bulk of the rock, even though, in the sampled zones of high yield, the actual pH values, if they could be measured, might be as much as 0.05 units lower.

Tables of data on the carbonate system for each interval are given in Chapters 5, 6, and 7. From them, the following general conclusions can be drawn:

pH measurements on surface samples are higher than those measured on the pressure sample, and all measured pH values are higher than those calculated at calcite saturation. Thus, CO_2 evolution is effecting all reported pH values;

The calculated concentrations of CO_2 at calcite saturation are the same or lower than those measured by gas analyses. The analyzed values thus appear to include some dissociated HCO_3^- in addition to the true dissolved CO_2 ; and

Petrographic and isotopic evidence suggests that water in the field fractures is saturated with calcite, but water from the zones of high water yield may be undersaturated. The chemical differences are too small to be measurable. The data from the samples taken is representative of water throughout the upper crystalline.

4.2.2 Oxidation - Reduction

A number of geochemically important elements can be present in minerals or in solution in more than one valence state. It is necessary to know the concentrations of each valence state present to adequately define the ground-water geochemistry of a system. The several valence states of some elements have such different chemical characteristics that separate analyses can be made for them. Nitrogen, for example, can be present as $\text{N}(-3)\text{H}_4^+$, $\text{N}(0)_2$, $\text{N}(+3)\text{O}_2^-$ and $\text{N}(+5)\text{O}_3^-$, and, as was done for the Boettstein samples, each can be analyzed separately. Similarly, individual analyses were made for both $\text{As}(+3)\text{O}_3^-$, and $\text{As}(+5)\text{O}_4^-$ and for

$S(+6)O_4^{2-}$ and $H_2S(-2)$. When direct analyses for several oxidation states of an element can be made, no additional information is needed to define the solution oxidation state for that element.

For certain other elements likely to be present in more than one oxidation state, only total concentrations or the concentration of one oxidation state can be measured. Uranium, for example, may be present as $U(+6)O_2^{2+}$, $U(+5)O_2^+$, or $U(+4)^{+4}$, but the analytical procedures give only total dissolved uranium concentrations. Likewise, while both Fe^{+2} and Fe^{+3} are important, the concentration of Fe^{+3} in non-acid waters is too low to measure and so only Fe^{+2} concentrations are available. Total iron values are often reported, and are frequently higher than the Fe^{+2} value for the same sample. The difference is usually not dissolved Fe^{+3} but rather should be attributed to particulate or colloidal iron dissolved by the acid used to preserve the sample.

4.2.2.1 Oxidation Potentials

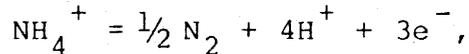
The value of an additional parameter, the oxidation potential, is required if only one analysis is available for an element present in more than one oxidation state. The oxidation potential (Eh, volts) of an oxidation-reduction reaction is described by the Nernst equation (Stumm and Morgan, 1981, Section 7.3),

$$Eh = E^0 + \frac{RT}{nF} \ln \frac{\prod_i a_{ox_i}^{n_i}}{\prod_j a_{red_j}^{n_j}}$$

where: Eh = oxidation potential, volts;
 E^0 = standard potential of the reaction, volts;
 R = Gas Constant = 8.3143 J/mol/K;
 T = Temperature, K = 273.15 + °C;
 F = Faraday constant = 96,487.0 J/V/mol;
 n = number of electrons transferred in the reaction;
 a_{ox_i}, n_i = activities and stoichiometric coefficients of oxidized species;
 and

$a_{\text{red}_j}, n_j =$ activities and stoichiometric coefficients of reduced species.

For example, for the reaction,



the Nernst equation becomes

$$E_h = E^0 + \frac{RT}{3F} \ln \left(a_{\text{N}_2}^{0.5} a_{\text{H}^+}^4 / a_{\text{NH}_4^+} \right)$$

The standard potential of reaction, E^0 , is related to its equilibrium constant, K , by the expression

$$E^0 = - \frac{RT}{nF} \ln K$$

and to its standard Gibbs energy of reaction, ΔG_r^0 , by:

$$\Delta G_r^0 = nE^0 F.$$

Oxidation states are also often specified using the pE notation. The pE, which in concept is analogous to pH, is related to Eh by:

$$\text{pE} = -\log a_{\text{e}^-} = \frac{F}{\ln 10} \frac{E_h}{RT}$$

The following relationship is provided for the temperature dependent conversion of pE to Eh:

$$E_h(\text{volts}) = \text{pE} \cdot (1.984\text{E}-04) \cdot T$$

If both a_{ox} and a_{red} are known, as they are for nitrogen and sulfur species in the Boettstein waters, for example, the Eh for these systems can be calculated using the Nernst equation. If, on the other hand, only one concentration value is available - a_{ox} , a_{red} , or a_{total} , for example - the system cannot be

completely defined unless an independent estimate of the oxidation potential for that reaction is available.

It has been routine geochemical practice for a number of years to measure the potential developed between a platinum and a reference electrode in water samples. These potentials, which can usually be measured reproducibly only with difficulty, are referred to as platinum electrode potentials, or measured Eh values. Such values are reported for most of the Boettstein samples.

It is not well established how the oxidation states of the many elements which may be present in a given ground water influence its platinum electrode potential. In waters in which iron is the dominant electro-active element (element present in more than one valence state), reproducible platinum electrode potential values have been reported which, when used with measured Fe^{+2} concentrations in the Nernst equation, give values for Fe^{+3} concentrations which are in reasonable agreement with those from mineral constraints on the ground-water chemistry.

Potentials calculated from other redox couples often are quite different from one another and from measured electrode potentials as well, as recently demonstrated by Lindberg and Runnells (1984). Several electro-active species and redox pairs were analyzed in the Boettstein samples. To delimit the range of oxidation states present in these samples, several oxidation potentials were calculated and are given in Table 4.1. Redox couples included are NH_4^+/N_2 , $\text{H}_2\text{S}/\text{SO}_4$, $\text{O}_2/\text{H}_2\text{O}$, Sato $\text{O}_2/\text{H}_2\text{O}$, CH_4/CO_2 and H^+/H_2 . Use of these sensitive species provides a range of redox state of the waters. Schweingruber (1984) has already presented the results of calculations of this type and reached conclusions similar to those given here.

The presence of dissolved oxygen in a water implies strongly oxidizing conditions. Two values for the $\text{O}_2/\text{H}_2\text{O}$ couple are given in Table 4.1. The first, which gives more positive oxidation potentials, is based on the thermodynamic properties of the species involved. The second, the Sato Eh, uses an empirical relationship proposed by Sato (1960) between oxygen content and "effective" Eh.

In general, the Sato value is the calculated value closest to that measured. Both the Sato and measured values are more oxidizing (positive) than those calculated from uranium solubility or the other redox pairs. The oxygen contents of the several samples

Formation Depth (m)	Sample	Date	Pt. Temp. (°C)	Electrode		NH ₄ ⁺ -N ₂		UO ₂ Solub- ility		H ₂ S-SO ₄		O ₂ -H ₂ O		Sato O ₂ /H ₂ O		CH ₄ -CO ₂		H ⁺ -H ₂		
				Meas. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)	Eh (volts)	Calc. (volts)		
<u>BOETTSTEIN</u>																				
Muschelkalk 163		1-Nov-82	19.7	+0.17	-0.16	-0.009	>-0.15	+0.80	+0.21	-0.18	-0.29									
Buntsandstein 313		20-Jan-84	26.0	-0.094	-0.24	-0.096	>-0.25	+0.71	+0.11	-0.27	-0.38									
Buntsandstein/ Weath. Cryst. 316		16-Nov-82	26.0		-0.22	-0.058	>-0.23	+0.73	+0.13	-0.25	-0.42									
Crystalline 399		14-Dec-82	30.0	+0.006	-0.27	-0.11	>-0.26	+0.68	+0.08	-0.29	-0.41									
Crystalline 621		22-Jan-83	37.0	+0.006	-0.27	-0.12	>-0.25	+0.68	+0.06	-0.29	-0.40									
Crystalline 619		9-Aug-83	31.0	-0.076	-0.26	-0.12	>-0.27	+0.67	+0.062	-0.29	-0.43									
Crystalline 792		16-Aug-83	31.0	-0.14	-0.27	-0.14	>-0.28	+0.66	+0.052	-0.30	-0.44									
Crystalline 1326		10-Oct-83	60.0	--	--	-0.052	--	--	--	--	--									
<u>ZURZACH</u>																				
Crystalline Boring #1			38.0	-0.042	-0.26	-0.11	>-0.27	+0.69	+0.068	-0.29	--									
Crystalline Boring #2			40.0	-0.065	-0.26	-0.11	>-0.27	+0.67	+0.036	-0.29	--									

Table 4.1: Oxidation potentials as measured and calculated from analyses of redox pairs.

given in Chapters 5 and 6 are variable suggesting that rather than being a constituent of the formation water, the oxygen results from drilling fluid or air contamination of the samples themselves. Contamination by 1 percent with oxygen-saturated water would give a sample concentration of 0.1 mg O₂/ℓ. For all samples, at least one analysis reported lower concentrations of oxygen, and so support this interpretation that no dissolved oxygen is present in the formation waters. Dissolved H₂S concentrations reported for the Boettstein samples were generally at the analytical detection limit. Thus the Eh values calculated from the H₂S/SO₄ couple are lower limiting values.

The NH₄⁺/N₂, H₂S/SO₄, and CH₄/CO₂ values are generally similar. These reactions are not coupled, except perhaps biologically, and, unless they do actually represent a fundamental equilibrium state of the system at depth, the reason for their similarity is not obvious. Their value has been chosen as the probable lower limit of possible oxidation states in the samples discussed below. As discussed in the following section, however, the metals, iron and uranium, appear to be responding to a more oxidizing environment.

The most reducing conditions are implied by the H⁺/H₂ couple. It is highly probable that the dissolved H₂ present in the Boettstein samples is not from the formation water but is a product of the corrosion of the iron tools and tubing present in the borehole during sampling. This same process is thought to produce the high iron concentrations discussed in the next section. The highly reducing conditions indicated by this couple can, therefore, be taken as not representative of the state of the formation.

4.2.2.2 Iron and Uranium

Iron can be present in solution in the +2, (ferrous) and +3, (ferric) states. Ferric iron forms oxide and hydroxide solids of limited solubility, and its concentration in neutral and basic waters tends to be below detection. Fe⁺² forms more soluble solids (except that when sulfide is present, the poorly soluble FeS may form), so when a water has a dissolved iron concentration of more than a few hundredths of a mg/ℓ, the iron must be in the ferrous form.

The samples from the Boettstein borehole were taken with iron tools and pipe placed in the borehole specifically for sampling and hydraulic testing. Metallic iron oxidizes in water until the exposed metal surfaces

are armored with a coating of ferric hydroxide, or "rust". Samples from boreholes with freshly-installed tubing or casing tend to have high initial iron contents which decrease with time as the iron in the borehole gradually becomes armored from further attack by water.

Table 4.2 gives the analyzed total iron and Fe^{+2} analyses of samples from the Boettstein crystalline section and from two thermal water boreholes at Zurzach. The Zurzach samples were taken as part of the NAGRA Regional Program (NTB 84-21) and were collected and analyzed by Institut Fresenius using the same procedures as for the Boettstein samples.

Borehole no.1 at Zurzach was drilled in 1955 and no. 2 in 1965 and both have been continuously producing water since being drilled. The chemistry of Zurzach water is identical in most respects to that from the upper crystalline section at Boettstein. The differences can be attributed to the presence of fresh iron in the Boettstein borehole which has not had sufficient time to become armored against further attack by formation water. The age of the Zurzach wells, however, is such that armoring would have become virtually complete and the samples from Zurzach should be representative of formation water chemistry.

As Table 4.2 shows, the iron content of Zurzach water is from 0.01 to 0.03 mg/l and the total iron and Fe^{+2} contents are the same. The Boettstein samples have much higher iron contents and in all cases the total iron is significantly greater than the Fe^{+2} concentration. These high iron contents are most probably not representative of formation water chemistry, but rather result from the presence in the samples of both dissolved and colloidal iron from the dissolution of the fresh iron metal in the boreholes. For the purpose of establishing the geochemistry of the formation water, the Boettstein iron values were not used, but instead, values of 0.02 mg Fe^{+2} /l were taken as representative based on the Zurzach analyses.

Schweingruber (1984) has employed iron, arsenic and uranium-based redox models in an intercomparison of calculated Eh's for three Boettstein waters. The upper limit of Fe^{+2} concentrations in the sample water was taken at FeCO_3 saturation. The resulting Eh's based on an $(\text{Fe}^{+2}/\text{Fe}(\text{OH})_3)$ couple compared with a UO_2 -saturation model differ by approximately 0.03 volts for the 400 m and 600 m waters. Assuming that the discrepancy between the two models is the result of an overestimate

Sample	Fe ⁺² (mg/l)	Fe _{tot} (mg/l)
<u>BOETTSTEIN CRYSTALLINE</u>		
Crystalline:		
399 m		
Flowing	1.2	4.1
Pressure vessel	--	1.3
621 m		
Flowing	1.2	2.1
Pressure vessel	--	1.3
619 m		
Pumping	1.0	2.3
Pressure vessel	--	0.63
792 m		
Pumping - 15-Aug	2.0	33.8
Pumping - 16-Aug	0.81	1.7
<u>ZURZACH</u>		
Borehole no.		
1 Oct-81	0.01	0.012
Aug-82	0.02	0.024
2 Oct-81	0.03	0.030
Aug-82	0.02	0.019

Table 4.2: Iron concentrations in Boettstein samples and from Zurzach thermal boreholes.

of Fe^{+2} concentration in the ground water, 0.02 mg Fe^{+2}/ℓ would have brought the two systems into agreement.

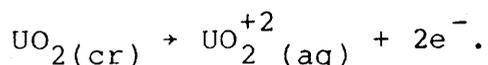
Uranium occurs in waters like those from the Boettstein crystalline section in both the $\text{U}(+4)^{+4}$ and $\text{U}(+6)\text{O}_2^{+2}$ states. Analytical techniques cannot distinguish between the two oxidation states, so only total uranium concentrations are reported. Analyses were made for uranium by Fresenius, EIR, and groups reporting to LLC, and, as discussed in Chapter 5 and 6 below, all agree reasonably well. The total uranium content of these waters ranges from 0.2 to 1.0 $\mu\text{g}/\ell$.

The geology report on the core from the Boettstein borehole (NTB 85-02) describes the presence of the uranium-bearing minerals:

Pitchblende: impure uraninite, UO_2 ;
 Brannerite: $(\text{U}, \text{Ca}, \text{Th}, \text{Ce})(\text{Ti}, \text{Fe})_2\text{O}_6$; and
 Coffinite: USiO_4

Only the thermodynamic properties of uraninite are known with much confidence. It is, however, the proper mineral to use in making solution control calculations.

The oxidation state of the dominant dissolved uranium species is $\text{U}(+6)\text{O}_2^{+2}$, while in uraninite, uranium is in the U^{+4} state. Thus uraninite dissolution is accompanied by uranium oxidation and, in a simplified form can be written:



Given knowledge of the thermodynamic properties of the solid UO_2 , the analyzed uranium concentrations can be used to calculate the oxidation potential for uranium in the samples. From the expression above,

$$\log K_T = \log a_{\text{UO}_2^{+2}} - 2pE - \log a_{\text{UO}_2\text{cr}}$$

and taking the activity of UO_2cr as 1,

$$\log K_T = \log a_{\text{UO}_2^{+2}} - 2pE$$

Rearranging:

$$pE = -0.5 \log K_T + 0.5 \log a_{\text{UO}_2^{+2}}$$

The potential shown in Table 4.1 is for the condition,

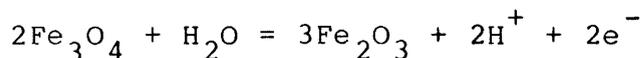
$$\log K_T = \log \text{IAP}$$

This oxidation potential estimated from the uranium content is likely to be similar to that to which other actinide elements respond. It should, therefore, have application to performance assessments.

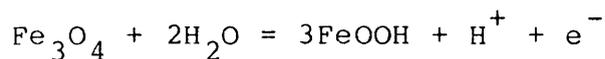
Oxidation potentials can also be defined by pairs of minerals if each member contains the same element in a different oxidation state. Pairs of iron minerals may play this role. The reduced ferrous-iron-bearing member is commonly magnetite (Fe_3O_4 or, alternatively, $\text{FeO}\cdot\text{Fe}_2\text{O}_3$). A number of oxidated minerals are possible including hematite (Fe_2O_3), goethite (FeOOH), and ferric hydroxide ($\text{Fe}(\text{OH})_3$).

Reactions between pairs of these minerals can be written:

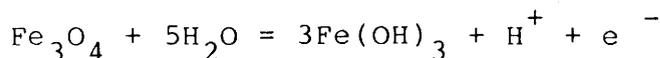
Magnetite - hematite:



Magnetite - goethite

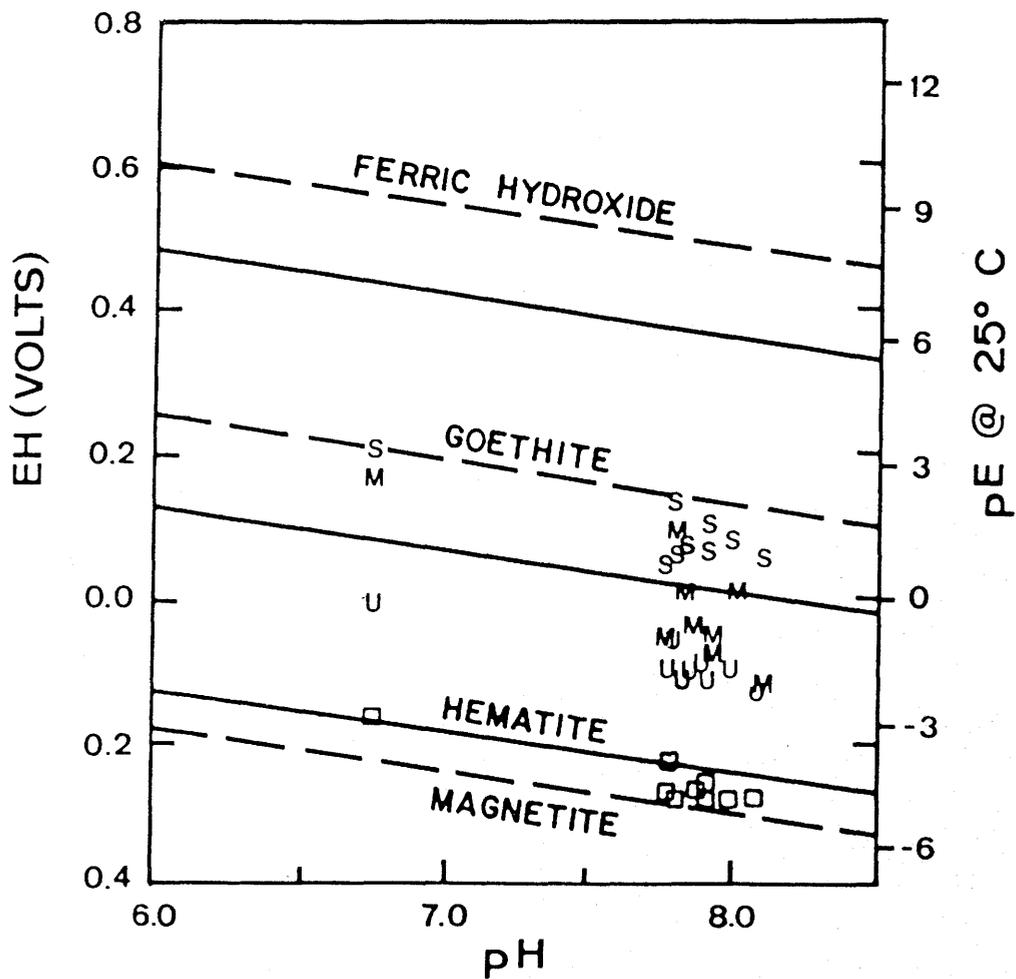


Magnetite - ferric hydroxide



The oxidation potential defined by each of these reactions depends only on the hydrogen ion activity (pH) of the system (given solutions like those discussed in this report in which the activity of water is virtually one).

Figure 4.1 is a diagram showing the relationship between pH and oxidation potential defined by each of the reactions written above. Oxidation potentials calculated for the Boettstein samples and given in Table 4.1 are also shown on the figure.



- NH₄⁺/ N₂ AND CH₄ / CO₂ COUPLES
- U UO₂ SOLUBILITY
- M MEASURED PLATINUM ELECTRODE POTENTIAL
- S H₂O / O₂ (SATO) COUPLE

STABILITY FIELD BOUNDARIES CALCULATED FROM DATA OF:

- SCHWEINGRUBER (1984)
- STUMM AND MORGAN (1981) AND BAES AND MESMER (1976)

Figure 4.1: Eh - pH diagram showing boundaries of iron mineral stability fields and Boettstein sample values.

The lines show the boundaries between the stability fields of magnetite (below) and hematite, goethite, and ferric hydroxide, respectively (above). Two lines are drawn for each boundary to indicate the uncertainties in the solubilities of the solid phases and in the equilibrium constants for the dissolved species. The solid lines are based on the data set selected and used by Schweingruber (1984) for his discussion of redox conditions at Boettstein. The dashed lines were calculated using data selected by Stumm and Morgan (1981) and Baes and Mesmer (1976). Trial calculations were made using data from other sources including the U.S. Geological Survey (Robie, and others, 1978) and National Bureau of Standards (Wagman, and others, 1982). These gave even wider ranges of uncertainty to the fields of stability of goethite and ferric hydroxide but were within the hematite range shown.

The potentials calculated from the NH_4^+/N_2 and CH_4/CO_2 redox pairs are consistent with those of the magnetite-hematite boundary. Magnetite is present throughout the crystalline section at Boettstein and hematite is common in the fractures above 1,000 m (NTB 85-02). The lower limit of the range of oxidation potentials in the upper crystalline, at least, thus appears to be related to this mineral pair. (Even lower potentials are calculated from the H^+/H_2 couple (Table 4.1). As mentioned, the H_2 measured is considered to be a product of iron corrosion and not representative of the oxidation state of the natural system.)

The other values in Table 4.1 plotted in Figure 4.1 indicate more oxidizing conditions. The range of values from the $\text{H}_2\text{O}/\text{O}_2$ (Sato) couple overlap those of the magnetite-goethite boundary. This is probably coincidence because the dissolved oxygen measured is considered to be an artefact of sampling and not representative of the formation water.

Oxidation potentials calculated assuming uraninite saturation are more positive than those along the magnetite-hematite boundary. The difference is too large to be attributable to analytical error or even to uncertainty in the thermodynamic data for uranium.

The oxidation potentials measured with a platinum electrode range between values similar to those calculated from the $\text{H}_2\text{O}/\text{O}_2$ (Sato) couple and lower values similar to those corresponding to uraninite saturation. The agreement between platinum-electrode and O_2 values is expected from Sato's (1960) experimental results. The reason for the lower values measured for some samples and the significance (if any) of their similarity to the uraninite values is not known.

4.2.2.3 Conclusions

A number of indicators of oxidation potential are available for the Boettstein samples. Their results are not entirely concordant. The probable lower limit of the range of oxidation potentials to be expected in formation water is that of the magnetite-hematite boundary which is virtually the same as the potentials calculated from the NH_4^+/N_2 and CH_4/CO_2 couples. The probable upper boundary is that defined by the uraninite solubility values. Some higher values measured with the platinum electrode represent oxygen dissolved in the sample but unlikely to have been present in the formation water itself.

4.2.3 Formation Temperature

The flow rate of water up the borehole while samples were being taken was relatively low, except during the large volume pump test of the Muschelkalk. Formation waters are thus likely to have been cooled during their travel up the borehole, and the surface-measured sample temperatures reported are likely to be lower than the formation temperatures.

Formation, not surface temperatures are of geochemical concern, so they have been evaluated using other available borehole temperature data.

Two sets of temperature data were used: those measured with the Lynes tool during hydraulic testing as evaluated by GTC (written communication to NAGRA, 27-August-84), and those from geophysical borehole logs reported in NTB 85-03. Figure 4.2 is a graph of the temperatures measured during hydraulic testing with borehole depths. Below about 700 m, where most of the hydraulic test data are available, the depth-temperature relationship is:

$$t(^{\circ}\text{C}) = 15.7 + 0.0333 * \text{depth (m)}$$

A similar relationship developed by Simond from temperature log data from 1,000 to 1,500 m depths is:

$$t(^{\circ}\text{C}) = 13.0 + 0.0356 * \text{depth (m)}$$

The differences between these two expressions result from the absence of careful calibration of the temperature transducers in the hydraulic test tools, and the neglect of borehole flow effects in considering the data above 1,000 m. The agreement is within one degree at any depth, however, which adequately defines the temperatures for geochemical purposes.

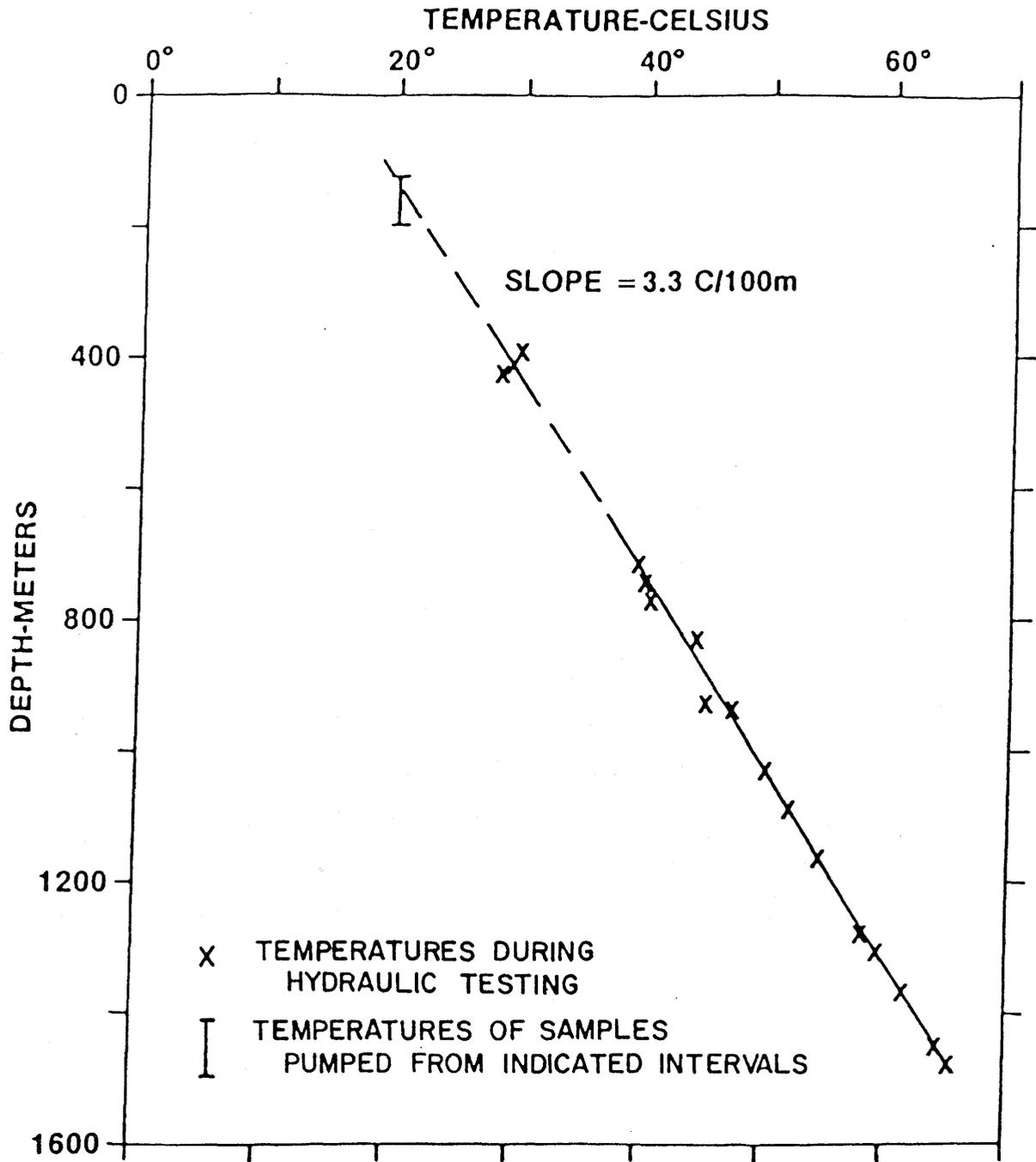


Figure 4.2: Boettstein borehole temperatures with depth.

Above 700 m, the data available comprise the large volume Muschelkalk pump test, two hydraulic tests at about 400 m and the crystalline pump test at 619 m, which are also shown in Figure 4.2. These points fall reasonably well on the temperature-depth line from the deeper crystalline section. If extended this line would intercept the ground surface at a temperature well above the mean annual value for this part of Switzerland. Thus the temperature gradient in the upper few hundred meters must be much steeper than at depth.

4.2.4 Other Mineralogical Constraints

Comparison between descriptions of the mineralogy of the water-bearing formations as given in NTB 85-02 and the results of mineral saturation calculations on the water samples identifies several minerals which appear to control or to be controlled by water chemistry. In the Muschelkalk these include the rock-forming minerals calcite and dolomite as well as the accessory mineral gypsum. Water-rock interactions in the Muschelkalk are discussed in detail in Section 5.1.3.

Crystalline rock-forming minerals are high temperature silicates whose influence on water chemistry is less direct. Minerals important to the chemistry of water in crystalline rocks are those in the fractures where the bulk of the water is found and where it moves. The discussion in this section focuses on the relationship between the water chemistry and these fracture minerals.

NTB 85-02 describes the alterations to which the Boettstein crystalline rock has been subjected and addresses fracture filling minerals. Most fractures are filled with clay minerals and calcite or with clay minerals, quartz and calcite. The exceptions are conduit-shaped open fractures which appear to be lined with drusy quartz crystals. Because of their open structure, these conduits yield water rapidly when a gradient is imposed on the system from the drilling operation. From its chemistry, however, it is clear that the water in the crystalline rock is reacting with, and so must have access to, minerals which occur in the fractures outside these quartz conduits.

In discussing the clay mineralogy of the fracture fillings, the geology report refers to a mineral diagram published by Aagaard and Helgeson (1983). This diagram is reproduced here as Figure 4.3 and on it are plotted values of $\log(a_{K^+}/a_{H^+})$ and $\log a_{SiO_2}$ from the crystalline samples from Boettstein. The result is a

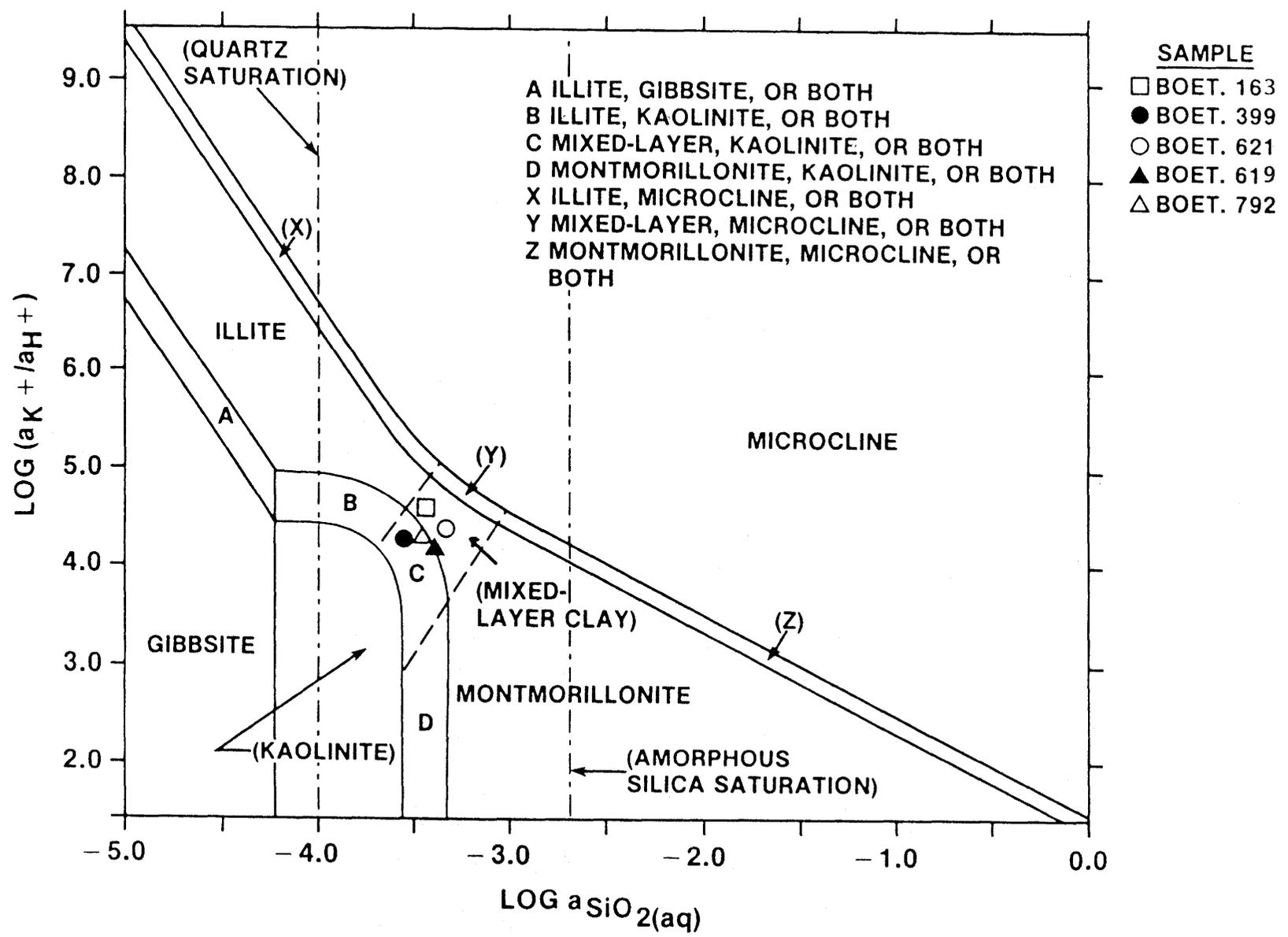


Figure 4.3: Clay mineral stability diagram of Aagaard and Helgeson (1983, Figure 14) with positions of Boettstein waters.

well defined area within the field of stability of mixed-layer clay and(or) kaolinite.

To examine the possible controls on the silica and aluminum contents of the formation waters, the geochemical model described above was used to calculate the concentrations of aluminum and silica which would be present in the waters if they were in equilibrium with kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and chalcedony (SiO_2). The pH values were those corresponding to calcite saturation, as described above.

In Table 4.3 the calculated and analyzed aluminum and silica contents are compared. The aluminum values calculated for all samples and the silica values calculated for the 399 m and 792 m samples agree with the analyzed concentrations within their stated precision. The reported silica values for the other two samples are significantly higher than those calculated.

From the description of the analytical techniques given in NTB 85-04, it appears that not all Boettstein samples were filtered before the silica analyses were made. The silica values measured in unfiltered samples are likely to be higher than the dissolved silica contents of formation water because of the possible inclusion in such samples of colloidal or particulate silica-bearing substances such as clay minerals. Thus, the silica values from the 621 and 619 m samples can probably be discounted as analytical artifacts.

The agreement between the calculated and analyzed values in Table 4.3 supports the hypothesis that the aluminum and silica contents of waters from the upper crystalline at Boettstein are controlled by the minerals kaolinite and chalcedony.

The following table shows the saturation indices for the mineral fluorite (CaF_2) as calculated by PHREEQE:

Sample	$\text{SI}_{\text{fluorite}}$
Muschelkalk	
163 m	+0.05
Crystalline	
399 m	-0.01
621 m	-0.02
619 m	+0.03
792 m	-0.06

Sample Depth	Aluminum (10^{-3} mmol/kg)		Silica (mmol/kg)	
	Anal. <u>1/</u>	Calc. <u>2/</u>	Anal. <u>1/</u>	Calc. <u>2/</u>
399 m	0.2	0.21	0.32	0.33
621 m	<0.2	0.31	0.49	0.40
619 m	0.3	0.22	0.47	0.35
792 m	<0.2	0.31	0.37	0.36

1/ Analytical values from NTB 85-01, Beilage 8.20
Detection limits and reproducibility of analyses
(NTB 85-04) are:

	Detection Limit	Repro- ducibility	Units
Aluminum	0.2	0.4	$\times 10^{-3}$ mmol/kg
Silica	0.004	0.004	mmol/kg

2/ Values calculated at equilibrium with calcite,
kaolinite and chalcedony.

Table 4.3. Analyzed and calculated dissolved aluminum
and silica concentrations in Upper
Crystalline waters.

Within the precision of the analytical data, all of the saturation indices are zero, which suggests that the waters are at equilibrium with fluorite. Studies of the Boettstein core material (NTB 85-02) have not found fluorite in the rock, however. Saturation indices calculated for fluorapatite, which is present in the rock have values upwards of +2. Fluorapatite can therefore not be a source of fluoride to the water nor a control on the concentration of fluoride. Fluorite, in spite of the fact that its presence has not been demonstrated, must be considered the probable control of the dissolved fluoride content of the waters of Boettstein.

5. CHEMISTRY OF SEDIMENTARY FORMATION WATER

This chapter describes the chemistry of water in the upper Muschelkalk and Buntsandstein/weathered crystalline horizons at Boettstein. The discussion of each zone includes a description of how the samples were collected and tables of the most probable chemical and isotopic composition of the formation waters. The chemical parameters were developed using the procedures and criteria described above. The data tables are heavily annotated to explain and support all parameter values included.

5.1 Muschelkalk, 163 m, Oct./Nov. 1982

Two samples were taken from the upper Muschelkalk from a zone extending from the 13 3/8 in casing shoe at 123.2 m to the borehole bottom, then at 202.3 m. Based on fluid-logging performed in the interval (NTB 85-01, Section 7.6), the water flow is from the Trochitenkalk below 171.5 m and from the upper part of the Trigonodus dolomite between 137 and 125 m.

The first Muschelkalk sample was taken on 29-October-1982 using Dowell-Schlumberger DST apparatus, and the second on 1-November-1982 by pumping. This interval was drilled with fresh-water mud but because it contained no tracer, no estimates of the amount of drilling fluid present in the samples could be made in the field. However, the tritium content of the pumped sample was found to be <1.0 TU. Based on a drilling-fluid tritium content of about 110 TU (see Table 7.5), this corresponds to a drilling-fluid content of less than 1 percent of the sample. The tritium content of the DST sample (NTB 85-01, Beilage 8.32) shows that it contained considerable drilling fluid. Thus, the discussion of water chemistry is based on the analyses of the pumped sample, which is given as sample no. 2 in Beilage 8.20 of NTB 85-01.

5.1.1 Chemical Analytical Results

Table 5.1 gives the concentrations of major dissolved species and values of other parameters for formation water from the upper Muschelkalk. The following notes describe the sources of data used and support the choices made in developing this table:

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	2.9	0.42	1
Sodium	Na ⁺	1,100.	47.96	1
Potassium	K ⁺	83.4	2.14	1
Ammonium	NH ₄ ⁺	1.2	0.067	1
Magnesium	Mg ⁺²	198.8	8.20	1
Calcium	Ca ⁺²	611.7	15.30	1
Strontium	Sr ⁺²	11.0	0.13	1
Barium	Ba ⁺²	0.015	0.11x10 ⁻³	1
Iron (Ferrous)	Fe ⁺²	0.05	0.90x10 ⁻³	2
Manganese	Mn ⁺²	0.034	0.62x10 ⁻³	1
Aluminum	Al ⁺³	0.017	0.63x10 ⁻³	1
CATION SUM (milliequivalents/l)			97.84	
Chloride	Cl ⁻	1,302.	36.82	1
Sulfate	SO ₄ ⁻²	2,624.	27.38	1
Bicarbonate plus Carbonate	HCO ₃ ⁻	391.	6.44	3
Fluoride	F ⁻	2.6	0.14	1
Bromide	Br ⁻	0.92	0.012	1
Phosphate	P	0.06	1.9x10 ⁻³	1
ANION SUM (milliequivalents/l)			98.16	
Dissolved Sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	<0.005	<0.15x10 ⁻³	1
Silica	H ₂ SiO ₃	26.4	0.34	1
Boron	HBO ₂	12.9	0.30	1
Iron (total)	Fe	1.4	--	1
Uranium	U	0.56x10 ⁻³	2.4x10 ⁻⁶	4
Dissolved Solids				
Sum		6,169.		
Residue at 110°C		6,480.		1
Temperature	°C	19.7		1
pH	pH	6.74		3
Density (20°C)	(mg/ml)	1.0037		1
Oxidation potential range:				
pE		-0.2 to - 3.2		6
Eh (volts)		-0.01 to - 0.19		6

Table 5.1: Major dissolved constituents and other parameters of water collected 1-November, 1982 from the 123.20 - 202.30 m interval of the Muschelkalk at Boettstein.

- 1) NTB 85-01, Beilage 8.20, Sample 2
- 2) The analytical results show 1.3 mg Fe⁺²/ℓ and 1.4 mg Fe_{total}/ℓ. To explore whether this could have been due in part to formation water attack on iron metal in the borehole (the cause of high iron values in samples from the crystalline), analyses of samples from other Muschelkalk wells taken as part of the Regional Program were examined. Samples chemically similar to that from Boettstein came from the Beznau and the 250 - 280 m Lostorf boreholes and from the springs at Baden. The iron content of the Beznau samples has been decreasing and may, therefore, not yet represent formation water chemistry. The Baden and Lostorf samples have remained reasonably steady during the period of sampling and a value representative of their iron content (0.05 mg/ℓ) was adopted.
- 3) Results important to the carbonate system are given in Table 5.2. The Fresenius results, given in the first column are internally inconsistent because the reported m-value and pH lead to a calculated dissolved CO₂ content (base capacity) of 1.42 mm and calcite and dolomite saturation indices of +0.21. Oversaturation with respect to these minerals is improbable in a carbonate aquifer, and the analyzed base capacity and CO₂ contents are higher than those calculated. Recalculation of the carbonate system assuming a pH of 6.74 leads to a base capacity of 1.97 mm, in much better agreement with the measured 2.02 mm, and to the more reasonable saturation indices of +0.07 for calcite and -0.07 for dolomite. The high dissolved CO₂ content of this water could have caused CO₂ loss during pumping and sampling which, in turn, would have produced the high Fresenius pH value reported and, perhaps, the low dissolved CO₂ and total CO₂ values reported by EIR as well.
- 4) The following uranium data are reported in NTB 85-01:

Analysis:	μg/ℓ	²³⁴ U/ ²³⁸ U
Fresenius Sample 2	<0.1	--
EIR Sample 2	0.55	9.0
LLC (Beilage 8.32)	0.57	11.81

The mean of the EIR and LLC results was chosen.

	Fresenius Analysis Sample 2	EIR Gas Analysis Sample 2	PHREEQE Calculation Results
m-value: (from the original analysis sheet)			
- meq/l	6.44		6.44
- mg/l as HCO_3^-	393.0		393.
$\text{HCO}_3^- + \text{CO}_3^{-2}$:			
- mm	6.37		6.42
- mg/l as HCO_3^-	387.5		391.
Dissolved CO_2 :			
calc - mm			1.97
Base Capacity:			
- mm	2.02		
- mg/l as CO_2	89.		
Gas Analyses:			
- mm		1.76	
mg/l CO_2		77.46	
Total CO_2 - mmol			
Sum of above	8.39		8.39
Analyzed		7.55	
pH	6.88		6.74
Saturation Indices:			
Calcite	+0.21		+0.07
Dolomite	+0.21		-0.07

Table 5.2: Carbonate system data for Boettstein Muschelkalk sample

5) The following dissolved gas concentrations (in mg/kg) are reported in NTB 85-01:

Analysis:	N ₂	O ₂	Ar	He	H ₂	CH ₄
Fresenius	34.	5.0	0.8	0.02	<0.0004	<0.008
Sample 2	28.	3.6	0.4	0.09	<0.0004	
EIR Sample 2	31.2	0.08	0.77	0.04	Tr	0.01
LLC (Beilage 8.32)			0.84	0.038		

Based on its tritium content, this sample could have included up to 1 percent drilling fluid. If the fluid contained 10 mg/l dissolved O₂, its presence could have given up to 0.1 mg/l O₂ to the sample. All oxidation state indicators are too low to support the presence of oxygen in the formation water, and so the oxygen reported must be taken as resulting from the presence of a minimal amount of drilling fluid or from sampling itself.

The EIR and Fresenius N₂ values are in reasonable agreement; the EIR value was used. The EIR and LLC results for Ar and He agree well. The EIR values were chosen for consistency with the other gas results.

6) The oxidation potential range reported is as discussed in Section 4.2.2.

5.1.2 Isotope Analytical Results

A number of isotope analyses were made on samples from all major water-bearing zones at Boettstein. This work was carried out or coordinated by the Low Level Counting Laboratory at the University of Bern. The significance of isotope techniques themselves is discussed in NTB 83-04 and details of the Boettstein isotope sampling and results in NTB 85-06.

Table 5.3 gives results of isotope analyses important in defining the evolution of the chemistry of the Muschelkalk water at Boettstein. The significance of these results is discussed in the following section.

5.1.3 Chemical and Isotopic Evolution

It is usually not possible to interpret the chemical evolution of water in an aquifer from a single sample. Fortunately, there is information available from Nagra's Regional Program on the chemistry and isotope content of

<u>Analysis</u>	<u>Units</u>	<u>Results</u>
$\delta^D_{H_2O}$	‰	-78.2
$\delta^{18}O_{H_2O}$	‰	-11.16
3H	TU	<1.0
$\delta^{13}C$	‰	-4.8
^{14}C	pmc	1.49 ± 0.12
$\delta^{34}S_{SO_4}$	‰	18.0
$\delta^{18}O_{SO_4}$	‰	13.7

Table 5.3: Selected isotope analytical results from Muschelkalk water and solutes (NTB 85-01, Beilage 8.32)

Muschelkalk water elsewhere in northern Switzerland which can be used to support an interpretation of the Boettstein results (NTB 84-21).

As mentioned above, the Boettstein Muschelkalk sample is from the Trigonodus dolomite and the Trochitenkalk. The Trigonodus dolomite is described as a marine dolomite with significant overgrowths of euhedral, clear calcite (NTB 85-02). The Trochitenkalk ranges from biomicrite to marly dolomite and contains gypsum and calcite pseudomorphs of gypsum.

The chemistry of the Boettstein sample is entirely consistent with its source in such rock. Geochemical calculations of the saturation state of waters with respect to minerals was discussed in Section 4.1.3 above. Such calculations for the water chemistry of Table 5.1 yield:

<u>Mineral</u>		<u>Saturation Index</u>
Calcite	- CaCO_3	+0.07
Dolomite	- $\text{CaMg}(\text{CO}_3)_2$	-0.07
Gypsum	- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.00
Fluorite	- CaF_2	+0.05
Chalcedony	- SiO_2	+0.13

Saturation indices in such carefully collected and analyzed samples as these should be precise to within ± 0.05 to ± 0.1 units. Thus within these limits, this water appears saturated with respect to calcite, dolomite, gypsum, fluorite and, probably with chalcedony as well.

The upper Muschelkalk itself and the chemistry of this Boettstein water are similar to gypsiferous dolomite aquifers elsewhere in the world such as parts of the Edwards aquifer system of central Texas, USA (Pearson and Rettman, 1976). These similarities include:

Aquifer mineralogy including primary dolomite, gypsum and secondary calcite;

Water saturated with respect to calcite, dolomite and gypsum; and

Dissolved carbonate species relatively enriched in ^{13}C .

In the Edwards system, a straightforward model describes the evolution of the formation water. Water in the recharge region after passing through the soil zone

rapidly reaches chemical equilibrium with calcite. The dissolved carbonate of this water is about equally derived from CO_2 in the soil atmosphere and from mineral carbonate from the formation and, as described by Balderer, (1983, Section 4.2.3.5) has a $\delta^{13}\text{C}$ of -12 to -15‰ and a ^{14}C content of 50 to 85 pmc.

In the gypsum-bearing, dolomitic part of the Edwards, the water reaches dolomite saturation relatively rapidly because of the large amount of dolomite available. It also dissolves gypsum, but reaches gypsum saturation only with considerable time and(or) flow because of the relatively smaller amount of gypsum present in the formation.

As gypsum dissolves, the calcium and sulfate content of the solution increases. To maintain calcite saturation as gypsum dissolves, calcite precipitates. This lowers the carbonate content of the water and permits additional dolomite to dissolve. This evolutionary process stops when the solution has become saturated with gypsum and the driving force for continued calcite precipitation and dolomite dissolution no longer is present.

5.1.3.1 Carbon Isotope Evolution

The concurrent calcite precipitation and dolomite dissolution have a profound effect on the isotopic chemistry of the dissolved carbonate and they must be quantitatively described before any attempt can be made to use ^{14}C to estimate ground-water residence times or flow rates. The dissolving dolomite adds marine carbonate ($\delta^{13}\text{C} \approx 0$ to $+20\text{‰}$, $^{14}\text{C} = 0$ pmc) while the precipitating calcite contains ^{14}C and stable carbon isotopes at isotopic equilibrium with the solution. This produces waters with $\delta^{13}\text{C}$ values of -5‰ or even more positive, and considerably lower ^{14}C contents than could be accounted for by water age alone. The procedures for calculating this effect have been described by Wigley, and others, (1978) and examples of their application given by Downing and others (1977, 1979).

This model of water chemistry evolution has been applied to the upper Muschelkalk, and leads to an internally consistent description of the Muschelkalk water at Boettstein. This makes it possible to separate the change in water ^{14}C content resulting from geochemical reactions from those due to radioactive decay. Only the latter change is indicative of water age or residence

time and separating it from geochemical effects is, therefore, of considerable importance.

Wells at Kaisten and Windisch, sampled during the Regional Program (NTB 84-21) appear to represent recharge waters to the Muschelkalk system. The following characteristics distinguish them as recharge samples:

	<u>Kaisten</u>	<u>Windisch</u>
Tritium - T.U.	69.8 ± 4.8	83.7 ± 5.6
^{14}C - pmc	75.6 ± 0.6	77.3 ± 0.6
$\delta^{13}\text{C}$ - ‰	-14.0	-13.4
Saturation Indices		
Calcite	-0.01	-0.12
Dolomite	-0.61	-0.80
Gypsum	-0.59	-0.85

The high tritium and ^{14}C contents show that the water has infiltrated since the beginning of nuclear testing - within the last few tens of years. The samples are at or only slightly under saturation with respect to calcite, and have $\delta^{13}\text{C}$ values in the -12 to -15 ‰ range typical of recharge waters. Both are significantly undersaturated with respect to dolomite and gypsum and have, therefore, not yet had opportunity to react significantly with these minerals.

Using these as representative recharge waters, the mass of mineral solution and deposition required to reach the Boettstein water composition can be calculated, as shown in Table 5.4. The calculations begin with the recharge water compositions. Because gypsum is virtually the only source of sulfate in this system, the recharge water must dissolve sufficient gypsum to bring sulfate to the concentration found at Boettstein. This brings an equivalent amount of calcium into solution.

Although some magnesium may be present in gypsum or other sulfate minerals, dolomite is by far the most important source of magnesium in the system. The amount of dolomite taken is that necessary to raise the magnesium content of the recharge to the concentration in the Boettstein sample. This brings an equivalent amount of calcium and twice as much carbonate into solution. The increase in m-value (alkalinity) is twice the carbonate increase.

The Boettstein water contains considerably more sodium and chloride than do the recharge water types which may well result from an admixture of high chloride brine of

	Ca ⁺² mmols	Mg ⁺² mmols	Na ⁺ , K ₁ ⁺ etc. mmols	m- value meq.	SO ₄ ⁻² mmols	Cl ⁻ , F ₂ ⁻ etc. mmols	CO ₂ total mmols
RECHARGE Kaisten	6.42	1.95	0.39	6.15	5.26	0.46	8.12

EVOLUTION:							
+ 22.13 mmol Gypsum	+22.13				+22.13		
+ 6.25 mmol Dolomite	+6.25	+6.25		+25.00			+12.50
+ 36.16 mmol Salts			+36.16			+36.16	
- 7.16 mmol Ca ⁺² - 2Na ⁺	-7.16		+14.32				
- 12.34 mmol Calcite	-12.34			-24.68			-11.90
+ 0.14 mmol CO ₂							+0.14

BOETTSTEIN	15.30	8.20	50.87	6.47	27.39	36.62	8.42

RECHARGE Windisch	4.91	1.58	0.99	6.40	3.22	1.13	8.82

+ 24.17 mmol Gypsum	24.17				24.17		
+ 6.62 mmol Dolomite	6.62	6.62		26.48			13.24
+ 35.49 mmol Salts			35.49			35.49	
- 7.195 mmol Ca ⁺² - 2Na ⁺²	-7.195		14.39				
- 13.205 mmol Calcite	-13.205			-26.41			-13.205
- 0.435 mmol CO ₂							-0.435

BOETTSTEIN	15.30	8.20	50.87	6.47	27.39	36.62	8.42

1/ Sum of other cations; 2/ Sum of other anions adjusted for charge balance.

Table 5.4: Mineral dissolution and precipitation reactions during evolution of Muschelkalk water of Boettstein chemistry.

the type found at depth and described in the Regional Program report (NTB 84-21). This increase is accounted for by adding an arbitrary salt of composition NaCl to bring the recharge chloride to the Boettstein level. This does not add sufficient sodium to reach the concentration in the Boettstein sample. It is likely that as calcium enters the solution through gypsum and dolomite dissolution, it exchanges with sodium-bearing clay in the formation, thus adding sodium to and removing calcium from the solution. The extent of this reaction given in Table 5.4 is that necessary to bring the sodium content up to that of the Boettstein sample.

At this point, the amount of calcium and carbonate calculated as entering the solution far exceed the amounts found in the Boettstein sample. Calcite precipitation accounts for the calcium difference and removes an equivalent amount of carbonate from the system as well. The m-values are now also in balance, as they must be from the algebra of Table 5.4. The total carbonate values are close to, but not identical with, those in the Boettstein sample, however. Water of the Kaisten type requires an additional 0.14 millimoles of CO₂ which could easily be derived from the oxidation of carbon-bearing material in the aquifer. Water of the Windisch type, however, must lose 0.435 millimoles of CO₂. As the table above shows, this water as analyzed was undersaturated with calcite. A certain amount of CO₂ is likely to be lost from this water in the recharge area as it reaches calcite saturation there, and so the loss appearing in Table 5.4 is not surprising.

The results give the amounts of minerals which dissolve and precipitate during the evolution of waters of the recharge type to that found at Boettstein. These amounts were developed here using a simple mass balance approach which requires no knowledge of geochemical modeling for its understanding. The same calculations have been made using PHREEQE in its reaction calculation mode, and the amounts of mineral solution and precipitation are found to be the same.

To calculate the carbon isotopic evolution of these waters using the equations developed by Wigley, and others, (1978), requires that the isotopic composition of the starting solution and of carbonate entering the system be known, along with the amounts of carbonate entering and leaving the solution. The carbonate amounts came from the mass balances in Table 5.4. The $\delta^{13}\text{C}$ values of the recharge water types were measured and are given in the table above. The ^{14}C contents of the recharge water types were also measured and appear above. These values, though, are for waters recharged during a time of high atmospheric ^{14}C contents resulting

from nuclear activities. Water recharged before man's influence on the carbon-cycle began is likely to have had a ^{14}C content closer to 55 pmc than to the measured 75 to 80 pmc. 55 pmc was used in the calculations below.

The isotopic composition of the carbonate entering the solution from dolomite dissolution is also required. Although values measured on material from the Boettstein core are not yet available, values can be estimated precisely enough to introduce little error into the calculations. The ^{14}C content of the dissolving dolomite will certainly be zero because of the age of the formation. Its $\delta^{13}\text{C}$ value is likely to be one typical of marine dolomite - in the range of 0 to 2 ‰.

The isotope calculations were made using the CARISOL program which evaluates the finite difference solution to the isotope evolution differential equation of Wigley and others, 1978. The finite difference solution, given in Appendix C of that paper, is used in preference to the closed form solutions also given because it permits changing fractionation factors with changing temperatures and distributions of dissolved carbonate species, and is able to include ^{14}C fractionation as well.

Calculations were made at several assumed values for the $\delta^{13}\text{C}$ of the dissolving dolomite, with the following results:

$\delta^{13}\text{C}$ of Dolomite (‰):	0.0	0.5	1.0
Calculated $\delta^{13}\text{C}$ ‰:			
Kaisten	-5.2	-4.8	-4.4
Windisch	-5.0	-4.7	-4.3
Calculated ^{14}C (pmc):			
Kaisten	11.8	11.8	11.8
Windisch	11.7	11.7	11.7

The measured $\delta^{13}\text{C}$ value of the total carbonate dissolved in the Boettstein Muschelkalk sample is -4.8 ‰. This is matched most closely by evolution from either recharge water type using a dolomite $\delta^{13}\text{C}$ of 0.5 ‰. The $\delta^{13}\text{C}$ values calculated with dolomite $\delta^{13}\text{C}$ values of 0.0 and 1.0 ‰ indicate the sensitivity of the system to this parameter, but also are close enough to the measured Boettstein value to confirm the chemical evolution described in Table 5.4.

The ^{14}C result is not dependent on the choice of dolomite $\delta^{13}\text{C}$, so all three calculations give the same value. This number, - 11.8 for Kaisten and 11.7 for Windisch - is the ^{14}C content of the dissolved carbonate which would result from the solution-precipitation reactions alone during the chemical evolution of the Boettstein water. It does not include any radioactive decay which would have occurred between the time of water recharge and its sampling at Boettstein. The measured ^{14}C of the Boettstein sample was 1.5 pmc while the model value calculated with no decay is 11.8 pmc. The difference between these values corresponds to approximately 17×10^3 years and represents the residence time of the water.

It is not possible to estimate precisely the uncertainty in the model evolution calculations, but it is most unlikely the error could be as much as a factor of two in the ^{14}C content. This would correspond to an error of $<6 \times 10^3$ years in the time calculated.

It is important to note that the calculations described here do NOT require that the actual path of water flow to Boettstein be from Kaisten or Windisch. They require only that the chemistry of the recharge region - wherever it may be - be similar to that at Kaisten and Windisch. This seems reasonable given the similarity in these waters in spite of their distance apart.

5.1.3.2 Sulfate Isotope Evolution

According to the model for chemical evolution of Muschelkalk water presented above, the source of virtually all the sulfate dissolved in it would be mineral sulfate (gypsum). Beilage 4.1 of NTB 85-01 shows that neither gypsum nor anhydrite is present in the water-bearing zones of the Trigonodus dolomite and the Trochitenkalk from which the Boettstein water sample was derived. Gypsum does occur, though, in the basel Gipskeuper, overlying the Trigonodus dolomite and near the top of the Mittlerer Muschelkalk, beneath the Trochitenkalk. The Trochitenkalk itself also contains solution pores in the shape of gypsum crystals. If the model of chemical evolution is correct, the isotopic composition of the sulfate dissolved in the water should be the same as that of mineral sulfate of these formations.

Sulfate isotope values ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) are not yet available on sulfate minerals from the Boettstein core. However, Beilage 8.36 of NTB 85-01 shows that the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the dissolved sulfate are squarely within the range of values reported for mineral

sulfates from the same formations elsewhere. This supports the proposed origin for the dissolved sulfate in the Boettstein Muschelkalk water sample.

5.2 Buntsandstein/Weathered Crystalline, 313 m, Jan. 1984 and 316 m, Nov. 1982

At Boettstein the Buntsandstein is in direct contact with the weathered surface of the crystalline basement rock. Thus while the Buntsandstein is an obviously definable lithologic unit, it appears to function with the weathered crystalline as a single hydrologic unit.

According to the Geology Report (NTB 85-02), the contact between the Buntsandstein and the crystalline basement is at a depth of 315.30 m. The section to 340.35 m was drilled with brine mud. The composition of this drilling fluid is poorly known, except that its "salt" content (based on a chloride ion analysis) was about 200 g/l, it contained no tracer, and its tritium content was probably about 110 TU.

Drilling of this section was completed on 11-November-82 and several samples were taken from it between 13 and 16-November. The analyses of the best two of these are shown as Samples 5 and 6 in Beilage 8.20 (NTB 85-01). The borehole was deepened to 340.35 m on 17-18 November, and another sample was taken on 19 November. The hole was cased and cemented to 339.90 m, and the crystalline drilling and testing program was carried out.

At the conclusion of the testing program the casing was perforated opposite the Buntsandstein at 313 m and, a final sample was collected on 20 January 1984. Its analysis is given as sample 25 in Beilage 8.20.

The tritium content of Sample 5 was less than 1 TU and so contained less than one percent drilling fluid. The quantity of most constituents added to the sample by this amount of contamination can be neglected. Thus most of the isotope results, for example, should be quite useful.

Because of its very high salt content, however, even this small amount of drilling fluid contamination could have seriously effected the chemistry of the sample. One percent of a 200 g/l salt solution would have added 1,200 mg Cl/l to a sample, an amount larger than that analyzed in Samples 5, 6, or 25. To correct the chemical analyses of the Buntsandstein samples for drilling fluid contamination would require a much more precise value for the extent of contamination than is measurable. Thus no detailed geochemical interpretation of these samples is warranted.

As mentioned, it is possible that the Buntsandstein and weathered crystalline at Boettstein form a single hydrogeologic unit. If so, the chemistry of water in this unit would be chemically similar to other water in the upper crystalline. The Buntsandstein/weathered crystalline analyses show higher constituent concentrations than the crystalline water analyses discussed in the next chapter. However, it is not possible to show that these increased concentrations could not be due to drilling fluid contamination and that the formation water chemistry is not the same as that from deeper samples.

The drilling fluid present in these samples is not sufficient to influence the major environmental isotopes, however. Because of their importance in interpreting the upper crystalline samples, they are discussed below.

6. CHEMISTRY OF UPPER CRYSTALLINE FORMATION WATER

This chapter describes the chemistry of water in the crystalline rock both at Boettstein above 1,000 m depth and at Zurzach. Each zone sampled is discussed separately in a similar format which includes a description of how the sample was collected and tables of the most probable chemical and isotopic composition of the formation water. The chemical parameters were developed using the procedures and criteria described in the previous sections of this report. The data tables are heavily annotated to explain and support all parameter values included.

The raw chemical analyses are given in Beilage 8.20 (NTB 85-01) and the sample numbers used below are those of that Beilage. Isotope results are given in Beilage 8.32 (NTB 85-01).

6.1 Crystalline, 399 m; Dec. 1982

6.1.1 Sample Collection

This interval flowed at about 1.3 l/min. Sample 8 was collected at the surface from this flow. Tracer measurement suggests that contamination by the deionized water drilling fluid was less than 1 percent (Beilage 8.10, NTB 85-01). Sample 9 was collected after sample 8 from a depth of about 90 m using GTC pressure sampling apparatus.

6.1.2 Chemical Analytical Results

Table 6.1 gives the concentrations of major dissolved species and values of other parameters for formation water from this zone. The following notes describe the sources of data used and support the choices made in developing this table.

- 1) Average of Fresenius analyses, Samples 8 and 9 (Beilage 8.20, NTB 85-01)
- 2) Fresenius analysis, Sample 8 (not analyzed in 9)
- 3) The following iron values were reported:

Fresenius, Sample 8 - Fe ⁺² ,	1.2 mg/l
Fresenius, Sample 8 - Total	4.1 mg/l
Fresenius, Sample 9 - Total	2.0 mg/l

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	2.0	0.29	1
Sodium	Na ⁺	356.2	15.52	1
Potassium	K ⁺	8.5	0.22	1
Ammonium	NH ₄ ⁺	0.37	0.021	1
Magnesium	Mg ⁺²	0.3	0.012	1
Calcium	Ca ⁺²	9.6	0.24	1
Strontium	Sr ⁺²	0.40	4.6x10 ⁻³	1
Barium	Ba ⁺²	0.040	0.29x10 ⁻³	2
Iron (Ferrous)	Fe ⁺²	0.02	0.36x10 ⁻³	3
Manganese	Mn ⁺²	0.120	2.2x10 ⁻³	1
Aluminum	Al ⁺³	0.0057	0.21x10 ⁻³	8
CATION SUM: (milliequivalents/l)			16.57	
Chloride	Cl ⁻	120.7	3.41	1
Sulfate	SO ₄ ⁻²	308.0	3.21	1
Bicarbonate plus carbonate	HCO ₃ ⁻	386.	6.33	4
Fluoride	F ⁻	12.35	0.65	1
Bromide	Br ⁻	0.83	0.010	2
Phosphate	P	0.006	0.2x10 ⁻³	2
ANION SUM: (milliequivalents/l)			16.83	
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	0.009	0.3x10 ⁻³	2
Silica	H ₂ SiO ₃	25.8	0.33	8
Boron	H ₃ BO ₃	4.2	0.068	1
Iron (Total)	Fe	0.02	--	3
Uranium	U	1.0x10 ⁻³	4.2x10 ⁻⁶	5
Total Dissolved Solids				
Sum		1,033.		
Residue at 110°C		1,045.		2
Temperature	°C	28.		7
pH	pH	8.00		4
Density (20°C)	(mg/ml)	0.9992		2
Oxidation Potential Range				
pE	-1.7 to -4.7			9
Eh(volts)	-0.11 to -0.28			9

Table 6.1: Major dissolved constituents and other parameters of water collected 13-15, Dec, 1982 from 393.9 to 405.1 m interval, crystalline section at Boettstein

As discussed in Section 4.2.2.2 above, these high iron values are most likely attributable to iron tools in the borehole. Formation water ferrous and total iron concentrations have, therefore, been taken as equal to those at Zurzach, 0.02 mg/l.

4) Results important to defining the carbonate system are given in Table 6.2. Because of the high pH of the water (>8), the amount of total carbonate present as dissolved CO₂ is very small and so difficult to analyze. PHREEQE calculation results describe a solution with m-value equal to the pressure vessel sample adjusted to calcite saturation. The pressure sample m-value was selected because it is less likely to have been effected by outgassing during flow up the borehole than the surface collected samples. The calculated dissolved CO₂ content is slightly below those measured by EIR. The EIR analytical technique may have included some dissociated HCO₃⁻ in its CO₂ result so the comparison is not surprising. The calculated values have been chosen for the results in Table 6.1.

5) The following uranium data were reported:

Sample	U (µg/l)	²³⁴ U/ ²³⁸ U
Fresenius: Sample 8, flowing	0.8	---
EIR Sample 8, Flowing	1.1	2.8
EIR Sample 9, Pressure vessel	1.0	---
LLC - (Beilage 8.32)	1.1	3.26 ± 0.05

The mean value of all results was used.

6) The following dissolved gas concentrations (in mg/kg) were reported:

Analysis	N ₂	He	Ar	O ₂	CH ₄	H ₂
Fresenius: Sample 8	25	0.02	0.7	0.9	<.004	<.00002
	20	0.1	0.4	0.7	<.006	<.0002
EIR: Sample 8	34.3	0.04	0.89	0.1	0.01	0.005
EIR: Sample 9	35.1	0.04	0.84	0.007	0.01	0.005
LLC, Flowing		0.034	0.99			
(Beilage 8.32)		0.040	1.02			
LLC, Press. vessel		0.029	0.942			
(Beilage 8.32)						

There is little difference between the EIR and LLC results for He and Ar, and little difference between the surface collected and pressure sample results. The concentrations of U and dissolved gases are not consistent with the measured concentrations of O₂ reported by Fresenius and EIR as discussed in Section 4.2.2.1. Means of the EIR N₂, H₂ and CH₄ values were

	Fresenius Analyses		EIR Gas Analyses		PHREEQE Calcula- tion Results
	Sample 8 Flowing	Sample 9 Pressure Sample	Sample 8 Flowing	Sample 9 Pressure Sample	
m-value (from original analysis sheet)					
- meq/l	5.82	6.40			6.40
- mg/l as HCO_3^-	355.	390.			390.
$\text{HCO}_3^- + \text{CO}_3^{-2}$					
- mm	5.32	6.39			6.33
- mg/l as HCO_3^-	325.	389.9			386.
Dissolved CO_2					
Calc - mm					0.11
Gas Analyses:					
- mm	0.00	0.05	0.14	0.29	
- mg/l as CO_2	<0.1	2.0	6.16	12.76	
Total CO_2 - mm					
Sum of above Analyzed	5.32	6.44	—	—	6.44
pH	8.27	8.14			8.00

Table 6.2: Carbonate system data for 399 m crystalline water

adopted. Low CH_4 and H_2 values in the Fresenius samples are likely the result of sample degassing.

7) The temperature of the surface sample 8 was 11.1°C when collected. The formation temperature, based on the considerations of Section 4.2.3 is 29.0°C using the first equation or 27.2°C using the second. A rounded mean value of $28.^\circ\text{C}$ was chosen.

8) Silica (H_2SiO_3) and aluminum concentrations are those calculated for the water at equilibrium with kaolinite, chalcedony and calcite as discussed in Section 4.2.2.

9) The Eh range reported is taken from Table 4.1.

6.2 Crystalline, 621 m, Jan. 1983

6.2.1 Sample Collection

This interval flowed at about 3 $\mu\text{L}/\text{min}$. Sample 12 was collected at the surface from this flow on 22-Jan-83. Sample 13 was then collected using the GTC pressure sampling tool from a depth of about 600 m.

Even though the interval had been swabbed and allowed to flow freely until nearly 18 m^3 of fluid had discharged, the tracer concentrations of both the surface and pressure samples indicated that they still contained as much as 3 percent drilling fluid (Beilage 8.10, NTB 85-01). However, the tritium concentration of the isotope sample taken during the same sampling period was only 1.0 ± 0.7 TU (Beilage 8.32, NTB 85-01). The tritium content of the de-ionized water used for drilling fluid was about 110 TU (see Table 7.5), so the samples are not likely to have contained more than 1. to 1.5 percent de-ionized water. The interval at 399 m was probably contributing to the fluid in the borehole while drilling proceeded. The difference between the contamination percents indicated by the concentrations of tracer and tritium concentrations could be due to the presence of 1.5 to 2. percent of water from 399 m in the sample.

The accuracy to be expected in water analyses is probably not less than one or two percent. This is the same level of error which could have been introduced by the presence of drilling fluid in the sample. Thus attempting to correct the reported analyses for their drilling fluid content is not justified.

6.2.2 Chemical Analytical Results

Table 6.3 gives the concentrations of major dissolved species and other parameters for formation water from this zone. The following notes describe the sources of data used and support the choices made in developing this table.

1) Average of Fresenius analyses samples 12 and 13 (Beilage 8.20, NTB 85-01)

2) Fresenius analyses sample 12. (Not analysed in 13).

3) The following iron concentrations were reported:
 Fresenius Sample 12 - Fe⁺², flowing, 1.2 mg/ℓ
 Fresenius Sample 12 - Total, flowing, 2.1 mg/ℓ
 Fresenius Sample 13 - Total, pressure, 1.3 mg/ℓ

As discussed in Section 4.2.2 above, these high iron values are attributable to iron tools in the borehole. Formation water ferrous and total iron concentrations have therefore been taken as equal to those at Zurzach, 0.02 mg/ℓ.

4) Results important to defining the carbonate system are given in Table 6.4. Because of the high pH of the water (>8), the amount of total carbonate present as dissolved CO₂ is very small and so difficult to analyze. PHREEQE calculation results describe a solution with m-value equal to the pressure vessel sample adjusted to calcite saturation. The pressure sample m-value was selected because it is less likely to have been effected by outgassing during flow up the borehole than the surface collected samples. The calculated dissolved CO₂ content is that from the pressure sample measured by EIR. The EIR analytical technique may include some dissociated HCO₃⁻ in its CO₂ result so the comparison is not surprising. The calculated values were chosen for the results in Table 6.3.

5) The following uranium data were reported:

Sample	μg/ℓ	²³⁴ U/ ²³⁸ U
EIR Sample 12, flowing	0.4	2.0
EIR Sample 13, pressure vessel	0.5	---
LLC, (Beilage 8.32)	0.42	2.59 ± 0.07

The mean of the EIR and LLC values was used.

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	2.5	0.36	1
Sodium	Na ⁺	364.0	15.86	1
Potassium	K ⁺	10.8	0.28	1
Ammonium	NH ₄ ⁺	0.17	9.4x10 ⁻³	2
Magnesium	Mg ⁺²	0.3	0.012	1
Calcium	Ca ⁺²	11.8	0.29	1
Strontium	Sr ⁺²	0.57	6.5x10 ⁻³	1
Barium	Ba ⁺²	0.045	0.33x10 ⁻³	2
Iron (Ferrous)	Fe ⁺²	0.02	0.36x10 ⁻³	3
Manganese	Mn ⁺²	0.099	1.8x10 ⁻³	1
Aluminum	Al ⁺³	0.0084	0.31x10 ⁻³	8
CATION SUM: (milliequivalents/ℓ)			17.14	
Chloride	Cl ⁻	130.9	3.70	1
Sulfate	SO ₄ ⁻²	333.	3.47	1
Bicarbonate plus carbonate	HCO ₃ ⁻	385.	6.32	4
Fluoride	F ⁻	12.35	0.65	1
Bromide	Br ⁻	0.88	0.011	2
Phosphate	P ⁱ	0.012	0.39x10 ⁻³	2
ANION SUM: (milliequivalents/ℓ)			17.63	
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	<5x10 ⁻³		2
Silica	H ₂ SiO ₃	31.2	0.40	8
Boron	H ₃ BO ₃	5.8	0.094	1
Iron (Total)	Fe	0.02		3
Uranium	U	0.44x10 ⁻³	1.8x10 ⁻⁶	5
Total Dissolved Solids				
Sum		1087.		
Residue		1017.		2
Temperature	°C	36.0		7
pH	pH	7.82		4
Density (20°C)	mg/ml	0.9992		2
Oxidation Potential Range				
pE		-1.9 to -4.7		8
Eh(volts)		-0.12 to -0.28		8

Table 6.3: Major dissolved constituents and other parameters of water collected 22-Jan-1983 from 618.5 to 624.1 m interval, crystalline section at Boettstein.

	Fresenius Analyses		EIR Gas Analyses		PHREEQE Calcula- tion Results
	Sample 12 Flowing	Sample 13 Pressure Vessel	Sample 12 Flowing	Sample 13 Pressure Vessel	
m-value (from original analysis sheet)					
- meq/l	6.33	6.39			6.39
- mg/l as HCO_3^-	386.	390.			389.
$\text{HCO}_3^- + \text{CO}_3^{2-}$					
- mm	6.30	6.40			6.32
- mg/l as HCO_3^-	384.4	390.4			385.
Dissolved CO_2					
Calc - mm					0.16
Gas Analysis					
- mm	0.07	0.07	0.15	0.30	
- mg/l as CO_2	3.0	3.0	6.6	13.2	
Total CO_2 - mm					
Sum of above Analyzed	6.37	6.47	6.05	--	6.48
pH	8.13	8.00			7.82

Table 6.4: Carbonate system data for 621 m crystalline water

6) The following dissolved gas concentrations (in mg/kg) were reported:

Analysis	N ₂	He	Ar	O ₂	CH ₄	H ₂
Fresenius	28	0.02	0.7	2.2	0.007	<.00002
Sample 12	22	0.01	0.4	1.6	0.01	<.0002
EIR Sample 12	34.8	0.04	0.90	0.01	0.02	0.004
EIR Sample 13	39.4	0.04	0.93	0.04	0.02	0.002
LLC - Flowing (Beilage 8.32)		0.038	0.93			
		0.036	0.92			
LLC - Press. vessel (Beilage 8.32)		0.035	0.91			

The EIR and LLC results for He and Ar are virtually identical, and show no systematic differences between surface collected and pressure vessel samples. Because the pressure vessel was filled with N₂ before sample collection, the EIR Sample 12 N₂ value was adopted. The Fresenius samples contained more O₂ but less than the other gases than do the EIR and LLC samples. They may have suffered either from outgassing before collection or from some exchange with the atmosphere. The EIR H₂, O₂, and CH₄ data were used.

The concentrations of U and dissolved gases are not consistent with the measured concentrations of O₂ reported by EIR as discussed in Section 4.2.2.1.

7) The temperature of sample 12 was 15.4°C when collected at the surface. The formation temperature based on the first equation of Section 4.2.3 is 36.4°C and, based on the second, 35.1°C. A rounded mean value of 36°C was chosen. Because of the low velocity of flow up the borehole, cooling of the sample during flow undoubtedly took place.

8) Silica (as H₂SiO₃) and aluminum concentrations are those calculated for the water at equilibrium with kaolinite, chalcedony, and calcite, as discussed above in Section 4.2.2.

9) The Eh range reported is from Table 4.1.

6.3 Crystalline; 619 m, Aug. 1983

6.3.1 Sample Collection

This interval was sampled on 9-August-83 during the test phase of the borehole program, some 200 days after the interval was first drilled. Straddle packers were set to isolate the same water-bearing zone sampled on 22-January-83 and described in Section 6.2.

Sample 16 was collected at the surface while the interval was being pumped with a submersible pump. Following pumping, sample 17 was taken at a depth of about 600 m using GTC pressure sampling apparatus.

After the packers were installed, about 40 m³ of water was allowed to flow from the interval before the pump was installed. At the time of pump installation, the tracer concentration of the flowing fluid indicated that it contained less than 0.2 percent borehole fluid. With pumping, the tracer level first fell by about a factor of 10, but then rose again, finally stabilizing at a level corresponding to a borehole fluid content of about 0.3 percent.

This behavior is interpreted as the result of fluid in the annular space bypassing the upper packer through the surrounding rock and entering the test interval. Because of discharge into the annular space from the open 399 m zone, this sample probably is more representative of water from the 399 m zone than of water from the 621 m horizon.

The ¹⁴C content of this and the other samples from the Boettstein crystalline section support this hypothesis, as described in Section 6.6.

6.3.2 Chemical Analytical Results

Table 6.5 gives the concentrations of major dissolved species and values of other parameters for formation water from this zone. The following notes describe the sources of data used and support the choices made in developing this table.

- 1) Average of Fresenius analyses samples 16 and 17.
- 2) Fresenius analysis sample 16. (Not included in sample 17.)

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	1.45	0.21	2
Sodium	Na ⁺	377.6	16.45	1
Potassium	K ⁺	9.8	0.25	1
Ammonium	NH ₄ ⁺	0.23	0.013	2
Magnesium	Mg ⁺²	0.2	0.010	1
Calcium	Ca ⁺²	11.8	0.30	1
Strontium	Sr ⁺²	0.34	3.9x10 ⁻³	1
Barium	Ba ⁺²	0.025	0.18x10 ⁻³	2
Iron (Ferrous)	Fe ⁺²	0.02	0.36x10 ⁻³	3
Manganese	Mn ⁺²	0.140	2.6x10 ⁻³	1
Aluminum	Al ⁺³	0.006	0.22x10 ⁻³	8
CATION SUM: (milliequivalents/l)			17.55	
Chloride	Cl ⁻	123.8	3.50	1
Sulfate	SO ₄ ⁻²	339.5	3.54	1
Bicarbonate plus carbonate	HCO ₃ ⁻	374.	6.14	4
Fluoride	F ⁻	12.05	0.64	1
Bromide	Br ⁻	1.0	0.013	2
Phosphate	P	0.06	1.9x10 ⁻³	2
ANION SUM: (milliequivalents/l)			17.37	
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	<5.x10 ⁻³		1
Silica	H ₂ SiO ₃	27.3	0.35	8
Boron	H ₃ BO ₃	6.2	0.10	1
Iron (Total)	Fe	0.02		3
Uranium	U	0.20x10 ⁻³	8.4x10 ⁻⁷	5
Total Dissolved Solids				
Sum		1089.		
Residue		1088.		2
Temperature	°C	31.0		7
pH	pH	7.92		4
Density (20°C)	mg/ml	0.9993		2
Oxidation Potential Range				
pE	-2.0 to -4.7			8
Eh(volts)	-0.12 to -0.28			8

Table 6.5: Major dissolved constituents and other parameters of water collected 9 August, 1983 from 609.0 to 629.7 m interval, crystalline section at Boettstein.

3) The following iron concentrations were reported:

Fresenius sample 16 - Fe ⁺² , pumping,	1.0 mg/ℓ
Fresenius sample 16 - Total, pumping	2.3 mg/ℓ
Fresenius sample 17 - Total, pres. sample,	0.63 mg/ℓ

As discussed in Section 4.2.2, these high iron values are most likely attributable to iron tools in the borehole. The ferrous and total iron concentrations of the formation water have therefore been taken as equal to those at Zurzach, 0.02 mg/ℓ.

4) Results important to defining the carbonate system are given in Table 6.6. Because of the high pH of the water (~8), the amount of total carbonate present as dissolved CO₂ is very small and so difficult to analyze. PHREEQE calculation results describe a solution with m-value equal to the pressure vessel sample adjusted to calcite saturation. The pressure sample m-value was selected because it is less likely to have been affected by outgassing during flow up the borehole than the surface collected samples. The calculated dissolved CO₂ content is that from the pressure sample measured by EIR. The EIR analytical technique may include some dissociated HCO₃⁻ in its CO₂ result so the comparison is not surprising. The calculated values have been chosen for the results in Table 6.5.

5) The following uranium data were reported:

Sample	μg/ℓ	²³⁴ U/ ²³⁸ U
EIR sample 16 pumping	0.21	2.5
EIR sample 16 pressure sample	0.25	---
LLC - (Beilage 8.32)	0.14	2.85 ± 0.15

The mean of the EIR and LLC values was used.

6) The following dissolved gas concentrations (in mg/kg) were reported:

Analysis	N ₂	He	Ar	O ₂	CH ₄	H ₂
Fresenius	20.5	0.02	0.6	<.1	.01	.007
Sample 16	16.4	0.1	0.3	<.7	.02	.08
EIR-Sample 16	33.6	0.04	0.90	<5x10 ⁻⁴	0.03	0.01
EIR-Sample 17	38.1	0.04	0.95	0.05	0.03	<5x10 ⁻⁴
LLC, Pumping		0.025	0.90			
(Beilage 8.32)		0.025	0.91			
LLC, Pres. vessel		0.025	0.91			
(Beilage 8.32)						

	Fresenius Analyses		EIR Gas Analyses		PHREEQE
	Sample 16 Pumping	Sample 17 Pressure Sample	Sample 16 Pumping	Sample 17 Pressure Sample	
m-value (from original analysis sheet)					
- meq/l	6.20				6.20
- mg/l as HCO_3^-	378.				378.
$\text{HCO}_3^- + \text{CO}_3^{2-}$					
- mm	6.20	6.00			6.14
- mg/l as HCO_3^-	378.3	366.0			374.
Dissolved CO_2					
Calc - mm					0.13
Gas Analysis					
- mm	0.07	0.30	<0.24	<0.41	
- mg/l as CO_2	3.07	13.0	<11.	<18.	
Total CO_2 - mm					
Sum of above	6.27	6.30			6.27
Analyzed			7.15	—	
pH	8.06	7.94			7.92

Table 6.6: Carbonate system data for 619 m crystalline water

The EIR and LLC values are in good agreement, but there is a greater difference in the He results than was present in the two previous sets of samples. No explanation for this observation is apparent. Because the pressure vessel was filled with N₂ before sample collection, the EIR sample 16 value was used.

As discussed in Section 4.2.2.1, the concentrations of U and dissolved gases are not consistent with the O₂ concentrations reported in Fresenius sample 16 and EIR sample 17. The trace O₂ value reported for EIR sample 16 was adopted. CH₄ concentrations of all samples were similar so a mean value was chosen. The presence of H₂ is considered a reduction by-product of iron in solution and, therefore, the lowest H₂ concentration was chosen.

7) The formation temperature at depth of 619 m from the first equation of Section 4.2.3 is 36.3°C and from the second, 35.0°C, but the temperature of the sample at the surface was only 31.0°C. Because the sample appears to contain some water from the less deep zone at 399 m where the formation temperature is about 28°C, the 31°C sample temperature seems representative and was used.

8) Silica (as H₂SiO₃) and aluminum concentrations are those calculated for the water at equilibrium with kaolinite, chalcedony and calcite, as discussed in Section 4.2.2.

9) The Eh range reported is taken from Table 4.1.

6.4 Crystalline, 792 m, Aug. 1983

6.4.1 Sample Collection

This interval was sampled from 14 through 16 August 1983 during the test phase of the borehole program, more than 200 days after the interval was drilled.

Sample 18 was collected at the surface while the interval was being pumped at 20 l/min with a submersible pump. Prior to the start of pumping, artesian discharge from the borehole annulus was measured at approximately 16.6 l/min. During pumping with the water level in the observation standpipe at 180 m, this discharge was observed to decrease to 11.2 l/min. It was therefore concluded that leakage was occurring into the packered interval from the open borehole as a result of pumping; no attempt was

made to sample the packered interval using GTC pressure sampling apparatus.

The ^{14}C data along with knowledge of the borehole sampling history suggests an explanation for the observed water chemistry. The long period of artesian discharge from the 619 m zone prior to pumping could have resulted in ground water entering the test interval from that zone. The observed tracer concentrations would result from borehole annulus fluid mixing with test interval water during pumping. GTC has made preliminary calculations of the radius region which could have been influenced by artesian discharge for this period of time. If the flow regime is treated as a porous medium, the range of influence depends on the porosity. A porosity of 0.1 percent would lead to a range of 208 m, while 0.5 percent would correspond to 93 m. A fracture flow model using an equivalent hydraulic conductivity for the zone of 10^{-6} m/s would give a radius of 2.2 km. These calculations are rough and the results should not be used for other purposes. They do support the conclusion that this sample could have had its source in a zone much higher in the borehole.

6.4.2 Chemical Analytical Results

Table 6.7 gives the concentrations of the major dissolved species and values of other parameters for the water sampled from this zone. The following notes describe the sources of data used and support the choices made in developing this table.

- 1) From Fresenius analysis sample 18
- 2) The reported iron results were:

Fresenius Sample 18	Fe^{+2}	0.81 mg/l
	Fe_{total}	1.7 mg/l

As discussed in Section 4.2.2, above, these high iron values are probably a consequence of the presence of iron tools in the borehole. The ferrous and total iron contents adopted were, therefore, those of the samples from Zurzach, 0.02 mg/l.

- 3) Values reported are those calculated with PHREEQE using Fresenius ($\text{HCO}_3^- + \text{CO}_3^{2-}$) sample data adjusted to calcite saturation. Additional data pertaining to the carbonate system for the Boettstein 792 m waters is presented in Table 6.8. An m-value for these waters was calculated, however, a comparative value was not reported for the test sample. The Fresenius ($\text{HCO}_3^- + \text{CO}_3^{2-}$) value is very similar to the

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	1.35	0.20	1
Sodium	Na ⁺	395.4	17.23	1
Potassium	K ⁺	8.3	0.21	1
Ammonium	NH ₄ ⁺	0.19	0.010	1
Magnesium	Mg ⁺²	0.2	6.6x10 ⁻³	1
Calcium	Ca ⁺²	8.5	0.21	1
Strontium	Sr ⁺²	0.09	1.0x10 ⁻³	1
Barium	Ba ⁺²	0.030	0.22x10 ⁻³	1
Iron (Ferrous)	Fe ⁺²	0.02	0.36x10 ⁻³	2
Manganese	Mn ⁺²	0.140	2.6x10 ⁻³	1
Aluminum	Al ⁺³	0.0084	0.31x10 ⁻³	7
CATION SUM: (milliequivalents/l)			18.10	
Chloride	Cl ⁻	141.8	4.01	1
Sulfate	SO ₄ ⁻²	339.0	3.54	1
Bicarbonate plus carbonate	HCO ₃ ⁻	372.9	6.12	3
Fluoride	F ⁻	12.9	0.68	1
Bromide	Br ⁻	1.2	0.015	1
Phosphate	P	0.04	1.3x10 ⁻³	1
ANION SUM: (milliequivalents/l)			17.90	
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	<5.x10 ⁻³		1
Silica	H ₂ SiO ₃	28.1	0.36	7
Boron	H ₃ BO ₃	5.36	.087	1
Iron (Total)	Fe	0.02		2
Uranium	U	0.12x10 ⁻³	0.50x10 ⁻⁶	4
Total Dissolved Solids				
Sum		1,120.		
Residue		1,119.		1
Temperature	C	31.		6
pH	pH	8.07		3
Density (20°C)	(mg/ml)	0.9993		1
Oxidation Potential Range				
pE		-2.30 to -4.81		
Eh(volts)		-0.14 to -0.29		8

Table 6.7: Major dissolved constituents and other parameters of water collected 16 August, 1983 from the 782.0 to 802.7 m interval, crystalline section at Boettstein.

	Fresenius Analyses Sample 18	EIR Gas Analyses Sample 18	PHREEQE Calculation Results (at calcite saturation)
m-value			
- meq/l			6.21
- mg/l as HCO_3^-			378.8
$\text{HCO}_3^- + \text{CO}_3^{-2}$			
- mm	6.20		6.12
- mg/l as HCO_3^-	378.2		372.9
Dissolved CO_2			
Calc - mm			.093
Gas Analyses			
- mm	<.045	<.11	
- mg/l as CO_2	<2.	<4.8	
Total CO_2 - mm			
Sum of above Analyzed	6.24		6.21
pH	8.25		8.07

Table 6.8: Carbonate system data for 792 m crystalline water

calculated m-value indicating that all of the measured alkalinity was attributed to aqueous carbonate species. The calculated difference between alkalinity and $(\text{HCO}_3^- + \text{CO}_3^{2-})$ in these waters is .09 meq/l.

4) The following uranium data were reported:

Sample	$\mu\text{g}/\ell$	$^{234}\text{U}/^{238}\text{U}$
EIR-sample 18	0.19	1.1
LLC-(Beilage 8.32)	0.05	2.69 ± 0.28

The mean value was used.

5) The following dissolved gas concentrations (in mg/kg) were reported:

Analysis	N_2	He	Ar	O_2	CH_4	H_2
Fresenius Sample 18	21.1	0.01	0.6	0.1	0.01	0.007
EIR sample 18	35.2	0.05	0.92	$<5 \times 10^{-4}$	0.03	0.05
LLC (Beilage 8.32)	--	0.026	0.91	--	--	--
	--	0.026	0.90	--	--	--

The Ar values of EIR and LLC are in good agreement, but the LLC He values are only half the EIR result. No reason for this difference is apparent. All Fresenius results are low, possibly because of outgassing at time of collection. The EIR N_2 value was selected. The concentrations of U and dissolved gases are not consistent with the measured concentrations of O_2 reported in the Fresenius sample as discussed in Section 4.2.2.1. The trace O_2 concentration reported for EIR Sample 18 was therefore adopted. Since all of the Fresenius results appear low in concentration, possibly because of outgassing, the EIR values for CH_4 and H_2 were also selected.

6) The formation temperature at 792 m from the first equation of Section 4.2.3 is 42.1°C and from the second, 41.2°C . The temperature of the surface sample was 31°C . The sample apparently included water from shallower depths where lower formation temperatures prevail, so the surface sample temperature was adopted.

7) Silica (as H_2SiO_3) and aluminum concentrations are those calculated for the water at equilibrium with kaolinite, chalcedony, and calcite, as discussed above in Section 4.2.2.

8) The Eh range reported is taken from Table 4.1.

6.5 Zurzach: Thermal Boreholes 1 and 2

6.5.1 Sample Collection

Zurzach is located approximately 6 km northeast of Baden. The baths there are supplied from boreholes yielding water from crystalline basement. Thermal borehole no. 1 was drilled in 1955 to a depth of 430 m and borehole no. 2 in 1965. The temperature of water from both boreholes is about 40° C.

Both boreholes are sampled frequently and analyzed by the Mineral Water Laboratory. They were also sampled as part of the NAGRA regional program in October 1981 and August 1982 and analyzed by Fresenius, EIR, LLC and other groups using the same procedures as for the Boettstein samples (NTB 84-21).

The chemistry of the Zurzach waters is virtually identical to that of water from the upper crystalline zones at Boettstein. Because the Zurzach boreholes have been operating for many years, the effects of borehole materials on sample chemistry should be minimal. They are thus useful to indicate how the Boettstein results need be corrected to eliminate effects of the borehole materials on the observed water chemistry, and are included here.

6.5.2 Chemical Analytical Results

Tables 6.9 and 6.10 give the concentrations of major dissolved species and values of other parameters for waters for Zurzach thermal boreholes numbers 1 and 2, respectively. Notes describing the sources of data and supporting the choices made follow. The procedures used to develop both Tables 6.9 and 6.10 were the same so the notes refer to both tables.

1) Average of Fresenius analysis of samples collected 27-Oct.-81 and 17-Aug.-82.

2) The following iron concentrations were reported:

Borehole	Date	Fe ⁺²	Fe _{total}
1	Oct-81	0.01	0.012
1	Aug-82	0.02	0.024
2	Oct-81	0.03	0.030
2	Aug-82	0.02	0.019
mean ± LSD		0.020 ± 0.008	0.021 ± 0.008

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	0.98	0.14	1
Sodium	Na ⁺	303.2	13.21	1
Potassium	K ⁺	7.4	0.19	1
Ammonium	NH ₄ ⁺	0.11	6.1x10 ⁻³	1
Magnesium	Mg ⁺²	0.3	0.012	1
Calcium	Ca ⁺²	14.2	0.35	1
Strontium	Sr ⁺²	0.64	7.3x10 ⁻³	1
Barium	Ba ⁺²	0.06	0.44x10 ⁻³	1
Iron (Ferrous)	Fe ⁺²	0.015	0.27x10 ⁻³	2
Manganese	Mn ⁺²	0.043	0.78x10 ⁻³	1
Aluminum	Al ⁺³	0.0105	0.39x10 ⁻³	7
CATION SUM: (milliequivalents/l)			14.31	
Chloride	Cl ⁻	136.	3.84	1
Sulfate	SO ₄ ⁻²	260.5	2.72	1
Bicarbonate plus carbonate	HCO ₃ ⁻	258.	4.24	3
Fluoride	F ⁻	9.8	0.52	1
Bromide	Br ⁻	0.75	9.4x10 ⁻³	1
Phosphate	P	0.012	0.39x10 ⁻³	1
ANION SUM: (milliequivalents/l)			14.04	
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	0.	0.	1
Silica	H ₂ SiO ₃	32.7	0.42	7
Boron	H ₃ BO ₃	2.44	0.040	5
Iron (Total)	Fe	0.018	0.32x10 ⁻³	2
Uranium	U	3.5x10 ⁻⁴	1.5x10 ⁻⁶	4
Total Dissolved Solids				
Sum (mg/l)		889.		11
Residue		869.		1
Temperature	°C	38.		6
pH	pH	7.86		3
Density (20°C)	(mg/ml)	0.9988		
Oxidation Potential Range				
pE	-1.81 to	-4.76		8
Eh(volts)	-0.11 to	-0.294		8

Table 6.9: Major dissolved constituents and other parameters of water collected October, 1981 and August, 1982 from Zurzach Thermal borehole no. 1.

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Lithium	Li ⁺	1.05	0.15	1
Sodium	Na ⁺	292.	12.73	1
Potassium	K ⁺	7.4	0.19	1
Ammonium	NH ₄ ⁺	0.11	6.1x10 ⁻³	1
Magnesium	Mg ⁺²	0.3	0.012	1
Calcium	Ca ⁺²	15.1	0.38	1
Strontium	Sr ⁺²	0.62	7.1x10 ⁻³	1
Barium	Ba ⁺²	0.055	0.40x10 ⁻³	1
Iron (Ferrous)	Fe ⁺²	0.025	0.45x10 ⁻³	2
Manganese	Mn ⁺²	0.045	0.82x10 ⁻³	1
Aluminum	Al ⁺³	0.011	0.41x10 ⁻³	7
CATION SUM: (milliequivalents/l)		13.87		
Chloride	Cl ⁻	133.7	3.78	1
Sulfate	SO ₄ ⁻²	265.5	2.77	1
Bicarbonate plus carbonate	HCO ₃ ⁻	267.	4.38	3
Fluoride	F ⁻	10.05	0.53	1
Bromide	Br ⁻	0.74	9.3x10 ⁻³	1
Phosphate	P	0.013	0.14x10 ⁻³	1
ANION SUM: (milliequivalents/l)		14.24		
Dissolved sulfide (H ₂ S, HS ⁻ , S ⁻²)	H ₂ S	0.	0.	1
Silica	H ₂ SiO ₃	34.3	0.44	7
Boron	H ₃ BO ₃	2.5	0.04	5
Iron (Total)	Fe	0.025	4.48x10 ⁻³	2
Uranium	U	2.5x10 ⁻⁴	1.0x10 ⁻⁶	4
Total Dissolved Solids				
Sum (mg/l)		887.		11
Residue		874.		1
Temperature	°C	40.		6
pH	pH	7.79		7
Density (20°C)	(mg/ml)	0.9989		1
Oxidation Potential Range				
pE	-1.84 to	-4.71		8
Eh(volts)	-0.11 to	-0.29		8

Table 6.10: Major dissolved constituents and other parameters of water collected October, 1981 and August, 1982 from Zurzach Thermal borehole no. 2.

The mean values for the two boreholes were adopted, because the standard deviation (SD) values suggest that all results are from the same population. As discussed in Section 4.3.2, these iron values are unlikely to have been influenced by borehole effects and should represent the formation water iron levels. Their grand mean value, 0.02 mg/l, was used for the other samples of upper crystalline water discussed in this chapter.

3) Values reported are those calculated with PHREEQE using Fresenius ($\text{HCO}_3^- + \text{CO}_3^{2-}$) sample data adjusted to calcite saturation. Additional data pertaining to the carbonate system for the Zurzach waters is presented in Table 6.11. M-values for these waters was calculated, although measured values for comparison were not reported for borehole no. 1 or no 2. Fresenius ($\text{HCO}_3^- + \text{CO}_3^{2-}$) values are similar or equivalent to calculated m-values indicating that all of the measured alkalinity was attributed to aqueous carbonate species.

The calculated dissolved CO_2 content of borehole no. 1 is slightly below that measured by EIR. This discrepancy is likely the result of the EIR analytical technique incorporating some dissociated HCO_3^- in its CO_2 result.

4) The following uranium data were reported:

Borehole	Date	$\mu\text{g/l}$	$^{234}\text{U}/^{238}\text{U}$
1:	Oct. 81	0.20	3.0
	Aug. 82	0.50	--
2:	Oct. 81	0.20	3.1
	Aug. 82	0.30	--

The mean value for each borehole was adopted.

5) The following gas concentrations (in mg/kg) were reported:

Analysis	N_2	He	Ar	O_2	H_2	CH_4
<u>Borehole no. 1</u>						
Fresenius: Oct. 81	19.8	0.01	0.8	0.3	<0.0002	0.01
Fresenius: Aug. 82	13.0	n.n.	0.5	0.2	<0.0002	0.005
EIR: Oct. 81	30.4	0.02	0.86	0.17	<0.0005	0.01
EIR: Aug. 82	29.2	0.03	0.83	0.04	<0.0005	0.01
<u>Borehole no. 2</u>						
Fresenius: Oct. 81	12.1	0.01	0.6	0.30	0.001	0.01
Fresenius: Aug. 82	--	--	--	0.60	--	--
EIR: Oct. 81	31.5	0.03	0.87	0.0005	<0.0005	0.01
EIR: Aug. 82	31.4	0.03	0.87	0.004	<0.0005	0.01

	<u>Borehole no. 1</u>			<u>Borehole no. 2</u>		
	Fresenius Analyses	EIR Gas Analyses	PHREEQE Calculation Results (at calcite saturation)	Fresenius Analysis	EIR Gas Analyses	PHREEQE Calculation Results (at calcite saturation)
m-value						
- meq/l	4.28	4.28		4.41		4.41
- mg/l as HCO ₃ ⁻	261		261	269		269
HCO ₃ ⁻ + CO ₃ ⁻²						
- mm	4.28		4.24	4.40		4.38
- mg/l as HCO ₃ ⁻	261		256	269		266
Dissolved CO ₂						
Calc - mm			.10			.12
Gas Analyses						
- mm		.11			.12	
- mg/l as CO ₂		4.84			5.28	
Total CO ₂ - mm						
Sum of above			4.34			4.50
Analyzed		4.15			4.32	
pH	7.81		7.86	7.99		7.79

Table 6.11: Carbonate system data for Zurzach thermal boreholes

Mean values of the N_2 , He and Ar EIR results for each borehole were adopted. The concentrations of U and dissolved gases are not consistent with the concentrations of O_2 reported by EIR. An O_2 value less than the minimum measured EIR value was adopted. Means of the H_2 and CH_4 values reported by EIR were used.

6) Water temperatures at the time of sampling were:

Borehole	Date	deg. C
1	Oct. 81	37.7
1	Aug. 82	41.8
2	Oct. 81	39.6
2	Aug. 82	42.4

Rounded mean values for each borehole were used.

7) Silica (H_2SiO_3) and aluminum concentrations are those calculated for the water at equilibrium with kaolinite, chalcedony and calcite.

8) The Eh range reported is taken from Table 4.1.

6.6 Isotope Analytical Results

Samples for analysis of concentrations and ratios of a number of stable and radio-isotopes were collected by the Low-Level Counting Department (LLC) of the University of Bern. The results of their own analyses and those of other laboratories in which some of the analyses were made are given in NTB 85-06 and in Beilage 8.32, NTB 85-01.

The results of selected isotope analyses from the Bundsandstein and upper crystalline section at Boettstein are given in Table 6.12. Results from the samples taken at 649 m which was analyzed only for isotopes are included in this table. Analyses of samples from Zurzach are given in Table 6.13.

The δD and $\delta^{18}O$ values of the waters can be summarized as:

		mean \pm 1 SD (per mil)
Boettstein	δD	-73.3 ± 0.7
	$\delta^{18}O$	-10.02 ± 0.04
Zurzach	δD	-75.5 ± 0.9
	$\delta^{18}O$	-10.12 ± 0.06

Sample	$\delta^D_{H_2O}$ per mil	$\delta^{18}O_{H_2O}$ per mil	3H Tritium Units	^{14}C Percent Modern Carbon	$\delta^{13}C$ per mil	$\delta^{34}S_{SO_4}$ per mil	$\delta^{18}O_{SO_4}$ per mil	$^{234}U/^{238}U$ Activity Ratio
<u>Buntsandstein and weathered crystalline</u>								
16-Nov-82	-73.7	-10.15	<0.7	12.1 ± 0.3	-6.3	16.13	6.92	3.0
20-Jan-84	-73.4	-10.06	0.2 ± 0.2	14.03 ± 0.13	-9.3			
<u>Crystalline</u>								
399 m Flowing	-72.7	-10.05	0.55 ± 0.29 0.23 ± 0.35	8.25 ± 0.13	-9.3	14.62	1.16	2.8 (3.26 ± 0.05)
621 m Flowing	-72.7	-10.04	(1.0 \pm 0.7)	<1.3	-8.8	13.56	-0.15	2.0 (2.59 ± 0.07)
619 m Pumped	-74.1	-10.01	(1.0 \pm 0.7)	7.89 ± 0.09	-9.0	14.09	-1.32	2.5
649 m Pumped				13.8 ± 0.1	-9.1			
792 m Pumped	-73.7	-9.96	(0.9 \pm 0.9)	7.64 ± 0.07	-9.1	14.12	-0.28	1.1

Table 6.12: Results of selected isotope analyses of Buntsandstein and Upper Crystalline Formation waters, Boettstein.

Sample	δD_{H_2O}	$\delta^{18}O_{H_2O}$	3H	^{14}C	$\delta^{13}C$
	per mil	per mil	Tritium Units	Percent Modern Carbon	per mil
No. 1 Oct-81	-76.8	-10.10	<0.3 (<0.7)	4.6 ± 0.16	-9.64
No. 1 Aug-82	-75.1	-10.06	(<0.9)		
No. 2 Oct-81	-75.6	-10.21	<1.2 (<1.2)	4.67 ± 0.16	-9.38
No. 2 Aug-82	-74.6	-10.12	(<1.1)		

Table 6.13: Results of selected isotope analyses of Crystalline Formation waters, Zurzach.

The Boettstein and Zurzach waters cannot be differentiated on the basis of their stable isotope compositions. Likewise, the samples from the several zones at Boettstein do not differ significantly one from the other.

The isotopic composition of the de-ionized water used for drilling fluid is given in Table 7.5. This water is derived from local surface water and is isotopically similar to the upper crystalline ground water, suggesting a similar geographic origin for both.

The tritium contents of all but the 619 and 621 m Boettstein samples are below detection. The drilling fluid contains about 110 TU, so no more than one percent of de-ionized water could have been present in any of these samples.

The $\delta^{13}\text{C}$ values of the total carbonate dissolved in these samples can be summarized:

	mean \pm 1 SD (per mil)
Boettstein	-9.1 \pm 0.2
Zurzach	-9.5 \pm 0.2

Like the δD and $\delta^{18}\text{O}$ values, the difference between the Boettstein and Zurzach mean values is only 1 SD so they cannot be differentiated. Likewise, the individual Boettstein samples cannot be distinguished one from the other.

$\delta^{13}\text{C}$ values provide information on the evolution of the chemistry of carbonate dissolved in groundwaters. If there are data on the isotopic compositions of carbonate minerals in the host rock, and a very general knowledge of the flow system, quantitative interpretation of $\delta^{13}\text{C}$ values is often possible.

It is often possible to interpret ground-water $\delta^{13}\text{C}$ values by assuming there are two sources of dissolved carbonate. The first is soil-air CO_2 which is plant CO_2 with $\delta^{13}\text{C}$ of ≈ -20 to -25 ‰ (per mil) and $^{14}\text{C} \approx 100$ pmc (percent modern carbon). The second source is mineral carbonate in the flow system which will contain no ^{14}C and a $\delta^{13}\text{C}$ value of ≈ 0 to $+2$ ‰, if it is of marine origin. Dissolved carbonate of $\delta^{13}\text{C} \approx -9$ to -10 ‰ would contain from 50 to 70% formation carbonate and 30 to 50% soil-air carbonate under this set of assumptions. The interpretation of carbon isotopes in ground waters is discussed in detail in NTB 83-04.

The ^{14}C data are of particular interest for two following reasons:

First samples from one of the major water-bearing zones at Boettstein (the zone between roughly 600 and 670 m as shown on Figure 1.1) had ^{14}C contents which varied with their time of collection; and,

Second, ^{14}C is one of the only constituents for which significant differences exist between Zurzach and Boettstein and among the samples from the Boettstein crystalline themselves.

Variation of ^{14}C with time in water from a single ground-water zone is unusual and requires an explanation. Here, the variation seems related to the time elapsed between drilling of an interval and its sampling. Table 6.14 gives the dates of drilling, sampling and the ^{14}C contents of samples from the Boettstein crystalline and from the Buntsandstein and Buntsandstein/weathered crystalline horizons.

Consider first the samples which were collected within a few days of drilling - the 316, 399 and 621 m samples. These show the expected decrease in ^{14}C with depth. As Table 6.14 also shows, the $\delta^{13}\text{C}$ and total dissolved carbonate contents of these samples are nearly identical so that the ^{14}C decrease can be taken as representing an actual increase in the residence time of water in the system with depth. Based on the data in Table 6.14, these differences would be:

316 m to 399 m	:	3 - 4,000 years
399 m to 621 m	:	>15,000 years

Later samples from the 600 - 670 m zones have higher ^{14}C concentrations. The sample from 619 m taken about 200 days after drilling has about 8 pmc, a value similar to that from the sample taken earlier from the 399 m zone. The 649 m sample taken some 260 days after drilling has nearly 14 pmc which is the highest ^{14}C content of any crystalline sample. The only samples with similar ^{14}C contents from the Boettstein borehole are those taken from Buntsandstein/weathered crystalline horizon shortly after drilling with about 12 pmc and that from the perforation to the Buntsandstein sampled 435 days after drilling with about 14 pmc. Note that although these Buntsandstein samples probably contain some drilling fluid and so are not suitable for detailed geochemical interpretations, the contamination amounts to less than 1 percent and so should not affect their ^{14}C contents.

Interval	Date		Days Elapsed	¹⁴ C	¹³ C	CO ₂ Total, milli- molality	
	Drilled	Sampled		Percent Modern Carbon	‰ per mil		
Bss	313 m	c. 11-Nov-82	20-Jan-84	435	14.03±0.13	-9.3	5.72
Bss-Cryst.	316 m	c. 11-Nov-82	16-Nov-82	5	12.1±0.3	-6.3	6.16
Crystalline	399 m	c. 10-Dec-82	15-Dec-82	5	8.25±0.13	-9.3	6.44
Crystalline	621 m	19-Jan-83	22-Jan-83	3	<1.3	-8.8	6.48
	619 m	19-Jan-83	9-Aug-83	200	7.89±0.09	-9.0	6.27
	649 m	c. 31-Jan-83	17-Oct-83	260	13.80±0.13	-9.1	--
Crystalline	792 m	20-Feb-83	16-Aug-83	175	7.64±0.09	-9.1	6.21

Table 6.14: Dates of drilling and sampling and ¹⁴C contents of samples from Buntsandstein and upper crystalline zones, Boettstein.

The system is shown diagrammatically in Figure 6.1. The stippled zone represents the Buntsandstein/ weathered crystalline horizon with a ^{14}C content of 12 to 14 pmc. The initial state of this system is shown by the three measurements taken shortly after drilling in which the ^{14}C content decreased with depth to essentially zero at the 621 m zone. The curved line shows the increasing ^{14}C concentration of the 621 m zone with time since drilling. It is also evident on this figure that the 792 m sample has a higher ^{14}C content than it would have had if it been sampled immediately after drilling.

The conclusion from these ^{14}C data is that the system has suffered profound disturbance as a result of the presence of the borehole. The rate of artesian flow from the borehole between the time when these zones were first drilled and when they were last sampled was probably of the order of 20 l/min. This is not a very large flow rate and yet, the fact that because of it, water from the upper weathered crystalline horizon was drawn at least at 600 - 650 m suggests a closely connected system with very low storage. The hydrologic implications of these data are profound but are not appropriate subjects for detailed discussion in a geochemical report.

As mentioned above, the $\delta^{13}\text{C}$ values of these samples suggest they contain from 30 to 50% soil air carbon. If this range is used to adjust the ^{14}C contents of the Buntsandstein/weathered crystalline samples, it suggests a residence time of from 6,000 to 12,000 years for water in this horizon.

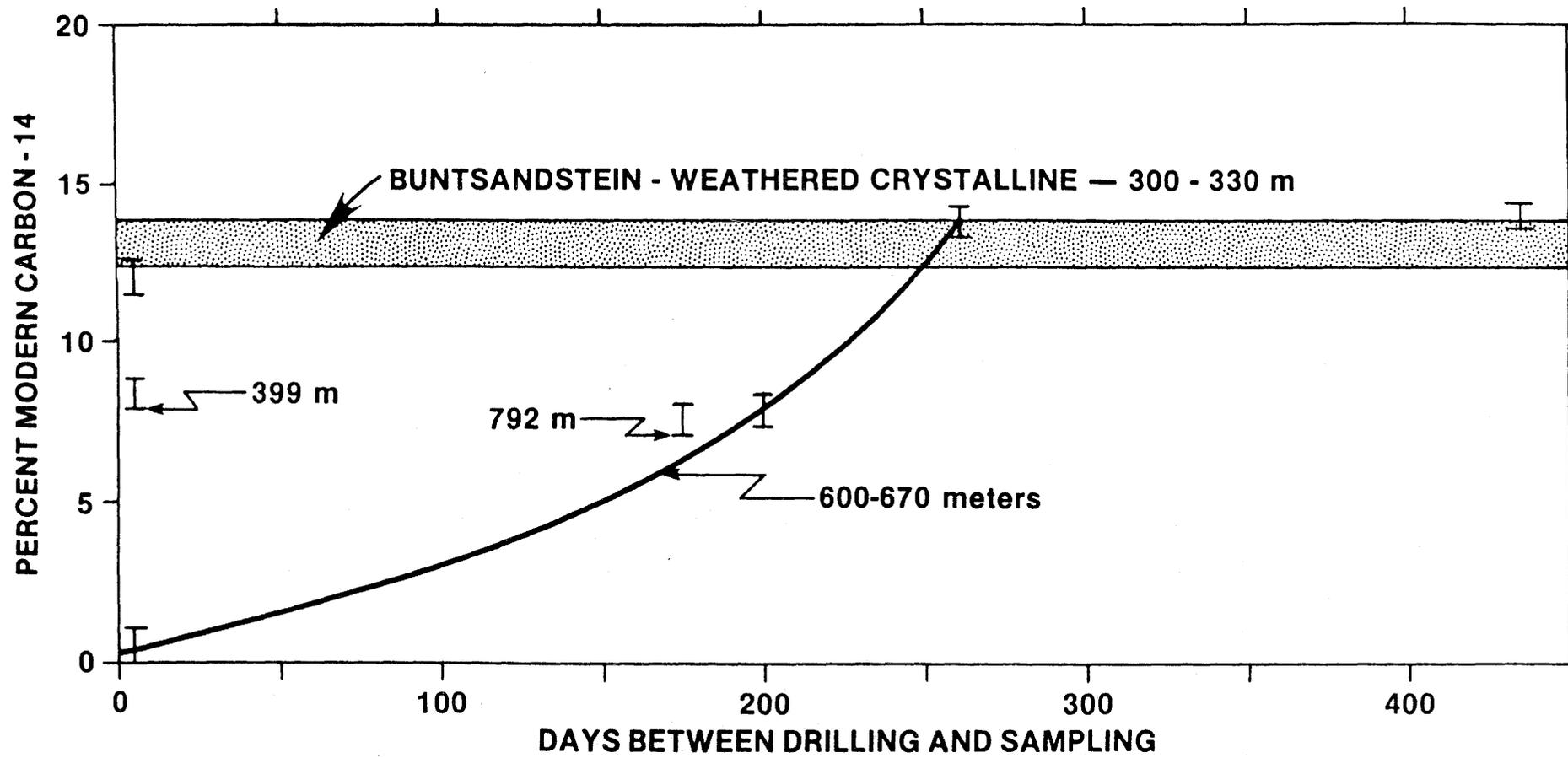


Figure 6.1: Content of ¹⁴C in waters from Buntsandstein and weathered crystalline with date sampled.

7. CHEMISTRY OF DEEP CRYSTALLINE FORMATION WATER

7.1 Crystalline, 1326 m, Sept/Oct, 1983

7.1.1 Sample Collection

The Boettstein borehole below about 800 meters yields little water and therefore can be sampled only with difficulty. To provide at least an estimate of the chemistry of the water in the deep crystalline environment, straddle packers were used to isolate the zone from 1321 to 1331 m depth. Even though this is the zone with the highest hydraulic conductivity below 800 m (see Figure 1.1), it yields only a few milliliters of water per minute. This low flow rate was not sufficient to flush or completely displace the fluid in the borehole between the packers and in the tubing during the time available for sampling.

The interval was packed off on 31-August and samples were taken from within the tubing beginning on 19-September. Samples through 28-September were collected from several depths using a bailer and were analyzed for uranine, conductivity, pH and m-value. On 30-September and 7 and 10-October, samples were collected for complete chemical analysis by Fresenius and for analyses by EIR and LLC, in addition to the field analyses. These samples were taken using the Pressag sampler at depths between 1,300 and 1,313 m in the tubing (NTB 85-01, Section 8.2.). The analytical results are given in NTB 85-01 in Beilage 8.20 (samples 19, 20, 21 and 22) and in Beilage 8.32.

7.1.2 Chemical Analytical Results

The field data used in preparing this report are given in Table 7.1. Equivalent laboratory data from Fresenius are also given along with the sample numbers for reference to the complete analyses.

The samples are mixtures of two waters, the borehole fluid containing the uranine tracer and the tracer-free formation fluid. As the table shows, the conductivities and constituent concentrations vary inversely with tracer concentration. This inverse relationship, when extrapolated to the point where the tracer concentration is zero, will yield the conductivity and concentrations of the other constituents in the formation water itself. This inverse relationship is illustrated in Figure 7.1.

DATE	Uranine mg/l	Conductivity mS/cm	Chloride mg/l	Sodium mg/l	Hardness mg/l	Sulfate mg/l	Alkalinity meg/l
17.09	18.2	2.02					
20.09	17.5	4.10	1200	753	436	160	0.33
21.09	17.8	4.10	1250	770	443	240	0.43
22.09	18.8	2.8	650	540	281	180	0.36
24.09	18.8	2.4	850	610	385	240	0.43
26.09	17.7	5.6	1400	978	601	380	0.45
28.09	14.4	6.4	1750	1207	695	[110]	
30.09	12.5	8.4	2300				
	<u>1/</u> 12.63	8.86	2824	1675	977	647	0.70
03.10	15.5	7.6	[2700]	1500			
05.10	12.4	9.6	2800	1880			
07.10	12.0	9.6	2850	1800			
	<u>2/</u> 11.94	10.20	3268	1935	1108	722	1.05
10.10	<u>3/</u> 12.08	11.00	3508	2085	1138	836	0.51
10.10*	<u>4/</u> 8.54	12.49	39.23	2345	1260	919	0.80

All samples from 1300 m depth in tubing except * which was taken at 1313 m.

Full analyses given in NTR 85-01, Beilage 8.20:

1/ Sample 19; 2/ Sample 20; 3/ Sample 21; 4/ Sample 22

Table 7.1: Field and laboratory data used in developing chemistry of formation water at 1326 m.

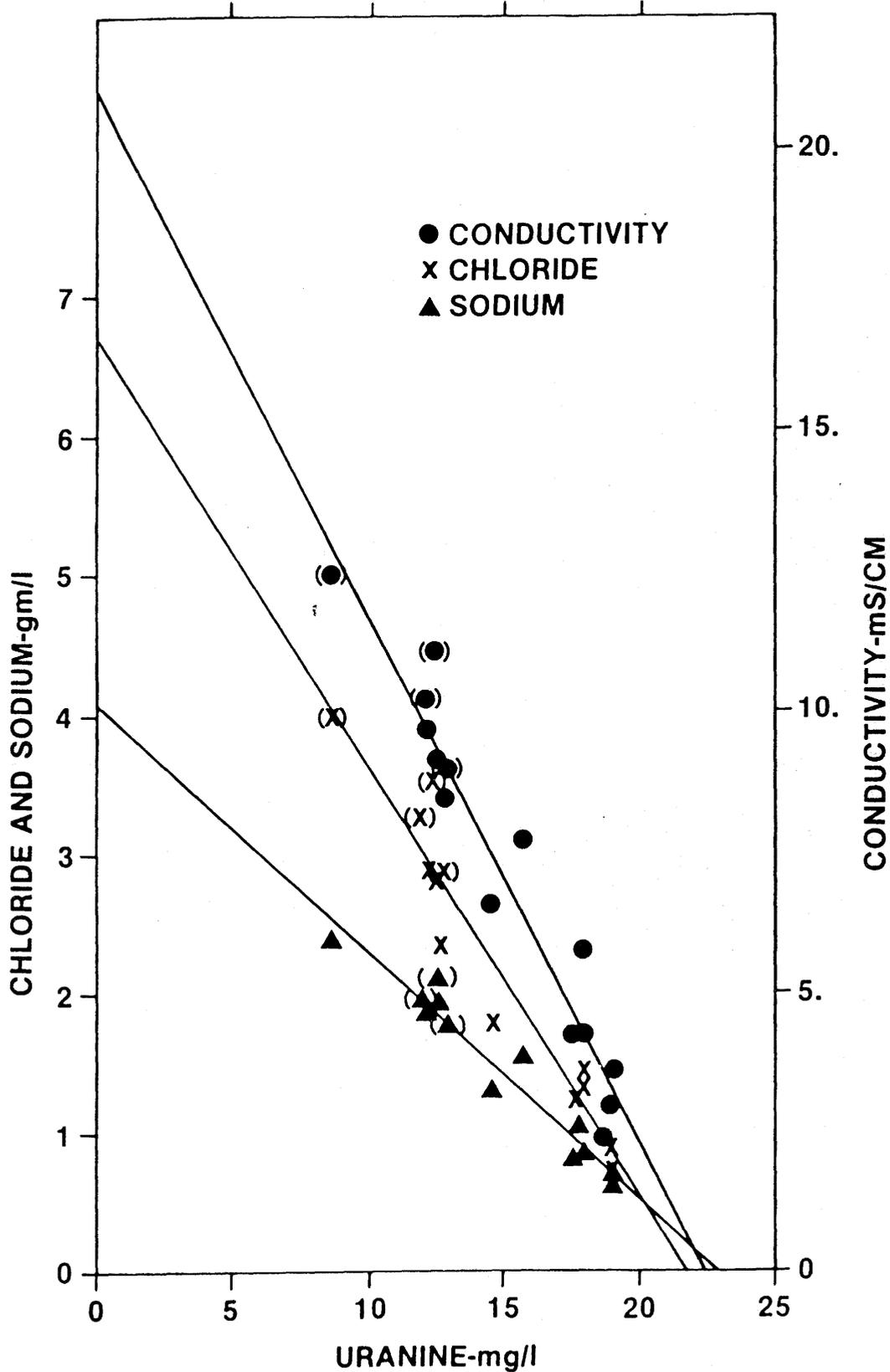


Figure 7.1: Graph of chloride, sodium, and conductivity against uranine content of samples from 1,326 m depth. Points in brackets are Fresenius Laboratory results.

To define the relationship between the tracer and the other analyzed constituents, least square regression lines were calculated. The equations for these lines have the form:

$$Y = B + A * \text{Uranine (mg/l)}.$$

where Y variously equals conductivity, chloride, sodium, hardness, sulfate or alkalinity.

Table 7.2 gives the calculated values of the coefficients B and A for each equation, the number of data pairs used (n), and the correlation coefficient (r). The absolute value of the correlation coefficients for all except alkalinity is greater than 0.96. A perfect correlation has an r value of 1.0. The high values of correlation coefficients for these equations suggest that, in spite of the apparent scatter in Figure 7.1, the regression lines are very well defined by the data.

The formation fluid has a uranine concentration of zero. In the equation above, the value of the dependent variable, Y, equals the coefficient B, when the independent variable, uranine concentration, is zero. The values of B in Table 7.2, therefore, represent the concentrations of the various species in pure formation water. The species given in Table 7.2 represent most of the dissolved material in common ground waters. It is thus possible to test the consistency of the water chemistry predicted from the values of B, by comparing the sums of the charges of cations and anions. As the second column of Table 7.3 shows, the cation sum is 220 milliequivalents per liter (meq/l), while the anion sum is 224 meq/l. This agreement is better than 2% and indicates the reliability of the field chemical data as well as of the regression equations based on them from which the formation water chemistry was estimated.

The relationships shown on Figure 7.1 and the regression lines Table 7.2 can be used to gain information about the borehole fluid as well as about the formation fluid. At the time the packers were installed for the collection of the samples being discussed here, the borehole fluid was reported to be deionized water to which some tracer had been added. The concentration of the tracer was nominally 20 milligrams per liter (mg/l) on 18-August, but no measurement is available at the time of sampling.

If the borehole fluid was traced deionized water, the concentrations of the various dissolved constituents would be zero at a uranine concentration equivalent to that of the initial undiluted borehole fluid. The uranine concentration corresponding to dissolved solids

Y (units)	n	B	A	r	Uranine Concentration at Y = 0
Conductivity (mS/cm)	15	21.2	-0.963	-0.962	22.0
Chloride (mg/l)	13	6.69	-0.312	-0.964	21.4
Sodium (mg/l)	13	4.04	-0.181	-0.970	22.3
Hardness (mg CaCO ₃ /l)	10	2.19	-0.0979	-0.970	22.6
Sulfate (mg/l)	9	1.63	-0.0763	-0.964	21.4
Alkalinity (meq/l)	10	1.34	-0.053	-0.804	25.6

Mean uranine concentration from Chloride, Sodium, Hardness, and Sulfate regressions: 21.9 ± 0.6 ($\pm 2.8\%$)

Table 7.2: Regression coefficients for equation:
 $Y = B + A * \text{Uranine (mg/l)}$

contents of zero equals $-B/A$ in the regression equation above. The uranine concentrations of the borehole fluid so calculated are shown in the last column of Table 7.2. The mean of the concentrations calculated from the chloride, sodium, hardness, and sulfate regressions is 21.9 ± 0.6 mg/l. This standard deviation is less than 3%, which adds additional confidence to the data set and estimating procedure used. This mean value, 21.9, is not significantly different from that calculated from the conductivity regression alone--22.0 mg/l, and both values agree with the nominal 20 mg/l value. That a differing value results from the alkalinity regression is also not unexpected given the relatively poor correlation between the alkalinity and uranine data.

Direct regression of analytical data against tracer concentrations produced the estimate of the major ion chemistry of the formation water shown in the first two columns of Table 7.3 and described above. To estimate the formation water concentrations of those minor elements which were analyzed by Fresenius but not in the field, a different technique was used. This technique involved developing a series of regression equations in the form:

$$\text{Concentration} = A * \text{Conductivity}.$$

The equation is the same as the regression equation above, but with the coefficient B constrained to equal zero. This constraint is physically reasonable, for as the dissolved solid concentration in a water approaches zero, so does its conductivity. Conductivity was chosen as the regression variable for these more detailed calculations because it is more precisely known than the uranine content.

Conductivities and concentrations from Fresenius analyses numbered 19, 20, 21 and 22 in Beilage 8.20 (NTB 85-01) 7.1 were used to calculate a value for the coefficient A for each dissolved constituent. As described above, the conductivity of the pure formation water is estimated to be 21.2 mS/cm (Table 7.2). The concentrations of each constituent in formation water were then calculated using the values of A and a conductivity of 21.2 mS/cm.

The composition of the formation water estimated by this procedure is given in the third and fourth columns of Table 7.3. This table shows that there is excellent agreement between the estimates of the major ions, sodium, hardness, chloride, and sulfate by this method and those from direct correlations with uranine concentration. The largest difference in any pair of esti-

	Field Concentrations at Uranine = 0 (table 7.2, col B)		Laboratory Concentrations at Conductivity = 21.2	
	mg/l	meq/l	mg/l	meq/l
Sodium	4,040.	176.	4,010.	174.
Potassium			45.	1.
Magnesium			2.6	0.
Calcium	2,190.1/	44.	870.	43.
Strontium			21.	1.
Total iron			0.45	0.
Manganese			3.1	0.
Aluminum			0.042	0.
Sum Cations		220.		219.
Chloride	6,690.	189.	6,720.	190.
Sulfate	1,630	34.	1,560.	32.
Alkalinity	82.	1.	95.	2.
Fluoride			3.0	0.
Sum Anions		224.		223.
Silica			12.2/ 4.73/	0.
Conductivity (mS/cm)	21.2		21.2	
pH (units)			7.0	

1/ Hardness as CaCO_3 = meq/l (Mg^{+2} + Ca^{+2} + Sr^{+2}) * 50.05

2/ Based on samples of 30-Aug-83 and 7-Oct-83.

3/ Based on samples of 10-Oct-83.

Table 7.3 Composition of formation water at 1326 m estimated from field and laboratory analyses.

mates, except for alkalinity, is in those for sulfate, and is less than 5 percent. The larger difference between the alkalinity estimates results from the poor correlation between alkalinity and uranium (Table 7.2).

Ion balances for this more complete estimation of the formation water chemistry are also given in Table 7.3. They show that the cation and anion charge balance is within 5 percent. This good balance together with the agreement between conductivity-calculated and uranium-calculated values for the major ion concentrations, adds confidence to this estimate of the major-ion composition of this ground water.

The concentrations of the minor ions in the ground water from 1326 meters cannot be estimated from the analytical data with as much precision as can the major ions. The minor species in Table 7.3 include magnesium, total iron, manganese, aluminum, and fluoride. The variability in the concentration of these ions reported in the analyses of the mixed samples is large enough that they give rise to errors between 15 and 30 percent in formation water concentrations calculated from them. These errors contrast sharply with errors of less than 5 percent in the major ions.

There is little consistency in the pH values reported from the four mixed samples. Furthermore, pH is not a quantity which behaves conservatively when waters are mixed and therefore, it is not possible simply to extrapolate from the analyzed values to the formation water chemistry. The value in Table 7.3 is simply the logarithmic mean of the measured pH's of the mixed water samples.

The major ion chemistry of this 1326 meter water is notably different from that of water found in the crystalline rock above 800 meters at Boettstein. However, there is no reason why the deeper water should not be in equilibrium with such minerals as calcite and fluorite, as are the shallower ones. Thus water-mineral equilibrium calculations were made to refine the estimate of the 1326 meter water composition (see 4.3, above).

Table 7.4 gives the final best estimate of the composition of water from 1326 meters. The following notes describe the selection of each value in that table:

- 1) Laboratory concentrations calculated at conductivity = 21.2 mS/cm, from Table 7.3, column 3.
- 2) Field and laboratory concentrations from Table 7.3, columns 1 and 3, adjusted for solution electroneutrality.

Parameter	Symbol	Milligrams/ Liter	Milli- molality	Note
Sodium	Na ⁺	4037.	176.52	2
Potassium	K ⁺	45.	1.16	1
Ammonium	NH ₄ ⁺	0.2	0.01	6
Magnesium	Mg ⁺²	2.6	0.11	1
Calcium	Ca ⁺²	870.	21.82	1
Strontium	Sr ⁺²	21.	0.24	1
Iron (Ferrous)	Fe ⁺²	0.01	0.2x10 ⁻³	3
Manganese	Mn ⁺²	3.1	0.057	1
Aluminun	Al ⁺³	0.04	1.5x10 ⁻³	1
CATION SUM: (milliequivalents/kg H ₂ O)			222.15	
Chloride	Cl ⁻	6,621.	187.74	2
Sulfate	SO ₄ ⁻²	1,560.	16.33	1
Bicarbonate plus carbonate	HCO ₃ ⁻	95.	1.56	1
Fluoride	F ⁻	3.6	0.19	1
Phosphate	P ³	0.06	1.9x10 ⁻³	
ANION SUM: (milliequivalents/kg H ₂ O)			222.15	
Silica	H ₂ SiO ₃	21.5		8
Iron (Total)	Fe	0.45	8.1x10 ⁻³	1
Uranium	U	0.06x10 ⁻³	0.25x10 ⁻³	5
Total Dissolved Solids				
Sum		13,230.		
Temperature	°C	60.		7
pH	pH	6.64		4
Density (20°C)	mg/ml	1.008		9
Oxidation Potential Range				
pE		-0.79 to -3.03		10
Eh(volts)		-0.052 to -0.20		10

Table 7.4: Composition of water from 1326 m depth at Boettstein. Estimated from samples taken between 17-September and 7-October, 1983.

- 3) The total iron content is probably a result of reactions with the iron tools in the borehole. An arbitrary ferrous iron concentration of 0.01 mg/l was chosen.
- 4) Using the geochemical model and the laboratory calcium and alkalinity values (note 1), the total dissolved carbonate was adjusted to achieve calcite saturation. The calculated total dissolved carbonate content is 1.94 mm.
- 5) NTB85-01 (Beil. 8.32) reports a uranium concentration of 0.03 ± 0.006 $\mu\text{g/l}$. Adjusting this to a uranine content of zero gives a formation water uranium content of 0.06 $\mu\text{g/l}$.
- 6) No ammonium concentrations were measured. The ammonium value was taken equal to that from the 619 and 621 samples.
- 7) The temperature at this depth is 59.9°C according to the first equation of Section 4.2.3 and 60.2°C according to the second. The rounded mean value was used.
- 8) The measured silica (H_2SiO_3) concentrations fall into two groups, from which formation water contents of 12 mg/l and 4.7 mg/l would be calculated (Table 7.3). These are both well below quartz saturation at 60°C , which is unlikely. The value given is that at quartz saturation at 60°C .
- 9) The density is that of a 1.3 weight percent solution of NaCl at 20°C .
- 10) Gas analyses were made on samples from this zone, but unlike the analyses for the other dissolved constituents, cannot be corrected to estimate the formation water concentrations because the gas content of the deionized water is not known. The oxidation potential which yields uraninite saturation and that for hematite/magnetite, which depends only on pH yield the range given.

7.1.3 Isotope Analytical Results

Analyses for tritium, D and ^{18}O were made on several mixed water samples and from them estimates of the isotopic composition of the formation water at 1,326 m can be developed using the same techniques as for the chemical analytical results.

The isotope results are given in Table 7.5. This table also includes values for the deionized drilling water which are needed in estimating the formation water composition.

Figure 7.2 shows the isotope data plotted against the uranium content of the samples. The tritium data support the initial hypotheses underlying the data interpretation -- that the samples are mixtures of two end members, one formation water, the other deionized water. The tritium data eliminate an alternate hypothesis -- that one end member was water from the upper crystalline region rather than deionized water. If the alternate hypothesis were even partly true, the samples would have had much lower tritium contents because water from the upper crystalline region has no tritium.

From the δD and $\delta^{18}O$ data, the isotopic composition of the 1,326 m formation water can be estimated to be:

$$\delta D = 49\text{‰} \text{ and } \delta^{18}O = -7.9\text{‰}$$

This water is enriched in the heavier isotopes compared with surface waters and ground waters from Northern Switzerland. The only waters which are similarly heavy have been collected from permo-carboniferous (Buntsandstein and below) zones at Weiach and Riniken.

7.2 Summary

The deep crystalline water represented by this sample is quite distinct from that in the upper crystalline zone. To attempt a detailed discussion of its origin or evolution would be too speculative an exercise to be worth while, but there are some points of its chemistry which are at least suggestive and should be mentioned.

Saline waters are normally associated with sedimentary (evaporitic) rock sequences, rather than in crystalline rock. Although saline crystalline waters do occur, they are either in shield environments (e.g., Canada) or can be traced to a sedimentary origin. A sedimentary source is available for this deep Boettstein water in the Permo-Carboniferous trough to the south of the borehole. While analyses of waters from this sequence are beginning to be available as a result of NAGRA drilling activity, they have not yet been examined closely enough to see whether a connection with the Boettstein deep water can be established.

One of the most striking features of this water is its relatively positive $\delta^{18}O$ and δD values. As pointed out, similar values (but less positive) are also found

Date (1983)	Depth (m)	Uranine (mg/l)	δD per mil	$\delta^{18}O$ per mil	Tritium	
					GSF, Neuherberg TU \pm 1 SD	LLC, Berne TU \pm 1 SD
30.09	1300	12.63	-62.3	-9.13	1 \pm 8	69 \pm 5
07.10	1300	11.94	-61.0	-9.05	-- --	-- --
07.10	1301	--	-60.5	-9.05	55 \pm 10	57 \pm 5
10.10	1301	11.25	-60.9	-9.04	58 \pm 8	57 \pm 5
10.10				8.92		64 \pm 11
<u>De-ionized drilling water</u>						
22.1		<u>1/</u>	-71.9	-10.05	121.7 \pm 9.5	
22.1		<u>1/</u>	-71.5	-10.03	105.2 \pm 7.8	
09.2		<u>1/</u>	--	--	103.7 \pm 7.9	
09.2		<u>1/</u>	-71.2	-10.04	105.5 \pm 8.1	
MEAN VALUE:			-71.6	-10.04	109.0 \pm 8.3	
			± 0.5	± 0.01	± 8.5	<u>2/</u>

1/ Uranine concentration in borehole prior to sampling was 22. ppm. See text.

2/ The mean of the reported errors is ± 8.3 . 1 SD for the group of four analyses is ± 8.5 .

Table 7.5: Isotopic composition of samples from 1,326 m zone at Boettstein and of de-ionized drilling water.

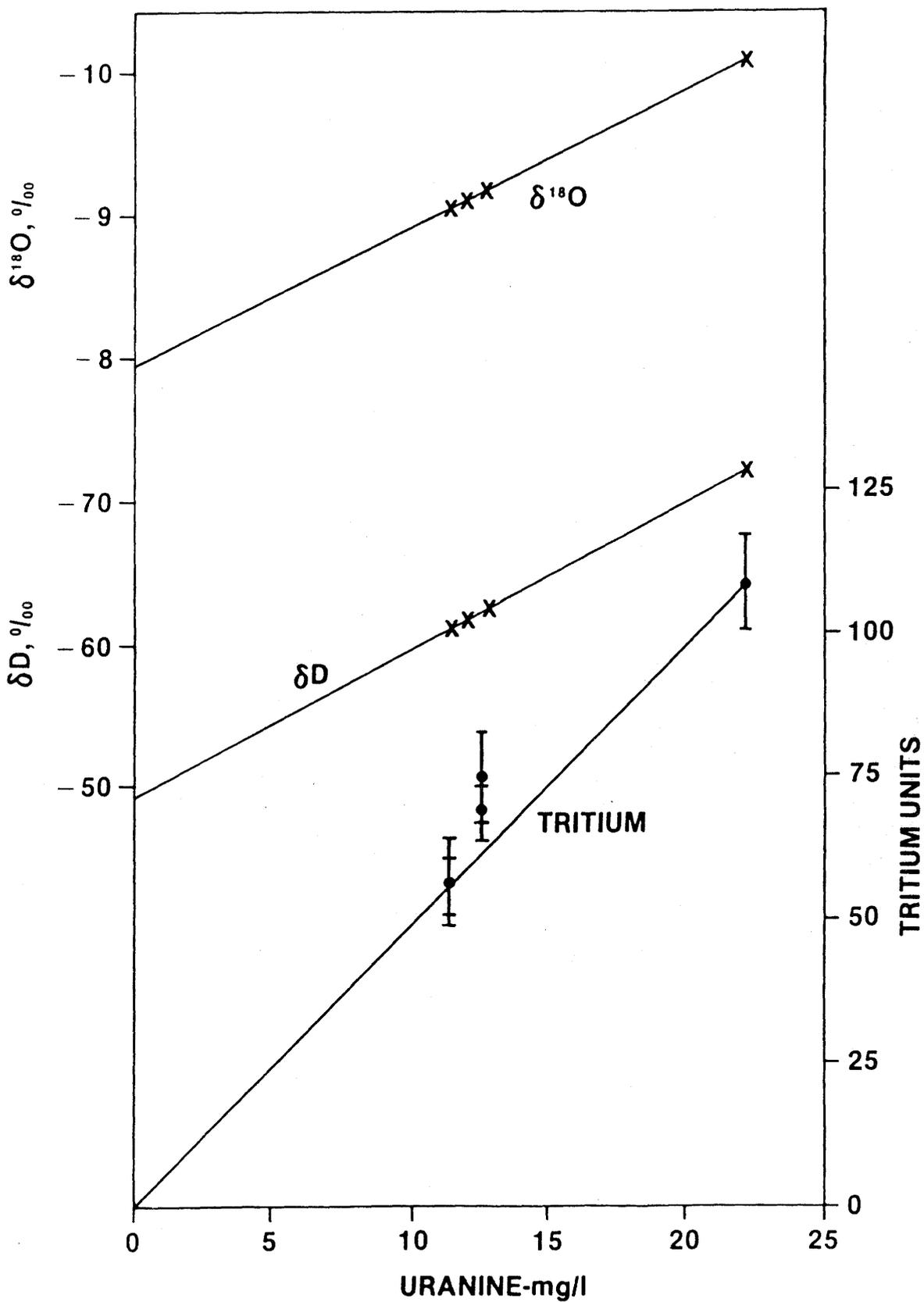


Figure 7.2: Graph of $\delta^{18}\text{O}$, δD , and tritium concentration against uranine content of samples for 1,326 m depth.

in a few samples of Permo-Carboniferous waters. When sulfate-sulfur isotope data are available, they too should be useful indicators of origin.

Other than in this general way, there is as yet too little data to address the origin of this deep crystalline water.

8. SUMMARY AND CONCLUSIONS

The sampling program carried out during drilling and testing of the Boettstein borehole has yielded water samples suitable for detailed geochemical interpretations. Such samples are available from the Muschelkalk, from the major zones of highest hydraulic conductivity in the upper crystalline, and from the zone of highest conductivity in the lower crystalline. Samples were also taken from the Buntsandstein and from the Buntsandstein/weathered crystalline zone. These last two samples contain a small amount of brine drilling fluid and are consequently unsuitable for geochemical interpretations. However, their isotope results were useful in understanding the behavior of the crystalline section under the stress of drilling and sampling.

The analyses were reviewed for internal consistency and for concordance among duplicate sets of results. Agreement among laboratories and between duplicate samples was generally good and the internal consistency of analyses, as judged by charge balance and total dissolved solids tests, was excellent.

A geochemical computer model (PHREEQE) was used to further test the internal consistency of the analyses and to examine water-rock reactions which could influence water chemistry. These tests revealed that:

The measured pH of all samples was higher than its probable in situ value, resulting from CO₂ loss from the sample at the time of pH measurement. Corrections could be made using measured dissolved CO₂ concentrations and(or) the assumption of water equilibrium with calcite;

Dissolved silica and aluminum concentrations in samples from the upper crystalline are consistent with equilibrium between water and the minerals, kaolinite and chalcedony;

All samples appear to be at equilibrium with fluorite; however, fluorite has not been observed in the core;

There are a number of redox-sensitive species present in the samples but they appear to be responding to different oxidation potentials. Thus the concept that these waters can be described by single values of oxidation potentials is not supported;

The dissolved oxygen present in most analyses appears to be from drilling fluid or air contami-

nation of the samples. The platinum electrode potentials seem to be responding to this oxygen, rather than reflecting any formation-water oxidation state;

The dissolved hydrogen reported and iron concentrations above a few hundredths of a mg/l do not reflect formation conditions, but result from corrosion of drilling and sampling tools in the borehole.

A probable range of oxidation potential values can be defined. The upper limit is the value at which the analysed uranium content is at saturation with uraninite (UO_2). The NH_4^+/N_2 , $\text{H}_2\text{S}/\text{SO}_4$, CH_4/CO_2 and hematite/magnetite couples give similar calculated potentials and define the lower end of the range. For the Boettstein crystalline waters, the probable oxidation potential range is from -0.1 volts to -0.3 volts.

Water from the Muschelkalk is saturated with respect to calcite, dolomite and gypsum. It appears to have evolved chemically as a result of gypsum and dolomite dissolution coupled with calcite precipitation. The $\delta^{13}\text{C}$ value calculated using this evolution model agrees with that measured and permits adjustment of the ^{14}C content for geochemical effects. Based on its corrected ^{14}C content, the Boettstein Muschelkalk water residence time is about 17,000 years.

The Buntsandstein/weathered crystalline horizon was drilled with brine mud. A number of samples were taken from this zone both during and after drilling. Although the tritium contents of several samples show that they contained less than 0.7 percent drilling fluid, this was still enough to have so seriously affected their chemistry that they are unsuitable for geochemical interpretation. Although these samples differ chemically from water from deeper crystalline horizons it is likely that if uncontaminated, they would be quite similar to the deeper waters. The isotope results are less affected by drilling fluid presence and are important to understanding the behavior of the upper crystalline system.

Samples suitable for geochemical analyses are available from all three major water-bearing zones of the upper crystalline. Those taken at 399 m and at 621 m during drilling are particularly important because only they represent water in place in the system. The remaining samples were taken after extensive flow into and pumping from the borehole. Their ^{14}C contents strongly

suggest that these samples are of water drawn from higher in the system.

The samples taken during drilling indicate a decrease in ^{14}C with depth from about 12 to 14 pmc in the Buntsandstein/weathered crystalline to <1.3 pmc at 621 m. After one-half to one year of flow, 14 pmc water was found at 649 m.

Water from all upper crystalline zones has virtually identical chemistry. Its pH is close to 8 and its total dissolved solids content is about 1,000 to 1,110 mg/l.

The composition of water from one deep crystalline zone at 1,326 m could be estimated from a series of samples. This water, with a salinity of over 13 g/l, is quite distinct from that in the upper crystalline. It is probable that this water is related to that found in Permo-carboniferous sediments in other boreholes, but to fully investigate this connection will require a more detailed study of the Permo-Carboniferous data than has heretofore been made.

9. REFERENCESNote regarding references in text to NAGRA documents:

Nagra Technische Berichte tend to be known by their document numbers. Thus text references to them are in that form, e.g. NTB 83-04. The full citation for these reports are given in the reference list as follows:

NTB 82-09: Nagra, 1982
NTB 83-04: Balderer, 1983
NTB 84-21: Schmassmann and others, 1984.
NTB 85-01: Nagra, 1985
NTB 85-02: Peters and others, 1985
NTB 85-03: Simond and others, 1985
NTB 85-04: Kussmaul and Antonsen, 1985
NTB 85-06: Balderer, 1985
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