nagra

Arbeitsbericht
NAB 09-15

Reference pore water for the Helvetic marls for the provisional safety analysis in the framework of sectoral plan - interim results (SGT-ZE)

January 2010

U. Mäder

RWI, Institute of Geological Sciences
University of Bern

nagra

Arbeitsbericht
NAB 09-15

Reference pore water for the Helvetic marls for the provisional safety analysis in the framework of sectoral plan - interim results (SGT-ZE)

January 2010

U. Mäder

RWI, Institute of Geological Sciences
University of Bern

Nagra Working Reports concern work in progress that may have had limited review. They are intended to provide rapid dissemination of information. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

Table of Contents

List of Tables

List of Figures

1   Summary

Four variants of a Na-Cl reference pore water (Table 6-2) are suggested for the marl stack (Palfris Formation, Vitznau Mergel) at the Wellenberg siting region. Low-pH and high-pH variants gauge the uncertainty with respect to alkalinity and P_{CO2}. The redox conditions are reducing and modelled at pyrite equilibrium, but with negligible methane for the "base-case". A more reducing variant accounts for the observed high partial pressures of methane, and it is also modelled at pyrite equilibrium (Table 6-2). A "High-Na-Cl" variant with a high salinity (Table 6-3) is also modelled to cover the uncertainty in salinity arising from poorly constrained porosity data.

A $Na-HCO_3$-type pore water in analogy to the $Na-HCO_3$ fracture water of Nagra (1997b) was not included because a planned repository will be located well within the rock volume containing Na-Cl-type pore water. This region is expected to extend upwards as matrix rock into the zone with $Na-HCO_3$-type fracture water.

The Na-Cl reference pore water proposed here has a somewhat higher pH and lower P_{CO2} compared to that of Nagra (1997b), but one of the different variants that bracket uncertainty is comparable. Redox conditions are modelled by mineral saturation constraints for all reference pore water compositions, or at a prescribed partial pressure of methane for the low-pε variant. All waters except the low-pε variant are sulphate-dominant compared to sulphide. The Na-Cl "base-case" reference pore water is similar (somewhat more saline) to that derived by Baeyens and Bradbury (1994) used to derive a sorption data base.

A detailed historical and factual account of the relevant geochemical issues is provided and discussed in detail. Uncertainties and open issues are also addressed.

2   Scope of this report

The scope of this report is to define – to the best of our current knowledge and scientific understanding – reference pore water compositions for the Helvetic marls as a constraint in deriving sorption data bases and solubility limits for radionuclides used in performance assessment calculations. This work is performed in the context of the proposed feasible siting regions and rock formations (Nagra 2008) for geologic disposal of radioactive waste in Switzerland in the framework of SGT-ZE (Sachplan Zwischenergebnis). SGT-ZE is an intermediate step of the Sachplan-procedure (sectoral plan) and the (provisional) safety assessment will be based on the presently available data set.

Only major components and some key geochemical parameters that are relevant for deriving sorption data bases and solubility limits are considered in this report.

The term "Helvetic marls" is used for marly strata of the Palfris Formation and Vitznau Mergel, formerly amalgamated as "Valanginien-Mergel", as occurring in the Drusberg Nappe of the Wellenberg siting region. Also part of the host-rock sequence are similar strata of Tertiary age that are part of the Axen Nappe and that are in tectonic contact with the Cretaceous Palfris Formation (see Section 5 and Figure 5-1 for details).

3   Introduction

The Helvetic marl sequence was proposed by Nagra (2008) as a potential host rock for low/intermediate-level radioactive waste (SMA) in the Wellenberg siting region.

One important reason for having to know – by measurement or interpretation – the pore water composition of a geologic formation is to be able to derive its radionuclide-specific sorption / retardation properties and solubility limits. In general, the sorption properties depend on geochemical parameters, most importantly mineralogy (sorption capacity), pH, ionic strength, redox state, and the speciation of the main dissolved constituents (potential ligands for radionuclides) of the pore water (Bradbury et al. 2008).

Because direct sampling of pore water in sedimentary formations of very low permeability is not feasible or subject to artefacts and contamination with drilling fluid, the process of deriving a pore water composition requires the integration of analytical data from diverse methods, and some kind of a geochemical model to integrate all constraints that are thought to be relevant for controlling the pore water composition. Prime examples of such an approach are that developed for Opalinus Clay at the Mont Terri Rock Laboratory (Pearson et al. 2003, Wersin et al. 2009) and that for the Callovian-Oxfordian claystone at Bure, France (Gaucher et al. 2009).

Reference compositions of fracture groundwater for the Wellenberg host rock were defined by Nagra (1997a, 1997b) in the Wellenberg geo-synthesis report, that was prepared in the context of the then proposed Wellenberg site for hosting a SMA repository. The Wellenberg project was stopped in 2002 by a public referendum in the Canton of Nidwalden. This report is an update to the work on ground water chemistry performed and summarized in Nagra (1997a, 1997b), and includes an estimate of the pore water composition bracketed by a range of reference pore water compositions.

The term pore water is used for the water-filled connected porosity of the rock matrix, as opposed to the groundwater or fracture water that is more mobile and resides in zones of higher transmissivity (Waber and Smellie 2008). While the latter can be sampled by conventional techniques, the former requires indirect methods or very long-term sampling to constrain its composition. In old systems where the fracture water is stagnant, it may be similar or even identical in composition to the adjacent pore water, and it may then be possible to sample it, as was the case for two intervals from borehole SB1 in the deep Na-Cl zone at Wellenberg (Nagra 1997a).

4   Approach

The generic approach to constraining a pore water composition in a low-permeability formation is to fix as many compositional parameters as possible by direct or indirect measurement, and provide substantiated constraints exerted by inferred mineral equilibria and ion exchange equilibria for all remaining parameters. The result is a geochemical model that is consistent with the principles of equilibrium thermodynamics and that fixes the pore water composition at a particular location in the formation. The model also explains the relevant mineralogical controls on the pore water composition. By the same token, such a model would also predict in principle how the pore water composition would react to external geochemical disturbances or on-going slow diffusion processes provided that kinetic effects can either be quantified or neglected.

Such models are established, well constrained and tested for the case of Opalinus Clay (Nagra 2002, Pearson et al. 2003, Wersin et al. 2009). While the Wellenberg area is also well-studied (Nagra 1997a), a number of now commonly employed sampling and analysis techniques to constrain pore water composition were not yet available at that time. The main geochemical focus during the Wellenberg project was to constrain the groundwater compositions and define different types of reference groundwater compositions. Exceptions were the studies of Baeyens and Bradbury (1994, pore water composition), Mazurek et al. (1994, chloride leaching), Hobbs et al. (2002) and Hobbs and Waber (2010, chloride and chloride isotopes), and Lippmann et al. (1998, stable isotopes, helium), and the study aimed at modelling the evolution of the chemistry in fracture waters (Pearson et al. 1998, Waber et al. 1998).

The concept of "geochemical porosity" was not yet fully established at that time, and the geochemical modelling techniques and tools were not as advanced as they are today. It is in this context that the original work on pore water and groundwater (or fracture water) is reviewed and re-interpreted where deemed necessary.

5   Region of interest and knowledge base

Figure 5-1 shows a geological overview map and profile of the proposed siting region Wellenberg (Nagra 2008). The thickness of the combined Palfris / Vitznau / Tertiary marl package is between 1000 and 1700 m and allows for flexibility in terms of depth and layout for a SMA repository. The thickness of the marl stack is 700-800 m measured between Eggeligrat and the level of the valley floor of the Engelberger Aa (ca. 500 m above sea level).
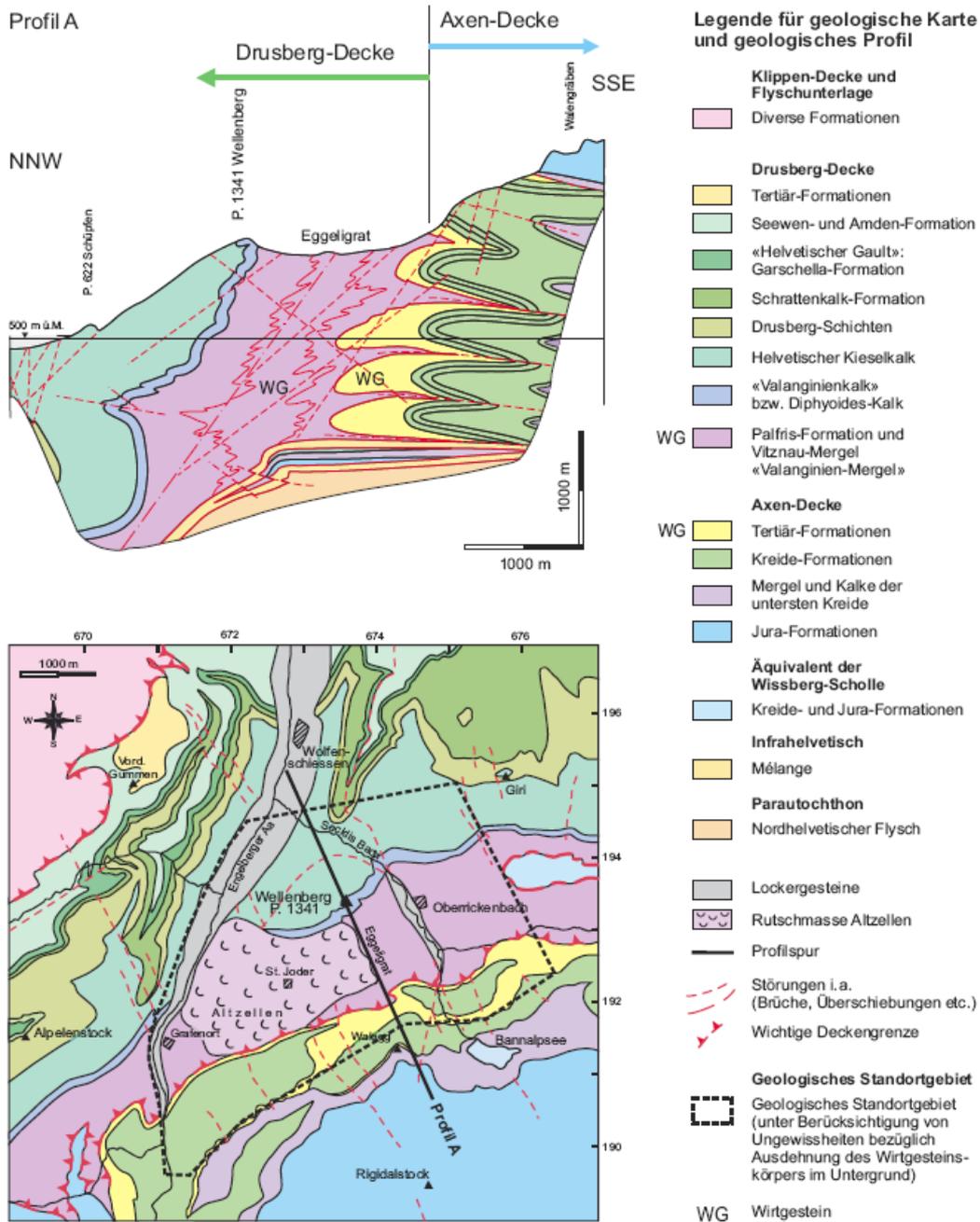

Fig. 5-1:   Suggested siting region Wellenberg for a SMA repository.

(Fig. 5.5-6 from Nagra 2008)

Nagra (1997a, 1997b) filed a geo-synthesis report to underpin the feasibility of building a repository for low- and intermediate-level radioactive waste within a thick sequence of subalpine marl formations in the area of Wellenberg (NW) near the community of Wolfenschiessen. The canton of Nidwalden voted against this undertaking in a public referendum in 2002. Research efforts aimed at geochemical aspects were largely discontinued (with few exceptions, notably including the concept of geochemical porosity) until a change in procedures prompted renewed interest in this rock formation in the framework of the proposed siting regions put forward by Nagra (2008).

The geological and tectonic framework is presented in detail in Nagra (1997a) and is summarized also in Nagra (2008). The Helvetic marls represent a tectonically thickened stack of rocks belonging to the Drusberg Nappe, but also comprising the youngest and outermost Tertiary marly rocks of the Axen nappe which is tectonically below the Drusberg nappe. The tectonic contact is a complex and multiply imbricated structure of overall vertical orientation in the Wellenberg region (Figure 5-1). The footwall of the Drusberg and Axen nappes is a thick tectonic interlayering of infrahelvetic Mélange, Flysch units and also Cretaceous and Jurassic limestone remnants (equivalent of the "Weissenberg Scholle").

In contrast to the other proposed siting regions (Nagra 2008), the rocks at Wellenberg underwent very low-grade metamorphism, and the pore waters evolved from originally marine water to diagenetic and finally metamorphic waters during the burial and deformation history. Estimates of maximum metamorphic temperature are 190-250 °C derived from the study of fluid inclusions (Diamond and Marshall 1994, Mullis 1997, Nagra 1997a, Mazurek 1999) ca. 18-24 Ma ago (early Miocene neoalpine metamorphism). A complex and largely ductile deformation history continued until ca. 5 Ma ago, after which brittle deformation continued during uplift and erosion during Pliocene and early Pleistocene time. Since then, meteoric water had started to infiltrate to greater depth along transmissive features and mixed with and overprinted the earlier fracture waters. The old Na-Cl type groundwaters at Wellenberg were shown to be remnants of metamorphic-type waters, and thus true pore waters (Nagra 1997a). The methane present in fluid inclusions (preserved metamorphic pore water) and in the fracture waters were generated in-situ during peak metamorphism (Diamond and Marshall 1994, Mullis 1997, Mazurek 1999).

Na-Cl-type pore waters are preserved in the low-permeability core-region of the marl stack, grading into ground waters with an increasingly dilute Na-bicarbonate and finally Ca-bicarbonate signature towards the top (Na-HCO_3-Cl / Na-HCO_3 / Ca-HCO_3). The Na-HCO_3-type groundwaters sampled from boreholes at shallower depths likely do not correspond to the pore water present in the nearby connected rock porosity, but to an evolutionary state between near-surface waters and the deeper Na-Cl-type pore water (Perason et al. 1998, Waber et al. 1998). The basal thrust zone represents a regional aquifer with younger (Pleistocene) and much less mineralized Na-HCO_3-type groundwaters (see details in Section 6) than the overlying Na-Cl-type.

Whereas the marly rocks are quite heterogeneous (clay content, limestone beds) and in parts strongly veined with abundant vugs, multiple lines of evidence attest the rocks a closed-system behaviour over considerable geologic time, including the preservation of "underpressures" (sub-hydrostatic) over potentially long time periods (Nagra 1997a, Diamond 1998, Mazurek 1999, Vinard et al. 1993, 2001). These observations, and directly measured very low hydraulic transmissivities attest a general low permeability for the marl sequence and renders the rocks feasible for long-term waste isolation, despite an apparently strong brittle overprint.

6   Reference porewaters for the Helvetic marl sequence

6.1   Existing data on groundwater and pore water composition

The hydrogeochemical data base was derived from 7 deep boreholes carried out within the Wellenberg Project (Nagra 1997a), with some additional sources of information from springs and shallow piezometers. Two boreholes (SB1, SB3) penetrated the entire stack of marly rocks (Palfris Formation and Vitznau Mergel) into its footwall in the central region of interest. Detailed references of the original data reports and interpretations are provided in section 6.3.1 of Nagra (1997a). The chemical analyses are based on water samples derived from packed-off sampling intervals. The groundwater samples are variably contaminated by drilling fluid, increasingly so in the tighter centre of the marl stack where the Na-Cl-type waters dominate and display a very low yield. Strictly speaking, these are samples of groundwater that need not be very similar to the pore water compositions present in the adjacent rock matrix. While a case was made that the deep Na-Cl fracture water reflects also the pore water composition, this is not the case for the shallower Na-HCO$_3$-Cl and Na-HCO$_3$-type fracture waters. For these waters to evolve from Ca-bicarbonate near-surface fracture waters, a certain amount of interaction with Na-rich clay is required most likely including also diffusive interaction with portions of the adjacent rock matrix that preserved some character of the original Na-Cl-type pore water (Pearson et al. 1998, Waber et al. 1998). This transition zone may therefore be rather heterogeneous, with good constraints on the composition of the fracture water, but not on the pore water composition in the less permeable portions in-between fracture systems. Concepts and techniques to determine pore water composition were not yet developed at that time.

Work that post-dates the geo-synthesis of Nagra (1997a) includes a leached chloride and chloride isotope study on the Wellenberg sample profile (Hobbs et al. 2002, Hobbs and Waber 2010), and the establishment of the concept of geochemical porosity (Pearson 1999).

A summary profile with the groundwater data classified and indicated along boreholes is reproduced in Figure 6-1. Here, the low-permeability core region with the Na-Cl-type groundwaters is overlain by a series of evolutionary waters, and underlain by younger Na-HCO$_3$-type groundwaters from within the infrahelvetic basal zone. While the sequence of groundwater types from near-surface Ca-HCO$_3$ waters to the Na-Cl waters in the low-permeability zone is relatively well constrained, the deep portions of the marl stack and its transition to the underlying infrahelvetic mélange is not resolved in detail, for lack of availability of sufficient sample volume to overprint the drilling fluid in these deeper parts of the Palfris Formation / Vitznau Mergel. The region with Na-Cl-rich pore waters in the matrix rock may extend well into the region where Na-HCO$_3$ and Na-HCO$_3$-Cl fracture waters were recovered.

The chemical and isotope composition of the Na-Cl groundwater and the underlying Na-HCO$_3$ groundwater exclude any interaction and active hydraulic connection between these two water types. The hydrochemical investigations of the fracture groundwaters further revealed that the time period since the activation of the present hydraulic system has not been long enough to substantially change the metamorphic pore water from the marl stack.

The pH and partial pressure of CO$_2$ are poorly constrained. At the shallower regions where sufficiently pure groundwater samples could be taken, the measured pH and dissolved constituents invariably were oversaturated with respect to calcite indicating loss of CO$_2$ during sampling and sample storage. Restoring calcite saturation by geochemical modelling led to pH values ranging from 7.71 to 8.70 for the Na-HCO$_3$ waters with associated P$_{CO2}$ ranging from $10^{-2.92}$ to $10^{-1.52}$ bars (Pearson 1994, Nagra 1997a, section 6.3.3). The Na-HCO$_3$ reference

groundwater has a pH of 8.33 and P_{CO2} of $10^{-2.37}$ bar (Nagra 1997b, Beilage A3.7-4b). The pH is not constrained for the contaminated samples of Na-Cl groundwaters. In this case, geochemical modelling using mineral saturations constraints were used (Pearson and Scholtis 1995, Waber et al. 1998), and the authors propose a pH of 6.69 and P_{CO2} of $10^{-0.937}$ bar for the reference groundwater (Nagra 1997b, Beilage A3.7-5b). Multiple evidence indicated that these Na-Cl waters were representative of old metamorphic formation waters at equilibrium with the rock system, and therefore represent also the pore water composition.
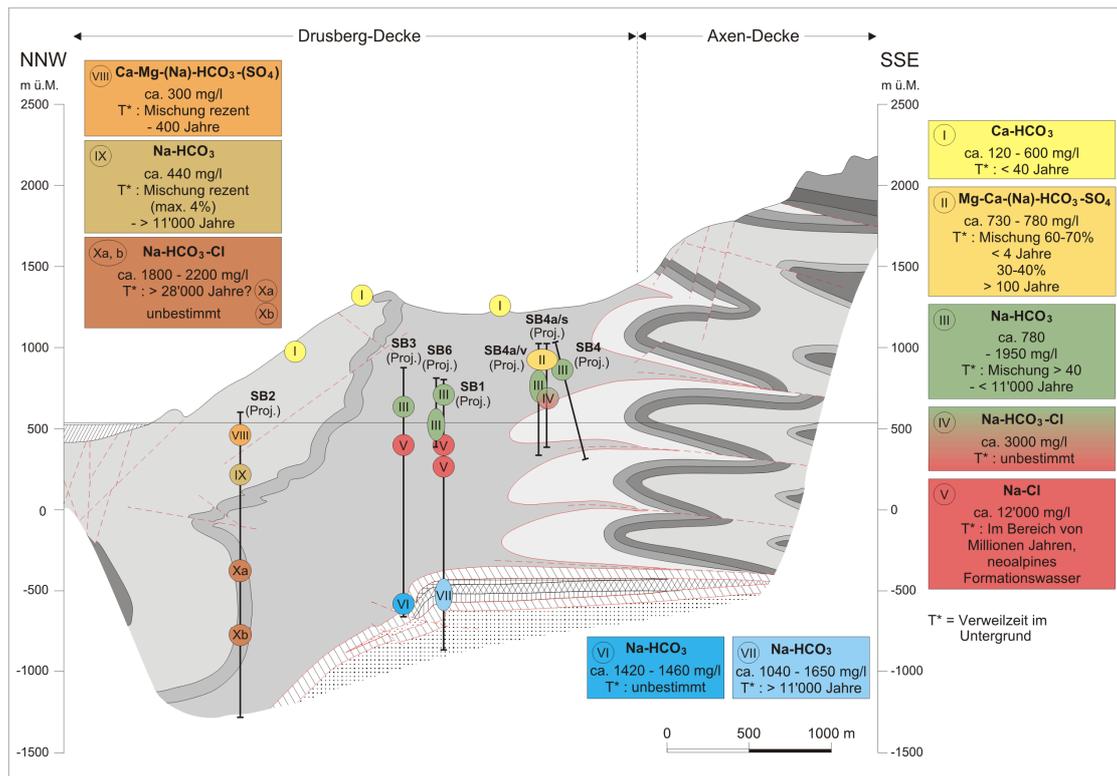
Fig. 6-1:   Hydrochemical summary diagram projected into a geological section across the Wellenberg region.

(Fig. 6.3-1 from Nagra 1997a)

Cation exchange capacities and cation site occupancies (and derived selectivities) were first determined on marl samples (Palfris Fm) from the Oberbauenstock area from borehole samples recovered from a service gallery to the Seelisberg motorway tunnel (Baeyens and Bradbury 1991). This locality is 10 km ENE of Wellenberg in a tectonically and geologically equivalent setting. This work was carried out at the Paul Scherrer Institut and was aimed at constraining a pore water composition for carrying out sorption-type laboratory experiments. New data on cation site occupancy and selectivity from a Palfris marl sample from borehole SB1 (Baeyens and Bradbury 1994) were used to constrain the Na-Cl-type reference groundwater of Nagra (1997a) because the large degree of contamination by drilling fluid precluded a direct method employing simple dilution corrections to all but the most conservative components, chloride and bromide. The sum of the displaced cations in the laboratory extract solutions was generally smaller than the nickel consumption measured when employing the Ni-ethylenediamine method for CEC determination. The work was carried out in a glove box to avoid effects from pyrite

oxidation, but the core material was not stored specifically to minimize air contamination. Details are reported in Baeyens and Bradbury (1991, 1994).

Drillcore samples from boreholes SB1 and SB3 (Figure 6-1) were analyzed for cation exchange capacity, cation site occupancy, aqueous leaching, mineralogy, porosity (Hg-injection) and stable isotope compositions (Mazurek et al. 1994). Only chloride and bromide data were interpreted from the aqueous extracts. The interpretation was hampered by the inferred inaccuracy of the applied porosity measurement method that was unable to determine the entire volume of connected porosity accessible to pore water in the rock matrix (large and variable proportion of micro-porosity not accessed by Hg-injection), and some analytical difficulties. There was a pronounced mismatch between the nickel consumption (Ni-ethylenediamine displacement method used for CEC determination) that was much smaller than the sum of the displaced cations. Work was not carried out in a glove box, and effects induced by pyrite oxidation did therefore lead to significant mineral-water interaction during aqueous extraction and cation exchange procedures. The CEC and site occupancies could not be interpreted with confidence and the data were not used in constraining pore water composition by geochemical modelling. At that time, careful on-site sample processing techniques to preserve the in-situ pore water were not yet established.

The only water-content measurements in the Wellenberg programme where those carried out in the context of stable isotope and He concentration measurements from borehole SB4a/s (Lippmann et al. 1998). The extraction method involved tight packaging and vacuum distillation at 105 °C. Seventeen values were obtained ranging from 0.3 to 1.8 wt%, of which fifteen are between 0.7-1.6 wt%, and twelve are between 1.0 and 1.3 wt%. Unfortunately, the lithology of the samples was not recorded, and it is unclear if these samples represent marly lithologies or also clay-bearing limestones.

While the mineralogy was examined on drill core samples of all boreholes, a very detailed examination was performed for boreholes SB1 and SB3 (Mazurek et al. 1994). Of importance is that the total clay content ranges from near-zero (limestone beds) to ca. 50% in argillaceous marls. The clay fraction is composed of similar amounts of illite, illite/smectite mixed layers and chlorite, with only negligible kaolinite. The smectite content is decreasing with increasing depth, and this is thought to be responsible for an observed general trend of a modest decrease in CEC (semi-quantitative data) with depth. Calcite is the dominant carbonate, but dolomite and ankerite or ferrous dolomite are present in significant amounts across the entire marl stack (Nagra 1997a). Pyrite is ubiquitous, ranging from 0.1 and 4.3 wt% in the Palfris Formation, for example. A new summary of mineralogical data, including porosity, is given by Mazurek (in prep.) for defining the reference mineralogy and some other relevant rock parameters.

Generally, measured Fe^{2+} concentrations (only available from the Na-HCO$_3$-type groundwaters and not in Na-Cl-type waters) are thought to be too high and affected by steel parts of the equipment, except for lowest values of less than 0.02 mg/l sampled with PVC tubing. The presence of measurable sulphide in some cases and the widespread occurrence of methane indicate reducing conditions for the entire marl stack, along with the ubiquitous presence of pyrite. The lowest pε measured in the boreholes with Na-HCO$_3$-type waters was -5.33, and this value was used as a constraint for both, the Na-HCO$_3$ and Na-Cl-type reference groundwaters of Nagra (1997b). While this very low redox potential is thermodynamically consistent with the relatively high levels of methane in many samples, it is not consistent with sulphate-dominant (relative to sulphide) waters observed in several boreholes. Constraints and issues related to sulphate, sulphide and methane concentrations are specifically discussed in the next section.

6.2   Existing models for pore water and groundwater composition

A modern view of and approach to pore water geochemistry was developed for the Wellenberg Project by Bradbury et al. (1990). The authors recognized the limited usefulness of drilling-fluid contaminated borehole samples from a low-permeability marl to define the in-situ pore water, and proposed to use instead data from the clay exchanger along with saturation constraints derived from the rock mineralogy. This approach was first applied to data from borehole rock samples from a service tunnel of the Seelisberg motorway tunnel by Baeyens and Bradbury (1991). It was then applied by Baeyens and Bradbury (1994) to a sample from the Nagra scientific drilling program at Wellenberg (borehole SB1) to characterise the Na-Cl type deep pore water in the low-permeability zone (Table 6-1). Their principle objective was to define a thermodynamically consistent pore water that could be used to perform relevant sorption experiments with marl samples, and use it as a basis to derive a sorption data base for this potential host rock. The authors performed aqueous extracts and determined cation occupancies by Ni-en displacement from which they determined selectivity coefficients. They then derived a model porewater in agreement with the selectivity coefficients by assuming a P_{CO2} and imposing calcite-dolomite saturation which allowed them to calculate Na in the pore water, and hence, total cation charge. All laboratory work was conducted under oxygen-free conditions in a glove box, but no special conservation was applied to the rock samples for the period between drillcore recovery and laboratory treatments. Various sources of uncertainty were discussed, and the results were also compared with the constraints imposed by leachable chloride content and averaged porosity data.

Efforts on groundwaters concentrated on the characterisation of the very old and saline Na-Cl-type water present in the low-permeability deep zone of the Palfris Formation and Vitznau Mergel, and the definition of a much more dilute and younger Na-HCO$_3$-type fracture water to represent the shallower regions of the marl stack below a near-surface zone with recent Ca-HCO$_3$-type groundwaters (Figure 6-1). A first set of Na-HCO$_3$-type and Na-Cl-type reference groundwaters were presented in Nagra (1993, section 5.1.4) constrained by water samples from the deep boreholes and some modelling assumptions. This work was superseded by later work as detailed below.

Expanding on the above efforts, Pearson et al. (1994), Pearson and Scholtis (1995) and Waber et al. (1998) broadened the approach to define and interpret all different types of groundwaters sampled during Nagra's drilling program at Wellenberg, and defined two end-member-type reference groundwaters, one for the deep (Na-Cl-type) and one for the more shallow regions (Na-HCO$_3$-type), respectively. The former could also represent rock portions at shallower regions at some distance to water conducting fractures, and that were not yet affected by surface-derived waters. A genetic interpretation that linked the different groundwater types of the marl formation was provided by Pearson and Scholtis (1995). A detailed account of the groundwater modelling efforts was provided by Pearson et al. (1998), Waber et al. (1998) and Pearson and Scholtis (1995). The work was presented in the Wellenberg geo-synthesis report by Nagra (1997a) with the detailed modelled and measured ranges of groundwater compositions given in Nagra (1997b). While the reference water for the Na-HCO$_3$-type groundwaters were derived from many sampled water compositions, the reference water for the Na-Cl-type was based on data from only two sampling intervals that were significantly contaminated. The cation contents of the latter were consistent with the cation exchange occupancy data of Baeyens and Bradbury (1994). Chloride concentration was based on one less-contaminated sample and an estimate of chloride content from aqueous leaching data (Pearson and Scholtis 1995). Some of the geochemical parameters for the two reference groundwaters of Nagra (1997a, 1997b) are given in Table 6-1.

The Nagra (1997b) Na-HCO$_3$-type reference groundwater (Table 6-1) is essentially a Na-HCO$_3$ solution with minor amounts of other constituents that are at equilibrium with calcite and dolomite. The pH is within the range reported for all samples (7.7-8.7) corrected for degassing by back-calculation to calcite saturation. The partial pressure of CO$_2$ of $10^{-2.37}$ bar is also within a range suggested for deep formations (e.g., Opalinus Clay). The stated value for Fe^{2+} of 0.56 mg/L is based on measurements, but was stated to lead to supersaturation with respect to pyrite and siderite at the given redox potential, and it was proposed that this value was likely too large due to contamination from sampling lines (Waber et al. 1998). It was suggested that a more appropriate value would be close to the detection limit of 0.02 mg/L which limited the measurement of Fe^{2+} in the long-term monitoring sampling from SB6 using PVC tubing. The lowest measured pε of -5.33 was quoted as reference value, but the concentrations of the redox species tabulated (Fe^{2+}, HS$^-$, SO$_4^{2-}$, CH$_4$(aq)) reflect the measurement values. The individual redox conditions derived from the sulphide/sulphate and methane/bicarbonate redox couples were -4.83 and -5.75 in pε, respectively. The water contains little total sulphur (< 0.073 mmol/L) and is sulphate-dominant relative to sulphide, and it is pyrite supersaturated at the measured pε. Pearson and Scholtis (1994) state that for all but one sample "SO$_4^{2-}$ appears to be a product of drilling fluid contamination and (or) of the oxidation of reduced sulphur in the formation during drilling or sampling". The dissolved methane content of 16.05 mg/L (1 mmol/L) yields a partial pressure of methane of $10^{-0.14}$ bar. Further details are given in Waber et al. (1998), Pearson and Scholtis (1994), and in the discussion below and in Section 6.4.

Tab. 6-1:   Na-HCO$_3$ and Na-Cl referenc groundwaters for Palfris Formation and Vitznau
            Mergel of the Wellenberg geosynthesis (Nagra 1997a, 1997b) and reference Na-Cl
            pore water of Baeyens and Bradbury (1994).

Parameter	Na-HCO$_3$-type (Nagra 1997b)	Na-Cl-type (Nagra 1997b)	Na-Cl-type (*) (B&B 1994)	Units / comments
Temperature	15.7 ºC	24.3 ºC	25 ºC	Estimated formation temp.
pH	8.33	6.69	7.5	
P$_{CO2}$	$10^{-2.37}$	$10^{-0.937}$	10^{-2}	Bar
HCO$_3^-$ (species)	16.06	12.76		mmol/kg$_{H2O}$
C^{IV} (total)	16.89	12.81	6.1	mmol/kg$_{H2O}$
Cl (total)	0.260	202	116	mmol/kg$_{H2O}$
S^{VI} (total)	0.0729	$1.05 \cdot 10^{-3}$ (set to 0.1 mg/L)	None	mmol/kg$_{H2O}$
S^{-II} (total)	$0.117 \cdot 10^{-3}$	0.0297	none	mmol/kg$_{H2O}$
SO$_4$/Cl	0.28	n.a.	n.a.	mol/mol
Na (total)	17.83	192.6	114	mmol/kg$_{H2O}$
K (total)	0.046	0.595	2	mmol/kg$_{H2O}$
Ca (total)	0.0499	6.23	1.6	mmol/kg$_{H2O}$
Mg (total)	0.0403	4.825	1.3	mmol/kg$_{H2O}$
Sr (total)	$5.7 \cdot 10^{-3}$	0.582	0.14	mmol/kg$_{H2O}$
Fe^{II} (total)	0.001	$0.724 \cdot 10^{-3}$		mmol/kg$_{H2O}$
Ca/Mg	1.24	1.29	1.23	mol/mol
Na^2/Ca	$6.37 \cdot 10^3$	$5.95 \cdot 10^3$	$8.12 \cdot 10^3$	mol^2/mol
pε (20 ºC)	-5.33	-5.33		Lowest measured value
SI (calcite)	0.00	0.00		
SI (dolomite)	0.05	0.04		
SI (gypsum)	-4.43	-8.54		
SI (celestite)	-3.36	-7.54		
SI (pyrite)	2.34	1.99		
SI (siderite)	1.21	-1.69		

Data are from Beilage A3.7-4b (Na-HCO$_3$) and A3.7-5b (Na-Cl) in Nagra (1997b). B&B 1994: Baeyens and Bradbury 1994: (*) Data set A, Table 13.

The Nagra (1997b) Na-Cl-type reference groundwater (Table 6-1) displays a rather large P$_{CO2}$ of $10^{-0.937}$ bar at a rather low pH of 6.69. Pearson and Scholtis (1995) used a leached chloride content of 0.7 mmol/kg$_{marl}$ derived by Baeyens and Bradbury (1994) for a drillcore sample collected at 539 m depth (SB1), and obtained a pore water chloride molality of 0.1 or 0.2, assuming a porosity of 2% or 1%, respectively. The latter value corresponds to the chloride concentration corrected for drilling fluid contamination of the groundwater sampled from 527 m depth in SB1 (VM-23b). This was also the value selected for the reference groundwater in Nagra (1997b): 200 mmol/kg$_{H2O}$, corresponding to 7090 mg/L. The reference groundwater was constrained at calcite saturation and by the cation exchange data of Baeyens and Bradbury (1994), and it is essentially at dolomite saturation (Table 6-1). The sulphate content was reduced

arbitrarily to 0.1 mg/L to satisfy the lowest measured $p\varepsilon$ constraint of -5.33 (same as used for the Na-HCO$_3$-type water). Measured sulphate values in the contaminated Na-Cl water samples were near 45 mg/L (0.5 mmol/kg$_{H2O}$), but these concentrations were considered to be artefacts of sulphide and pyrite oxidation induced by the drilling process. The value for Fe^{2+} is near that measured in sample VM-23b in SB1 (Nagra 1997b, Beilage A3.7-5a) corrected for contamination. A sulphide concentration of 1 mg/L was assumed and a sulphate concentration of 0.1 mg/L, and the resultant sulphide/sulphate $p\varepsilon$ is -3.98, and pyrite is oversaturated at these conditions. There is no data on dissolved gases from the Na-Cl waters. It was observed that in the gas phase sampled from boreholes there was 100 times the partial pressure of methane compared to CO$_2$, and this was used to model dissolved CH$_4$. The result was 237 mg/L CH$_4$(aq), a partial pressure of CH$_4$ of $10^{1.06}$ bar, and a $p\varepsilon$ of -4.08 (Waber et al., 1998). In conclusion, Waber et al. (1998) state that the redox situation in the Na-Cl groundwater is not well understood. They state that the $p\varepsilon$ is likely less negative in the Na-Cl groundwater compared to the Na-HCO$_3$ groundwater. This can also be understood by recognizing the large difference in pH between the two water types (1.64 pH units) and the intrinsic $p\varepsilon$-dependence on pH relative to the stability of water. Adopting the same $p\varepsilon$ (-5.33) for Na-Cl as for Na-HCO$_3$ groundwater led intrinsically to a much more sulphidic and methanic system for the Na-Cl groundwater at this lower pH. It was stated in Waber et al. (1998) that although graphite was not known to precipitate from groundwater, the large degree of graphite oversaturation implied by the methane/CO$_2$ ratio (SI = 7.6) seemed unlikely and suggested that the absolute redox state and gas concentrations were not yet well understood.

It is interesting to note that all reference waters of Nagra (1997b) derived from water samples and that of Baeyens and Bradbury (1994) derived from the exchanger population display similar Na^2/Ca molal ratios (Table 6-1). This implies that the Na/Ca population on the clay exchanger is also similar, because it is linked to the aqueous concentrations by the Na-Ca ion-exchange equilibrium (activity coefficients and aqueous speciation are ignored here, and the Gaines-Thomas convention is assumed). This is an indication that in the Na-HCO$_3$ region the clay exchanger still has the character that originated from an Na-Cl-type pore water (see also section 5 by Pearson, in Waber et al. 1998).

An issue that could not be satisfactorily constrained by the Wellenberg studies is that of the presence or concentrations of sulphate in the Na-HCO$_3$ and Na-Cl-type pore waters, and likewise many other details regarding the redox conditions.

- Baeyens and Bradbury (1991) interpreted the aqueous leaching behaviour of a sample from the Oberbauenstock as providing evidence for the presence of a limited amount of suspected celestite, and therefore used celestite saturation as a constraint on sulphate to model their Na-Cl-type pore water compositions MPW-1 and MPW-2. The resultant molal SO$_4$/Cl ratios were approximately 0.1 at chlorinities of 0.13-0.14 molal.

- Baeyens and Bradbury (1994) applied their pore water modelling technique to a rock sample from borehole SB1 from the Na-Cl-zone. Here, they interpreted that the sulphate generated in the aqueous extracts (2.2 meq/kg$_{marl}$) was an artefact (most likely due to pyrite oxidation), and used evidence from a water sample from borehole SB6 (Na-HCO$_3$-type locality) where no sulphate was detected (cited as pers. comm. at that time). The two resultant variants of modelled pore waters were free of sulphate. Concentrations of SO$_4^{2-}$ measured during monitoring sampling at SB6 (Nagra 1997b, Beilage A3.7-4a, Na-HCO$_3$-type) were approximately 1-10 mg/L, and a range for sulphide was observed from below detection to 3.4 mg/L. Relatively contaminated water samples from the Na-Cl-zone from SB1 (Nagra 1997b, Beilage A3.7-5a) ranged in sulphate concentrations from 43-48 mg/L, but reduced sulphur was not analyzed for.

- The Na-HCO$_3$-type reference groundwater of Nagra (1993) contained 11 mg/L of sulphate, and that of Nagra (1997b, Beilage A3.7-4b) 7 mg/L (Table 6-1) and only 0.004 mg/L of total sulphide. Analysed water samples from several SB boreholes range from 0.8-26 mg/L of sulphate, but also contain a sample with 98 and another one with 120 mg/L (Nagra 1997b, Beilage A3.7-4a). Concentrations of reduced sulphur ranged from 0.0076-3.4 mg/L, reached 40 mg/L in one case, or were below detection or not measured in other cases. In the majority of samples where reduced and oxidized sulphur was analyzed, reduced sulphur was dominant on a molal basis.

- For the Na-Cl-type reference groundwater of Nagra (1997b, Beilage A3.7-5b) a total sulphur content of 1 mg/l was assumed, and a redox potential of -5.33 (pε) was adopted, which would reduce sulphate essentially to zero. This redox condition corresponded to the most reduced pε measured in a borehole within the Na-HCO$_3$-type groundwater (at higher pH). Concentrations of 1 mg/L and 0.1 mg/L were adopted for dissolved sulphide and sulphate, resepectively, for the reference Na-Cl-type composition, and this defined a pε of -3.98 that is distinctly less negative than the one adopted from the Na-HCO$_3$-type sample (-5.33). Measured sulphate contents from three samples from two intervals in SB1 range from 43-48 mg/L (0.5 mmol/kg$_{H2O}$), but reduced sulphur was not analyzed. The range of contaminated samples from SB1 is plotted near 1 mmol/kg$_{H2O}$ (96 mg/L) in Nagra (1997a, figure 6.3-10). The contamination by drilling fluid in the three samples from SB1 is estimated to 20-65%. Pearson and Scholtis (1994) state that "it is likely that the oxidation state of these waters in situ, like that of the upper Na-HCO$_3$ waters, is reducing enough to favour sulphide over sulphate". It is stated in Nagra (1997a) that the concentrations of redox-sensitive components were disturbed in all samples. It was argued that the presence of non-corroded pyrite was an indication of the presence of reduced sulphur rather than sulphate, and that reducing conditions were also indicated by the presence of methane. Consequently, sulphide-dominant redox conditions were adopted to explain the high concentrations of dissolved methane. While the presence of thermodynamically stable pyrite alone does not require a sulphide-dominant sulphur system (e.g. Opalinus clay, Pearson et al. 2003, Mäder 2009b), the presence of appreciable methane at thermodynamic equilibrium with pyrite does. The consequence of a methane-sulphide-dominant system in equilibrium with pyrite would be that dissolved Fe^{2+} concentrations would become extremely small if assuming thermodynamic equilibrium.

The situation with respect to sulphate and sulphide and redox in general, including methane, is therefore rather unclear, and it is not constrained by direct measurements of pε or concentrations of redox-sensitive species for the Na-Cl-type groundwater. The Na-HCO$_3$-type groundwaters may be reducing enough to render sulphate smaller than sulphide or at least at a comparable concentration. The deeper Na-Cl-type groundwaters may be relatively more reducing (pε could be less negative in absolute terms due to the pH effect) to support a high P_{CH4} with only sulphide present, but there is no direct information on the presence or absence of reduced sulphur. The sulphate-sulphide speciation is very dependent on the assumed redox potential (and so is the saturation state of pyrite, for example), and the sulphate/sulphide transition occurs across a very narrow range of pε values. In the modelling approach below, this uncertainty in pε and methane/sulphide/sulphate is accounted for by defining a range of reference pore water compositions.

The pH is not directly constrained for the Na-Cl-type groundwaters. The contaminated borehole samples do not permit to re-construct pH in a straightforward way. The pH in the samples may also be affected by the bentonite component in the drilling mud and by other complex mineral-water interactions. The pH of the Nagra (1997b) reference water is a modelling result and it is dependent on the details and assumptions underpinning the approach. The details of the

modelling steps are not reported, but it is stated in Nagra (1997b) that pH, alkalinity and P_{CO2} are modelling results. Clearly, an additional assumption for one of the three parameters besides imposing calcite saturation at a given Ca concentration is required to constrain the system (see Pearson et al. 2003 for details of the approach). Scholtis (1992) provides details of modelling an earlier version of the Na-Cl reference groundwater: P_{CO2} was fixed at $10^{-2.3}$ bar, a value obtained for the better constrained Na-HCO$_3$ groundwater, and this resulted in a pH of 7.5 and a total alkalinity of 4.01 mmol/L. Clearly, the reference groundwater given by Nagra (1997a, b) was based on different assumptions (Table 6-1).

The concept of geochemical porosity (e.g., anion-accessible or chloride-accessible porosity) did not fully enter the Wellenberg work as it did in the case of Opalinus Clay (Pearson et al. 2003, Nagra 2002) a few years later. A first mention of such a concept in the case of the Helvetic marls was included in Baeyens and Bradbury (1991) where the authors reconstructed a marl pore water from aqueous leachate data, cation site occupancies and derived ion-selectivities combined with geochemical modelling. They associated the leached chloride by some amount of "free water" to match the modelled chlorinity. The available porosity data was not good enough to examine if this amount of "free water" was different from the total water contained in the connected physical porosity.

The concept of geochemical porosity was addressed in the context of marl from Wellenberg by Pearson (1996) and first published by Pearson (1998) and more fully by Pearson et al. (in: Waber et al. 1998) and in a broader context by Pearson (1999). The issue was not critical for the case of Wellenberg for defining the Na-HCO$_3$-type groundwaters because it was largely based on measured compositions. The understanding of geochemical porosity as it is today would have been helpful for interpreting the Na-Cl-type waters from the low-permeability zone by connecting the pore water samples with the aqueous leaching data and porosity. Determination of water-content (and related porosity) were not part of the analytical program, and only Hg injection porosity data was available which did bear a substantial uncertainty of not accessing a portion of the clay-related porosity. One data set from SB4a/s aimed at stable isotope and He determination via vacuum distillation included water-content determinations of 1.0-1.3 wt% on average (Lippmann et al. 1998). The concept of a reduced geochemical porosity due to the effect of permanently charged clay surfaces did not enter the Wellenberg synthesis (Nagra 1997a), but was later clearly identified for the case of the Helvetic marls at Wellenberg in Pearson (1999) along with examples from Opalinus Clay and Boom Clay, among others. Pearson (1999) suggested a geochemical porosity of ca. 0.3(±0.1) times water-loss porosity, comparing aqueous leaching data with a moderately contaminated borehole groundwater sample from the low-permeability zone containing the Na-Cl-type pore water.

The chlorinity value of 7090 mg/L (0.2 mol/kg$_{H2O}$) for the Na-Cl reference water hinges essentially on three analyses from two sampling intervals from SB1 (Nagra 1997b, Beilage A3.7-5a). Pearson and Scholtis (1995) and Waber et al. (1998) state that for interval VM-13 (two samples reported) the chlorinity could be back-calculated to zero-contamination with some confidence based on the observed linear evolution of electric conductivity during sampling (Pearson 1994). The sample from interval VM-23 was used for some modelling constraints (cation ratios, no bentonite in the drilling mud), but was treated in terms of dilution to match the chlorinity of 0.2 mol/ kg$_{H2O}$. This data, combined with a chloride content of marl derived from leaching experiments by Bayens and Bradbury (1994) of 0.7 mmol/kg$_{marl}$ and an average Hg-injection porosity of 2.9% for clay-rich marl (or 3.3% derived from water-content measurement) led to the determination of a geochemical porosity that was only about 30% of the total connected porosity by Pearson (1999). The aqueous leaching data and porosity data obtained on drillcore samples (Mazurek et al. 1994) were not constraining enough to further elucidate on salinity variations with depth or on additional constraints on the geochemical

porosity. Based on independent evidence, Baeyens and Bradbury (1994) calculated an ionic strength (chlorinity) based on the cation site occupancy and constraints from aqueous leaching data and an assumed P_{CO_2}, and bracketed the chloride concentration between about 0.1 and 0.16 mol/l. Both, the chlorinity and geochemical porosity hinge on a very limited set of measurements and some underlying assumptions.

6.3   Reference pore waters for Helvetic marls of the Wellenberg region

The arguments (Nagra 1997a, and references therein) that led to the definition of the Na-HCO$_3$ and Na-Cl as representative end-member reference groundwaters are valid and cover the range expected in the context of the Wellenberg siting region. Intermediate groundwaters of Na-HCO$_3$-Cl-type as found in some borehole intervals are genetically linked to the reference waters, and assume intermediate chemical compositions. While the Na-Cl-type reference groundwater is also representative of the pore water composition of the formation, this is likely not the case for the Na-HCO$_3$ waters except perhaps for the near-surface zone and fractured rock portions within and very near the water-conducting features. These latter waters are inferred to be of ages ranging from >40 to <11'000 years (Nagra 1997) and it is therefore possible or even likely that more saline pore waters are preserved away from water-conducting features, as is commonly observed in crystalline fractured rock systems (Waber and Smellie 2008). An indication for this is that chloride content data derived from leaching show elevated values also from a depth range where associated fracture waters are of Na-HCO$_3$-type (Mazurek et al. 1994, Hobbs and Waber, 2010). Such aspects were not examined during the Wellenberg project because the concept of pore water and fracture water (groundwater) was not yet commonly adopted at that time. The repository level foreseen for Wellenberg will be well within the Na-Cl region. It is therefore justified to consider a Na-Cl-type pore water and its uncertainty range as being present in the rock matrix of this region, and to omit a very dilute version with an Na-HCO$_3$-type character.

The key uncertainty with respect to the Na-Cl reference water is the salinity which hinges presently on very few critical measurements supported by the strong similarity in chemical, isotopic and gas composition to that of fluid inclusions in fracture minerals. There is a lack of a well-constrained pH-P_{CO_2}-alkalinity system (Section 6.3.1) and the redox conditions are also not well constrained (apart from being reducing) and so need to be bracketed by the available data and observations (Section 6.3.2).

6.3.1   Na-Cl reference pore water

The aim of the approach taken here is to arrive at fully modelled reference pore water compositions, including the redox state, but that are also consistent with the constraints imposed by the Wellenberg studies. Because cation concentrations are not well constrained by the contaminated water samples, the exchanger composition of Baeyens and Bradbury (1994) is used to model the initial cation ratios in solution in combination with the generic selectivity coefficients of Appelo and Postma (2005). This constraint is relaxed during subsequent modelling steps such that the final cation ratios are slightly different compared to the initial ones, and also the exchanger population would slightly adjust accordingly (maintaining the selectivity coefficients). The same chlorinity (0.2 mol/kg$_{H2O}$) as that proposed by Nagra (1997b) is used for all variants of the reference case. The uncertainty in the alkalinity system is reflected by bracketing P_{CO_2} by two variant compositions and thus also pH and carbonate alkalinity. The uncertainty in redox conditions is treated by modelling two states - both reducing: (1) assuming siderite-pyrite equilibrium (less reducing), and (2) specifying a partial pressure for methane while maintaining pyrite saturation (more reducing). While the former yields a water with

sulphate > sulphide, the latter is sulphidic with methane present. In both cases, an initial total sulphur content of 0.2 mmol/kg$_{H2O}$ was assumed which is an arbitrary choice that lies below the ca. 45 mg/L reported for the water samples (Nagra 1997b), but that are assumed to be a contamination by Waber et al. (1998).

Dissolved iron concentrations are handled differently for the less reducing variants (sulphate>sulphide) and the more reducing variant (methane-sulphide). While in the former case a dissolved Fe^{2+} activity can be conveniently defined by linking it to siderite saturation (as proxy for Fe-carbonate), this is not possible for the latter case, because Fe-bearing carbonates are thermodynamically not stale in the presence of substantial sulphide activities while maintaining equilibrium with respect to pyrite. Pyrite equilibrium would force dissolved Fe^{2+} activities to be extremely small in the presence of substantial sulphide activities, and this will be incompatible with siderite equilibrium and the constraints imposed on alkalinity by calcite equilibrium.

Because the available salinity constraints are very few and subject to uncertainty, a high-salinity variant with a chlorinity of 0.5 mol/ kg$_{H2O}$ is also provided and discussed as an upper limit in Section 6.3.2.

The following constraints were implemented in the Phreeqc model:

- Chlorinity was fixed at 0.2 mol/kg$_{H2O}$ as in Nagra (1997b, Beilage A3.7-4b).

- A small amount of total sulphur is included (0.2 mmol/ kg$_{H2O}$). The speciation is subsequently based on pyrite-siderite equilibrium.

- Sodium is added to charge balance.

- Initial dissolved inorganic carbon was added to satisfy a specific partial pressure of CO$_2$. It is initially set to $10^{-1.7}$ bar for the reference water to reach a target value near 10^{-2} bar.

- The initial pH is set to 7.0. This pH is a free variable during later modelling steps.

- The above solution is equilibrated with an exchanger of the composition measured by Baeyens and Bradbury (1994, page 22) using their data set A. The necessary data base entries for the exchange calculations are provided in the input file. The cation selectivity constant for K$^+$=Na$^+$ ion-exchange is adjusted (see discussion below).

- The above solution is equilibrated with calcite, siderite, pyrite and quartz, whereby small amounts of these minerals are either brought into or removed from solution. This reference pore water is also the less reducing variant with sulphate dominant compared to sulphide.

- Redox (pε) is initially fixed at -3 (to keep sulphate stable) and later constrained to be at sulphate/sulphide in equilibrium with siderite and pyrite.

- Solutions at higher initial P$_{CO2}$ (lower pH) and at lower initial P$_{CO2}$ (higher pH) are generated in analogous fashion to gauge the uncertainty with respect to pH and alkalinity (total inorganic carbon) as a function of P$_{CO2}$. This done by specifying different amounts of total inorganic carbon compared to the reference case (see commented-out lines [preceded by #] in the input file below).

- The more reducing variant with sulphide dominant and appreciable methane is implemented by specifying a partial pressure of methane that is two orders of magnitude above P$_{CO2}$ as proposed in Nagra (1997b).

The Nagra-PSI thermodynamic data base was used (Hummel et al. 2002), and all calculations were performed at 25 °C for lack of temperature dependency coefficients available in the data

base. This may lead to some minor deviations in cases where the formation temperature is more than 10 K below or above 25 °C. The exchanger data are taken from the Phreeqc default data base, where the generic selectivity coefficients of Appelo and Postma (1993, 2005) are implemented. The selectivity coefficient for potassium (log-K for exchange-reaction relative to sodium) is adjusted from 0.7 to 0.94 as adopted by Mäder (2009) for the case of the Opalinus Clay reference pore water. This is close to the lower limit of the range of 1-1.4 suggested most recently by Tournassat and Pearson in Wersin et al. (2009) for Opalinus Clay. This adjustment is an arbitrary decision not supported by independent evidence, but does not significantly affect the results except for reducing somewhat the dissolved potassium concentrations.

The Phreeqc input file is reproduced below, and the computed composition of the Na-Cl reference pore water is listed in Table 6-2. The command lines activated or de-activated in the Phreeqc input to obtain the high-P_{CO2} and low-P_{CO2} variants as well as the low-$p\varepsilon$ variant are indicated (preceded by # symbol), and results are also listed in Table 6-2. Detailed speciation information and saturation indices for all variants are provided in Appendices 1-4.

```
DATABASE NAPSI_300401DAV.DAT
TITLE  Na-Cl Ref pore water for Helvetic marl
# add ion exchange equilibria from PhreeqC default data base
EXCHANGE_MASTER_SPECIES
    X  X-
EXCHANGE_SPECIES
    X- = X-
    log_k   0.0
    Na+ + X- = NaX
    log_k   0.0
    -gamma  4.0   0.075
    K+ + X- = KX
#   log_k   0.70     # Appelo & Postma 1993
    log_k   0.95     # adjusted as for OPA pore water
    -gamma  3.5   0.015
    Ca+2 + 2X- = CaX2
    log_k   0.80     # Appelo & Postma 1993
    -gamma  5.0   0.165
    Mg+2 + 2X- = MgX2
    log_k   0.60     # Appelo & Postma 1993
    -gamma  5.5   0.2
    Sr+2 + 2X- = SrX2
    log_k   0.91     # Appelo & Postma 1993
    -gamma  5.26  0.121
SOLUTION 1 Na-Cl # Nagra 1997b Beilage A3.7-5b
    pe       -3.0  # set some initial reducing pe
    temp     25.0
    -units   mmol/kgw
    pH       7.0
    Cl       202.0
    Na       202.0    charge # initial Na-Cl-(SO4-HCO3) water
    S        0.2
    C 5.0   CO2(g) -1.7 # log(PCO2)=-2.10, pH=7.467 (ref water)
#   C 10.0  CO2(g) -1.2 # log(PCO2)=-1.21, pH=7.012 (low-pH)
#   C 5.0   CO2(g) -2.2 # log(PCO2)=-3.05, pH=7.948 (high-pH)
EXCHANGE 1 B&B94 # Baeyens&Bradbury NTB 94-22, data set A, p.22
    NaX      41.6
    KX       4.6
    MgX2     1.7   # 3.4 eq
    CaX2     4.95  # 9.9 eq
```

```
    SrX2     0.45  # 0.9 eq
EQUILIBRIUM_PHASES 1
    calcite        0.0
    siderite       0.0    # disable for low pe variant
    pyrite         0.0
    quartz         0.0
#   CH4(g)        -0.1    # enable for low pe variant
END
```

The "base-case" Na-Cl reference pore water chosen here (Table 6-2) has a higher pH and lower P_{CO2} compared to that of Nagra (1997b). This is not a modelling result but simply reflects a preference for more moderate partial pressures of CO_2 ($10^{-2.09}$ bar) compared to a value of $10^{-0.937}$ bar adopted in Nagra (1997b). There is no compelling argument for this other than that it is also supported by arguments of Coudrain-Ribstein and Gouze (1993), and this P_{CO2} is nearly the same as that adopted by Baeyens and Bradbury (1994) in their derivation of the Na-Cl type pore water (Table 6-1). The high-P_{CO2} variant (Table 6-2) is similar to the reference ground-water of Nagra (1997b) with respect to alkalinity and pH. The low-P_{CO2} variant represents the high-pH variant to span a reasonable range of uncertainty with respect to alkalinity/P_{CO2} and pH. This range of uncertainty is not known from measurements, and so it is simply a best guess, avoiding seemingly "extreme" combinations of pH and P_{CO2}.

Looking more closely at the reference groundwater of Nagra (1997b, Beilage A3.7-5b), one notes that the modelled composition contains distinctly more carbonate alkalinity compared to the range suggested in the measured and corrected-for-contamination compositional range given, and the pH is just below the lowest inferred value. While all these properties may be variably affected by borehole contamination, it may be an indication that the chosen modelling approach resulted in a reference composition slanted towards the low-pH/high-alkalinity/high-P_{CO2} extreme of the range permissible by the data. The exact details of the modelling steps are not described in Pearson and Scholtis (1995) or Waber et al. (1998) such that it is difficult to reconstruct the detailed procedures followed.

The modelled concentrations of the divalent cations that are tied to ion exchange (Ca^{2+}, Mg^{2+}, Sr^{2+}) are only about half of that given in the Nagra (1997b) reference groundwater. The concentrations adopted for the Nagra (1997b) reference water were based on a measured water sample but were said to be consistent with the cation site occupancies of Baeyens and Bradbury (1994). The generic cation distribution constants adopted for this work are sufficiently different from those derived by Baeyens and Bradbury (1994) to explain this difference. For example, only the selectivity constant for Sr^{2+} of Appelo and Postma (1993, 2005) is within that bracketed by Baeyens and Bradbury (1994) for all divalent cations with their data set A and B, but those for Ca^{2+} and Mg^{2+} are distinctly different.

Equilibrium with respect to dolomite (ordered dolomite) was not enforced. The Ca/Mg ratio for the Na-Cl water is determined by the exchanger site occupancy and the exchange distribution constants. This results in a slight undersaturation with respect to ordered dolomite, and a Ca/Mg ratio that is a bit higher (1.7) than if it were at dolomite saturation (~ 1.4).

Tab. 6-2:   Na-Cl referenc porewaters for Palfris Formation and Vitznau Mergel, and variants
with respect to CO_2 partial pressure and redox potential.

Parameter	Na-Cl "Base-case"	Na-Cl High-P_{CO2}	Na-Cl Low-P_{CO2}	Na-Cl Low-pϵ	Units
Temperature	25	25	25	25	ºC
pH	7.467	7.012	7.948	7.456	
Ionic strength	0.211	0.219	0.208	0.211	molal
pϵ (25 ºC)	-3.418	-2.897	-3.968	-4.841	
P_{CO2}	$10^{-2.10}$	$10^{-1.21}$	$10^{-3.05}$	$10^{-2.070}$	bar
P_{CH4}	$10^{-11.6}$	$10^{-11.2}$	$10^{-12.0}$	$10^{-0.1}$	bar
HCO_3^-	4.740	12.73	1.606	4.862	mmol/kg$_{H2O}$
C^{IV} (total)	5.413	15.86	1.800	5.558	mmol/kg$_{H2O}$
Cl (total)	202	202	202	202	mmol/kg$_{H2O}$
S^{VI} (total)	0.2	0.2	0.2	$2.51 \cdot 10^{-6}$	mmol/kg$_{H2O}$
S^{-II} (total)	$51.7 \cdot 10^{-9}$	$58.9 \cdot 10^{-9}$	$43.1 \cdot 10^{-9}$	0.2	mmol/kg$_{H2O}$
Na (total)	197.7	206.5	194.7	197.6	mmol/kg$_{H2O}$
K (total)	2.338	2.420	2.306	2.337	mmol/kg$_{H2O}$
Ca (total)	2.273	2.512	2.182	2.267	mmol/kg$_{H2O}$
Mg (total)	1.320	1.459	1.268	1.316	mmol/kg$_{H2O}$
Sr (total)	0.162	0.180	0.155	0.161	mmol/kg$_{H2O}$
Si (total)	0.178	0.177	0.180	0.178	mmol/kg$_{H2O}$
Fe^{II} (total)	0.0110	0.0140	0.0100	$0.549 \cdot 10^{-12}$	mmol/kg$_{H2O}$
Fe^{III} (total)	$0.918 \cdot 10^{-9}$	$0.204 \cdot 10^{-9}$	$6.14 \cdot 10^{-9}$	$1.61 \cdot 10^{-21}$	mmol/kg$_{H2O}$
SO_4/Cl	0.001	0.001	0.001	0	mmol/kg$_{H2O}$
Ca/Mg	1.72	1.72	1.72	1.72	mmol/kg$_{H2O}$
SI (dolomite, ord.)	-0.10	-0.10	-0.11	-0.10	
SI (gypsum)	-2.94	-2.92	-2.95	-7.85	
SI (celestite)	-2.04	-2.02	-2.04	-6.94	
SI (strontianite)	-0.36	-0.36	-0.36	-0.36	
SI (graphite)	-4.29	-3.67	-4.96	1.47	
Cl-porosity	0.009 / 30%	0.009 / 30%	0.009 / 30%	0.009 / 30%	Abs./proportion

Calculations performed with Phreeqc (version 2.15.07) and Nagra-PSI data base Version 01/01.
All pore water compositions are at equilibrium with respect to calcite, siderite (except for low
pϵ variant), quartz and pyrite. Cl-porosity: absolute vale and proportion of total accessible
porosity, based on Nagra (1997a) and Mazurek (in prep.).

The choice made here for the "base-case" reference pore water with respect to redox assumes
that the pore water is reducing but sulphate-dominant, rather than sulphide-dominant as
proposed in Nagra (1997b). Some sulphate was measured in the contaminated Na-Cl-type
borehole samples, and this was considered here. Methane is confined to a very low partial
pressure at the chosen conditions, and this is not consistent with the measureable methane
obtained from borehole sampling. The "base-case" and its variants at different P_{CO2}/pH

conditions are likely a bit less reducing than the expected in situ conditions but bracket the overall range of compositions given together with the more reducing variant elucidated on below.

The variant at more reducing conditions (Table 6-2) was defined by setting the partial pressure of methane ($10^{-0.1}$ bar) two orders of magnitude larger than P_{CO2}, as was argued by Waber et al. (1998), based on the observed gas composition. The condition of siderite (or any other Fe-carbonate) saturation has then to be relaxed if saturation with pyrite is to be maintained. The reason for this is the modelled extremely low dissolved iron concentration imposed by pyrite equilibrium at this low pε. All sulphur is reduced and the model is not sensitive to the assumed total sulphur (0.2 mmol/kg$_{H2O}$ as in the "base-case"). Graphite is supersaturated, but this is a technical issue because crystalline graphite is not expected to form at low temperatures. The dissolved methane content is 1.1 mmol/kg$_{H2O}$, which is similar to measured values in the Na-HCO3-type groundwaters (not measured in the Na-Cl-type water samples). This variant is quite similar to the reference pore water of Nagra (1997b) in terms of pH, redox, and alkalinity, such that arguments put forward on the basis of this pore water remain valid within the range of pore water composition considered in this report. The partial pressure of methane is an order of magnitude lower compared to that of the Nagra (1997b) reference groundwater because also the P_{CO2} is an order of magnitude lower in this case.

While pyrite is ubiquitously present throughout the marl stack, siderite is not reported as a mineral phase (Mazurek, in prep.). Siderite functions as a proxy for a Fe-bearing carbonate phase for the purpose of constraining the redox system thermodynamically. While dolomite and ankerite (or ferrous dolomite) are quite wide spread and may be the controlling phase, the lack of detailed knowledge of its composition (Ca-Fe-Mg-Mn solid solution) preclude it from thermodynamic calculations. The only analysis of ankerite were reported from fracture mineralisation (Mazurek and Bläsi 1992). A similar approach with respect to Fe-carbonate was used in the case of Opalinus Clay (Pearson et al. 2003) and results suggest that this is a reasonable assumption, and that the results are not overly sensitive to this approximation.

There are no independent constraints on the sulphide / sulphate system for the Na-Cl-type waters. The two variants differing in redox do bracket the extreme cases, with a range of -3.4 to -4.8 in pε at a pH of 7.5. If one were to assume graphite saturation (not a reasonable assumption), the resultant P_{CH4} would be only $10^{-3.1}$ bar at a dissolved methane concentration of $1.1 \cdot 10^{-6}$ mol/kg$_{H2O}$, and a pε of -4.43. Also in this case, measureable iron and sulphate would not be present at these conditions when assuming pyrite equilibrium.

6.3.2   High-Na-Cl variant of the reference pore water

The upper limit of salinity is poorly known in the absence of better constraints on geochemical porosity and physical porosity. A salinity of 2.5 times that of the reference pore water is chosen, namely 0.5 mol/kg$_{H2O}$, and 0.4 mmol/kg$_{H2O}$ of sulphate are prescribed (not a critical parameter). This value for chloride corresponds to the maximum observed equivalent salinities in fluid inclusions (Diamond and Marshall 1994) that document metamorphic conditions and different phases of carbonate formation in veins. This issue is further discussed in Section 6.4. Scholtis (1992) proposed a reference water with almost 0.5 mol/kg$_{H2O}$ of chloride, but this value was later stated to be based on an erroneous extrapolation to correct a contaminated water sample. The range of chlorinity reported by Nagra (1997b) for the Na-Cl reference groundwater is 4990-16775 mg/L (0.14-0.47 mol/kg$_{H2O}$) and its upper limit is also close to the here assumed 0.5 mol/kg$_{H2O}$.

The modelling approach is the same as that presented for the Na-Cl reference pore water in Section 6.3.1. The same arguments and comments apply, and these are not repeated here. Only the variant with intermediate pH and P_{CO2} is detailed here computed at a pε assuming equilibrium with siderite rendering sulphate stable and yielding a very low partial pressure of methane. The initial P_{CO2} was set such as to reach a final value very similar to that of the reference pore water.

The Phreeqc input file is listed below and the results are shown in Table 6-3. An initial P_{CO2} of $10^{-2.0}$ bar is chosen that brings the final P_{CO2} to $10^{-2.14}$ bar at a pH of 7.156. Detailed speciation information and saturation indices are provided in Appendix 5.

```
DATABASE NAPSI_300401DAV.DAT
TITLE  High-Na-Cl variant of ref pore water for Helvetic marl
# add ion exchange equilibria from PhreeqC default data base
EXCHANGE_MASTER_SPECIES
    X  X-
EXCHANGE_SPECIES
    X- = X-
    log_k   0.0
    Na+ + X- = NaX
    log_k   0.0
    -gamma  4.0   0.075
    K+ + X- = KX
#   log_k   0.70     # Appelo & Postma 1993
    log_k   0.95     # adjusted as for OPA pore water
    -gamma  3.5   0.015
    Ca+2 + 2X- = CaX2
    log_k   0.80     # Appelo & Postma 1993
    -gamma  5.0   0.165
    Mg+2 + 2X- = MgX2
    log_k   0.60     # Appelo & Postma 1993
    -gamma  5.5   0.2
    Sr+2 + 2X- = SrX2
    log_k   0.91     # Appelo & Postma 1993
    -gamma  5.26  0.121
SOLUTION 1 Na-Cl # Nagra 1997b Beilage A3.7-5b
    pe   -3.0  # set some initial reducing pe
    temp 25.0
    -units   mmol/kgw
    pH 7.0
    Cl 500.0
    Na 500.0    charge # initial Na-Cl-(SO4-HCO3) water
    S  0.4
    C  5.0   CO2(g) -2.0  # final log(PCO2)=-2.14, pH=7.156
EXCHANGE 1 B&B94 # Baeyens&Bradbury NTB 94-22, data set A, p.22
    NaX       41.6
    KX        4.6
    MgX2      1.7
    CaX2      4.95
    SrX2      0.45
EQUILIBRIUM_PHASES 1
    calcite       0.0
    siderite      0.0
    pyrite        0.0
    quartz        0.0
END
```

Tab. 6-3:   High-Na-Cl variant of referenc porewater for Palfris Formation and Vitznau
            Mergel.

Parameter	Na-Cl Reference	**High-Na-Cl**	Units
Temperature	25	25	ºC
pH	7.467	7.156	
Ionic strength	0.211	0.521	molal
pε (25 ºC)	-3.418	-2.995	
P_{CO2}	$10^{-2.10}$	$10^{-2.14}$	bar
HCO_3^-	4.740	2.092	mmol/kg$_{H2O}$
C^{IV} (total)	5.413	2.794	mmol/kg$_{H2O}$
Cl (total)	202	500	mmol/kg$_{H2O}$
S^{VI} (total)	0.2	0.4	mmol/kg$_{H2O}$
S^{-II} (total)	$51.7 \cdot 10^{-9}$	$22.5 \cdot 10^{-9}$	mmol/kg$_{H2O}$
Na (total)	197.7	460.6	mmol/kg$_{H2O}$
K (total)	2.338	5.155	mmol/kg$_{H2O}$
Ca (total)	2.273	11.15	mmol/kg$_{H2O}$
Mg (total)	1.320	6.843	mmol/kg$_{H2O}$
Sr (total)	0.162	0.780	mmol/kg$_{H2O}$
Si (total)	0.178	0.174	mmol/kg$_{H2O}$
Fe^{II} (total)	0.0110	0.0546	mmol/kg$_{H2O}$
Fe^{III} (total)	$0.918 \cdot 10^{-9}$	$1.637 \cdot 10^{-9}$	mmol/kg$_{H2O}$
SO_4/Cl	0.001	0.0008	mol/mol
Ca/Mg	1.72	1.63	mol/mol
SI (dolomite)	-0.10	-0.08	
SI (gypsum)	-2.94	-2.17	
SI (celestite)	-2.04	-1.26	
SI (strontianite)	-0.36	-0.36	
Cl-porosity	0.009 / 30%	0.009 / 30%	Abs./proportion

Calculations performed with Phreeqc (version 2.15.07) and Nagra-PSI data base Version 01/01. All pore
water compositions are at equilibrium with respect to calcite, siderite, quartz and pyrite. Cl-porosity:
absolute value and proportion of total accessible porosity, based on Nagra (1997a) and Mazurek (in
prep.).

In analogy to the treatment of the normal-salinity pore waters, also a range in pH / P_{CO2} and a
variant at lower pε with appreciable methane could be generated for the high-Na-Cl version of
the reference pore water. It will depend on the sensitivity of resultant sorption parameters or
solubility limits to the uncertainties in pH / P_{CO2} or pε if such an additional variant needs to be
specified.

6.4   Discussion and uncertainties

The stack of marl that is containing an Na-Cl pore water is quite thick and likely extends upwards into the groundwater mixing zone defined in Nagra (1997a) where Na-HCO$_3$ and Na-HCO$_3$-Cl-type waters were sampled from fractures.

The reference pore water suggested in Table 6.2 has the same salinity as that of the Nagra (1997b) groundwater, but here a higher pH and lower P$_{CO2}$ was thought to be more appropriate. Compositions for low-pH-high-P$_{CO2}$ and high-pH-low-P$_{CO2}$ variants are provided to cover some reasonable range of uncertainty. The "base-case" reference pore water is less reducing than that proposed by Nagra (1997b) but it is similar to that of the Na-HCO$_3$ reference groundwater of Nagra, namely with more abundant sulphate than sulphide. The low-pε variant accounts for a more reduced state with sulphide dominant and a large partial pressure for methane, but it reduces iron to trace concentrations when assuming pyrite saturation. This variant is similar to the reference pore water of Nagra (1997b) in terms of pH, redox, and alkalinity, such that arguments put forward on the basis of this pore water remain valid within the range of pore water composition considered in this report.

The high-Na-Cl pore water is a more saline variant (Table 6-3) to cover the range of uncertainty with respect to the presently not well constrained salinity which is mostly rooted in difficulties interpreting the Hg-injection porosity measurements and uncertainty related to the extent of the anion exclusion effect that controls the chloride-accessible porosity proportion. A simple way to gauge the uncertainty is to assume an average water content from Lippmann et al. (1998) for porosity (avoiding Hg-injection data) that is quite well constrained, and an average Cl-content per gram of rock derived from aqueous leaching studies (Baeyens and Bradbury 1994, Mazurek at al. 1994, Hobbs and Waber 2010) that show large ranges but the means are constrained by many samples. One can then combine this average porosity and chloride content with an estimate of the chloride-accessible porosity proportion of 30% suggested by Pearson (1999), and arrive at different averaged chloride concentrations for pore water. This ignores large expected sample-to-sample variations in porosity, but may provide some rough bounds on this issue.

The scatter of the water content data of Lippmann et al. (1998) is limited and averages 1.0-1.3 wt%, corresponding to a porosity range of 2.5-3.3%, here interpreted as accessible transport porosity. Their data is from borehole SB4a/s (Figure 6-1) from a depth range of 215-860 m that also extends into the Na-Cl core region, but that also contains a section of marls of Tertiary age from the Drusberg nappe (Figure 5-1). So, clearly, there is some uncertainty in combining this data set with leaching data from borehole SB1. The Cl-content measured by Baeyens and Bradbury (1994) is 0.7 mmol/kg$_{rock}$, that of Mazurek et al. (1994) average 0.25 mmol/kg$_{rock}$ (10 samples) and that of Hobbs and Waber (2010) average 0.35 mmol/kg$_{rock}$ (14 samples), for a depth interval of 230-730 m along borehole SB1. This depth range corresponds to a "core region" that is loosely characterized by generally elevated chloride contents compared to the sections above and below. It is interesting that the sample of Baeyens and Bradbury (536 m, SB1) has a Cl content that is more than twice that of the average of Mazurek et al. (1994) and that is larger than all but one of all measured samples (range: 0.14 to 0.68 mmol/kg$_{rock}$) for the quoted depth range. The chloride concentration in the pore water (Cl$_{pw}$, [mmol/kg$_{H2O}$]) can be calculated from the chloride-accessible porosity (n$_{Cl}$, [volume fraction]), the bulk density (ρ_{bulk}, [g/cm^3]) and the chloride concentration in the (dry) rock (Cl$_{rock}$, [mmol/kg$_{rock}$]) according to (e.g., Pearson et al. 2003, Annex 10):

$$Cl_{pw} = Cl_{rock}\, \rho_{bulk} / n_{Cl}$$

Table 6-4 summarizes the averaged data and the resultant pore water chloride concentrations. Note that this is only a rough estimate that ignores sample-to-sample variations in accessible porosity.

Tab. 6-4:   Estimated Cl concentration in pore water based on averaged data from different sample series.

Parameter Data set	Porosity (WC)	Porosity (Cl-accessible)	Cl_{rock} (aq. leaching)	Cl_{pw} (tot. poros.)	Cl_{pw} (Cl-poros.)
Units	fraction	Fraction	$mmol/kg_{rock}$	$mmol/kg_{H2O}$	$mmol/kg_{H2O}$
B&B'94	0.03	0.009	0.7	63	209
H&W'10	0.03	0.009	0.35	31	105
Maz'94	0.03	0.009	0.25	22	75

A bulk density of 2.69 g/cm^3 is assumed (Mazurek, in prep.). WC: average water content based on Lippmann et al. (1998), borehole SB4a/s, 215-860 m, 12 samples. Cl-accessible: 30% of water-content porosity (Pearson 1999). All data from borehole SB1. B&B'94: Baeyens and Bradbury (1994), 536m, 1 sample; Maz'94: Mazurek et al. (1994), 230-710 m, 15 samples; H&W'10: Hobbs and Waber (2010), 230-710 m, 10 samples.

The 200 $mmol/kg_{H2O}$ chloride concentration assumed for the reference Na-Cl pore water of Nagra (1997b, Table 6-1) and this work (Table 6-2) is reconciled by the leaching data of Baeyens and Bradbury (1994) and a chloride-accessible porosity of 0.9% (absolute) that is compatible with the average water content of samples measured by Lippmann et al. (1998) and an accessible porosity fraction of 30% for chloride according to Pearson (1999). This chloride composition is also equal to that measured in the best-constrained groundwater sample from the Na-Cl zone. This is not surprising, because this type of analysis led Pearson to his estimate of the anion exclusion effect for Wellenberg marls. It is difficult to identify the hen and egg in this line of arguments. The average total accessible porosity of 3 % is compatible with the average total mercury injection porosity for marly samples of the Palfris Formation (2.9 %, Mazurek in prep.), assuming that the samples studied were biased towards marly lithologies rather than limestone beds. If average porosities were smaller, the calculated chlorinities would be scaled accordingly, e.g., doubled for an average accessible total porosity of 1.5 % (Cl-accessible porosity of 0.45 %).

Baeyens and Bradbury (1994) calculate chloride concentrations of 107-116 $mmol/kg_{H2O}$ at pH 7.5 and an assumed P_{CO2} of 10^{-2} bar. This concentration is derived by the calculated cation concentrations constrained by the composition of the clay exchanger, calcite-dolomite equilibrium and a prescribed P_{CO2}. The associated chloride-accessible porosity would be ca. 1.5% based on their leached chloride content of 0.7 $mmol/kg_{rock}$. Their model is quite sensitive to pH (or assumed P_{CO2}) because it is linked to the fixed measured cation occupancy on the clay exchanger. A change in pH (or P_{CO2}) induces a change in Ca and Mg concentration (constrained by calcite-dolomite equilibrium) and thus shifts the Na content calculated from the selectivity coefficients, and hence, also total cation charge to be balanced by chloride.

The chloride contents in the leaching data of Mazurek et al. (1994) and Hobbs and Waber (2010) for the depth interval of the Na-Cl core region (ca. 230-710m) are distinctly lower and would suggest pore water chloride concentrations of 75 and 105 $mmol/kg_{H2O}$, respectively,

assuming the same porosity and anion-exclusion effect. These values would be more in line with the calculations of Baeyens and Bradbury (1994) but would be smaller than the best constrained water sample from the Na-Cl zone. For comparison, the total open porosity measured by Hg-injection (Mazurek et al. 1994) ranges from 0.7-3.6% with an average near 2.3% that is a bit smaller than the average water content porosity of Lippmann et al. (1998), but it is close to the average for marly samples (Mazurek, in prep.). Assuming this smaller porosity of 2.3% but the same anion-exclusion effect would yield chloride concentrations that are correspondingly higher. The data of Mazurek et al. (1994) and Hobbs and Waber (2010) hint at a curved profile with higher concentrations in the centre (Hobbs and Waber 2010), and so the apparent discrepancy stated above may be locally smaller.

The combined uncertainties on the average water-content data and the anion accessible porosity (30%±10% of total porosity, Pearson 1999) is likely a factor of two. It appears therefore that the adopted value of 200 mmol/kg$_{H2O}$ of chloride is permissible by the combined data sets, but that there is not much room for distinctly higher concentrations. The value of 500 mmol/kg$_{H2O}$ adopted for the high-Na-Cl variant (Table 6-3) is likely outside this uncertainty range, but it is an upper limit that corresponds to reported maximum NaCl equivalent salinities observed in fluid inclusions (Diamond and Marshall 1994), and is also close to the upper range stated in Nagra (1997b). The fluid inclusion data constrain the maximum concentration that the pore fluid in the rocks of the Palfris-Formation ever had during its evolution.

There is a possibility that the Na-Cl core region at the Wellenberg site is not as homogeneous as depicted here or generally implied by the available reports. Pearson and Scholtis (1994) comment on suspected heterogeneities within the Na-Cl zone. Generally, the very old age or residence time for the fracture water and pore water are thought to imply also the absence of salinity gradients other than at formation scale. It should be kept in mind that the history is very complex, with peak metamorphic conditions dating as far back as 20 Ma, and ongoing ductile deformation to ca. 5 Ma (Nagra 1997a, Mazurek 1999). Evidence for boiling conditions was found in fluid inclusions from the latest generations of vein calcite (Mazurek 1999, Diamond and Marshall 1994, Mazurek at al. 1994). It is therefore possible that heterogeneities in salinity could have been generated up to less than 5 Ma ago. Lippmann et al. (1998) interpret their measured He isotope profile in terms of He-loss with a simple advective-diffusive block model. They constrain block sizes of 90-270 m in the Na-Cl region, and minimum residence times of ca. 1 Ma in the pore water.

The field data from the Wellenberg boreholes are presently not tightly constraining the issue of anion-accessible porosity. The porosities are also not constrained well enough to demonstrate clearly the presence or absence of a salinity profile at Wellenberg across the low-permeability central portion where Na-Cl-type old pore waters are present. Some curvature with higher salinity in the centre was recently suggested by Hobbs and Waber (2010) based on previously unpublished data and some re-interpretation. The composition of cations in the Na-Cl pore water is presently only constrained by the measured cation occupancies on one sample by Baeyens and Bradbury (1994) and the extrapolated concentrations measured in one borehole interval. The redox system is not directly constrained in the Na-Cl water, and there is a discrepancy between the presence of relatively abundant methane and sulphate in water samples, as well as the presence of Fe-bearing carbonates in equilibrium with pyrite that would not allow for such methane-rich reducing conditions within the thermodynamic stability field of graphite (in reality, reduced solid carbon is present in some form of kerogen). It is possible that long-lived metastable states are preserved in the HCO_3-CH_4 and/or SO_4/H_2S redox subsystems, and therefore a thermodynamic equilibrium approach may have its limitations. Such issues, and the general fluid evolution through metamorphism with sulphate reduction and methanogenesis

would deserve some attention for a better understanding also of today's pore water present in the Na-Cl zone at Wellenberg.

The field and sampling techniques that were developed or advanced more recently for the Opalinus Clay Project would provide a significant improvement of the quality and interpretability of the analytical data compared to the state-of-the-art during the Wellenberg Project. Most of the above addressed uncertainties and apparent inconsistencies could be resolved with today's techniques.

7   Acknowledgements

8   References cited

Appelo, C.A.J., and Postma, D. (1993): Geochemistry, Groundwater and Pollution. Leiden, The Netherlands, A.A. Balkema, 536 p.

Appelo, C.A.J., and Postma, D. (2005): Geochemistry, Groundwater and Pollution, 2nd Edition. Leiden, The Netherlands, A.A. Balkema, 649 p.

Bradbury, M.H., Baeyens, B. and Alexander, W.R. (1990): Experimental proposals for procedures to investigate the water chemistry, sorption and transport properties of marl. Nagra Technical Report NTB 90-16, Nagra, Switzerland.

Baeyens, B. and Bradbury, M.H. (1991): A physico-chemical characterisation technique for determining the porewater chemistry in argillaceous rocks. Nagra Technical Report NTB 90-40, Nagra, Switzerland.

Baeyens, B. and Bradbury, M.H. (1994): Physico-chemical characterisation and calculated in situ porewater chemistries for a low permeability Palfris marl sample from Wellenberg. Nagra Technical Report NTB 94-22, Nagra, Switzerland.

Bradbury, M.H., Baeyens B. and Thoenen T. (2008): Sorption data bases for generic Swiss argillaceous, crystalline and calcareous rock systems. Nagra Working Report, Nagra, Wettingen, Switzerland.

Coudrain-Ribstein, A., and Gouze, P. (1993): Quantitative study of geochemical processes in the Dogger aquifer, Paris Basin, France. Applied Geochemistry, 8, 495-506.

Diamond, L.W. and Marshall, D.D. (1994): WLB: Fluid inclusions in vein samples from boreholes at Wellenberg, Switzerland. Unpublished Nagra Internal Report. Nagra, Wettingen, Switzerland.

Diamond, L.W. (1998): Underpressured paleofluids in a planned radwaste host rock. In: G.B. Arehart and J.R. Hulston (eds.), Proceedings of the 9th International Symposium on Water-Rock Interaction, WRI-9, Taupo, New Zealand. Balkema, Rotterdam, 669-772.

Gaucher, E.C., Tournassat, C., Pearson, F.J., Blanc, P., Crouzet, C., Lerouge, C., and Altmann, S. (2009): A robust model for pore-water chemistry of clayrock. Geochimica et Cosmochimica Acta, 73, 6470-6487.

Hobbs, M.Y., Waber, H.N. and Frape, S.K. (2002): Cl-isotope signatures of groundwaters, pore waters and calcite fluid inclusions: constraints on fluid origin and transport in a marl sequence. Abstract volume, GSA Annual Meeting, 2002, Denver, Colorado.

Hobbs, M.Y. and Waber, H.N. (2010): Chlorine and chlorine isotope signatures in groundwater, porewater and calcite veins from Wellenberg, Switzerland. RWI Technical Report, Institute for Geological Sciences, University of Bern, Switzerland

Hummel, W.H., Berner, U., Curti, E., Pearson, F.J., and Thoenen, T. (2002): Nagra/PSI Thermochemical Databes 01/01. Nagra Technical Report NTB 02-16, Nagra, Wettingen, Switzerland. Also issued by Universal Publishers, Parkland (FL), USA.

Lippmann, J., Osenbrück, K., Rübel, A., Sonntag, C., Lehmann, B., Purtschert, H., Loosli, H. and Tolstikhin, I. (1998): WLB: Stabile Isotope und Edelgasgehalte von Porenwässern und Gesteinen aus Bohrkernen der SB4a/s am Wellenberg. Unpublished Nagra Internal Report. Nagra, Wettingen, Schweiz.

Mäder, U. (2009): Reference pore water for the Opalinus Clay and "Brown Dogger" for the provisional safety analysis in the framework of sectoral plan – interim results (SGT-ZE). Nagra Working Report. Nagra, Wettingen, Switzerland.

Mazurek, M. and Bläsi, H.R. (1992): WLB: Sondierbohrung SB4, Geologische und mineralogische Laboranalysen. Unpublished Nagra Internal Report. Nagra, Wettingen, Schweiz.

Mazurek, M., Waber, N. and Bläsi, H.R. (1994): WLB: Geology, mineralogy and geochemistry of the Wellenberg. Unpublished Nagra Internal Report. Nagra, Wettingen, Switzerland.

Mazurek, M. (1999): Evolution of gas and aqueous fluid in low-permeability shales during uplift and exhumation of the central Swiss Alps. Applied Geochemistry 15, 223-246.

Mazurek, M. (in prep.): Referenzmineralogie der Wirtgesteine. Nagra Arbeitsbericht, Nagra, Wettingen, Schweiz.

Mullis, J. (1997): WLB: Fluideinschluss-Untersuchungen in Ankerit, Calcit und Quarz der Sondierbohrung SB4. Unpublished Nagra Internal Report. Nagra, Wettingen, Switzerland.

Nagra (2002): Projekt Opalinuston: Synthese der geowissenschaftlichen Untersuchungsergebnisse; Entsorgungsnachweis für abgebrannte Brennelemente, verglaste hochaktive sowie langlebige mittelaktive Abfälle. Nagra Technical Report NTB 02-03, Switzerland.

Nagra (1993): Untersuchungen zur Standorteignung im Hinblick auf die Endlagerung schwach- und mittelaktiver Abfälle – Geologische Grundlagen und Datensatz zur Beurteilung der Langzeitsicherheit des Endlagers für schwach- und mittelaktive Abfälle am Standort Wellenberg (Gemeinde Wolfenschiessen, NW). Nagra Technical Report NTB 93-28, Nagra, Wettingen, Switzerland.

Nagra (1997a): Geosynthese Wellenberg 1996, Ergebnisse der Untersuchungsphasen I und II. Textband. Nagra Technical Report NTB 96-01, Nagra, Switzerland.

Nagra (1997b): Geosynthese Wellenberg 1996, Ergebnisse der Untersuchungsphasen I und II. Beilageband. Nagra Technical Report NTB 96-01, Nagra, Switzerland.

Nagra (2008): Vorschlag geologischer Standortgebiete für das SMA und HAA-Lager. Geologische Grundlagen. Nagra Technical Report NTB 08-04, Switzerland.

Parkhurst, D.L. and Appelo, C.A.J. (1999): User's guide to PHREEQC, a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: – U.S. Geol. Surv. Water-Resources Invest. Rep.: 99-4259 (v.2.15; 2008).

Pearson, F.J. (1994): WLB: Quality of groundwater samples from Wellenberg; Estimation of contamination by drilling fluid using tracers and stable and radioactive isotopes. Unpublished Nagra Internal Report. Nagra, Wettingen, Switzerland.

Pearson, F.J., Mazurek, M., and Waber, H.N. (1994): WLB: Geochemical properties of the Palfris Formation at Wellenberg and their use in modelling pore water compositions. Unpublished Nagra Internal Report, Nagra, Wettingen, Switzerland.

Pearson, F.J. and Scholtis, A. (1995): Controls on the chemistry of pore water in a marl of very low permeability. In: Y.K. Kharaka and O.V. Chudaev (eds), Proceedings of the 8th International Symposium on Water-Rock Interaction, WRI-8, Vladisvostok, Russia. Balkema, 35-38.

Pearson, F.J. (1996): Ruminations on porosity and salinity in WLB marl. Unpublished PSI AN-44-96-05, Paul Scherrer Institut.

Pearson, F.J. (1998): Geochemical and other porosity types in clay-rich rocks. In: G.B. Arehart and J.R. Hulston (eds.), Proceedings of the 9th International Symposium on Water-Rock Interaction, WRI-9, Taupo, New Zealand. A.A. Balkema, Rotterdam, 259-262.

Pearson, F.J., Waber, H.N., and Scholtis, A. (1998): Modelling the chemical evolution of porewater in the Palfris Marl, Wellenberg, Central Switzerland, *in* McKinley, Ian G., and McCombie, Charles, editors, Scientific Basis for Nuclear Waste Management XXI, Davos, Switzerland, Warrendale, PA, Materials Research Society, Materials Research Society Symposium Proceedings 506, 789-796.

Pearson, F.J. (1999): What is the porosity of a mudrock? In: A. Aplin, A.J. Fleet and J.H.S. Macquaker (eds), Muds and mudstones: physical and fluid flow properties. Geological Society of London, Special Publications, 158, 9-21.

Pearson, F.J., Arcos D., Bath, A., Boisson, J.Y., Fernandez, A.M., Gaebler, H.E., Gaucher, E.C., Gautschi, A., Griffault, L., Hernan, P. & Waber, H.N. (2003): Mont Terri Project – Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. Reports of the Federal Office of Water and Geology (FOWG), Geology Series No. 5.

Scholtis, A. (1992): WLB: Reference Waters NaHCO3-Type and NaCl-Type. Unpublished Nagra Internal Report, Nagra, Wettingen, Switzerland.

Vinard, P., Blümling, P., McCord, J.P. and Aristorenas, G. (1993): Evaluation of hydraulic underpressures at Wellenberg, Switzerland. International Journal of Rock Mechanics and Sciences and Geomechanics, 30, 1143-1150.

Vinard, P., Bobet, A. and Einstein, H.H. (2001): Generation and evolution of hydraulic underpressures at Wellenberg, Switzerland. Journal of Geophysical research, 106, 30593-30605.

Waber, H.N., Pearson, F.J., Eichinger, L. and Scholtis, A. (1998): WLB: Reference compositions of the groundwater types and geochemical modelling of groundwater evolution at Wellenberg. Unpublished Nagra Internal Report. Nagra, Wettingen, Switzerland.

Waber, H.N. and Smellie, J.A.T. (2008): Characterisation of pore water in crystalline rocks. Applied Geochemistry, 23, 1834-1861.

Wersin, P., Gaucher, E., Gimmi, Th., Leupin, O., Mäder, U., Pearson, F.J., Thoenen, T. and Tournassat, Ch. (2009): Geochemistry of pore waters in Opalinus Clay at Mont Terri: experimental data and modelling. Mont Terri Project, Technical Report 2008-06.

Appendix 1 – Reference pore water (Helvetic marls)

Listing of part of the Phreeqc output file giving a full description of the solution, aqueous speciation and mineral saturation indices. Select values are given in Table 6-2 (column "Base-case").

```
--------------------------Description of solution--------------------------

                                    pH   =   7.467     Charge balance
                                    pe   =  -3.418     Adjusted to redox equilibrium
                      Activity of water  =   0.993
                          Ionic strength =   2.110e-01
                      Mass of water (kg) =   1.000e+00
                 Total alkalinity (eq/kg) =   5.184e-03
                    Total CO2 (mol/kg) =   5.413e-03
                   Temperature (deg C) =  25.000
                 Electrical balance (eq) =  -2.734e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|) =  -0.00
                             Iterations =  13
                                Total H = 1.110229e+02
                                Total O = 5.552601e+01

--------------------------Distribution of species--------------------------

                                           Log      Log      Log
   Species          Molality    Activity  Molality Activity  Gamma

   OH-              3.915e-07   2.916e-07   -6.407   -6.535   -0.128
   H+               4.579e-08   3.410e-08   -7.339   -7.467   -0.128
   H2O              5.551e+01   9.930e-01    1.744   -0.003    0.000
C(-4)        3.505e-15
   CH4              3.505e-15   3.505e-15  -14.455  -14.455    0.000
C(4)         5.413e-03
   HCO3-            4.740e-03   3.529e-03   -2.324   -2.452   -0.128
   NaHCO3           2.917e-04   2.917e-04   -3.535   -3.535    0.000
   CO2              2.725e-04   2.725e-04   -3.565   -3.565    0.000
   CaHCO3+          4.126e-05   3.072e-05   -4.384   -4.513   -0.128
   MgHCO3+          2.203e-05   1.641e-05   -4.657   -4.785   -0.128
   NaCO3-           1.783e-05   1.328e-05   -4.749   -4.877   -0.128
   CO3-2            1.579e-05   4.853e-06   -4.802   -5.314   -0.512
   CaCO3            5.549e-06   5.549e-06   -5.256   -5.256    0.000
   SrHCO3+          3.511e-06   2.614e-06   -5.455   -5.583   -0.128
   MgCO3            1.840e-06   1.840e-06   -5.735   -5.735    0.000
   FeHCO3+          1.258e-06   9.366e-07   -5.900   -6.028   -0.128
   FeCO3            3.089e-07   3.089e-07   -6.510   -6.510    0.000
   SrCO3            1.500e-07   1.500e-07   -6.824   -6.824    0.000
Ca           2.273e-03
   Ca+2             2.220e-03   6.824e-04   -2.654   -3.166   -0.512
   CaHCO3+          4.126e-05   3.072e-05   -4.384   -4.513   -0.128
   CaSO4            6.055e-06   6.055e-06   -5.218   -5.218    0.000
   CaCO3            5.549e-06   5.549e-06   -5.256   -5.256    0.000
   CaSiO(OH)3+      1.168e-08   8.694e-09   -7.933   -8.061   -0.128
   CaOH+            4.429e-09   3.298e-09   -8.354   -8.482   -0.128
   CaSiO2(OH)2      2.996e-11   2.996e-11  -10.524  -10.524    0.000
Cl           2.020e-01
   Cl-              2.020e-01   1.504e-01   -0.695   -0.823   -0.128
   FeCl+            7.400e-07   5.510e-07   -6.131   -6.259   -0.128
   FeCl+2           1.430e-21   4.397e-22  -20.845  -21.357   -0.512
   FeCl2+           3.967e-22   2.954e-22  -21.401  -21.530   -0.128
   FeCl3            4.444e-24   4.444e-24  -23.352  -23.352    0.000
Fe(2)        1.099e-05
   Fe+2             8.632e-06   2.654e-06   -5.064   -5.576   -0.512
   FeHCO3+          1.258e-06   9.366e-07   -5.900   -6.028   -0.128
   FeCl+            7.400e-07   5.510e-07   -6.131   -6.259   -0.128
   FeCO3            3.089e-07   3.089e-07   -6.510   -6.510    0.000
   FeOH+            3.282e-08   2.444e-08   -7.484   -7.612   -0.128
   FeSO4            2.098e-08   2.098e-08   -7.678   -7.678    0.000
   FeHSO4+          6.320e-15   4.706e-15  -14.199  -14.327   -0.128
```

```
Fe(3)             9.177e-13
   Fe(OH)3              6.584e-13   6.584e-13   -12.181   -12.181    0.000
   Fe(OH)2+             2.357e-13   1.755e-13   -12.628   -12.756   -0.128
   Fe(OH)4-             2.348e-14   1.749e-14   -13.629   -13.757   -0.128
   FeOH+2               5.920e-17   1.820e-17   -16.228   -16.740   -0.512
   FeSiO(OH)3+2         1.269e-18   3.900e-19   -17.897   -18.409   -0.512
   FeCl+2               1.430e-21   4.397e-22   -20.845   -21.357   -0.512
   Fe+3                 1.375e-21   9.680e-23   -20.862   -22.014   -1.153
   FeCl2+               3.967e-22   2.954e-22   -21.401   -21.530   -0.128
   FeSO4+               6.338e-23   4.719e-23   -22.198   -22.326   -0.128
   FeCl3                4.444e-24   4.444e-24   -23.352   -23.352    0.000
   Fe(SO4)2-            6.166e-26   4.591e-26   -25.210   -25.338   -0.128
   FeHSO4+2             1.402e-29   4.312e-30   -28.853   -29.365   -0.512
   Fe2(OH)2+4           9.982e-31   8.916e-33   -30.001   -32.050   -2.049
   Fe3(OH)4+5           5.201e-40   0.000e+00   -39.284   -42.486   -3.202
H(0)              1.250e-11
   H2                   6.251e-12   6.251e-12   -11.204   -11.204    0.000
K                 2.338e-03
   K+                   2.338e-03   1.741e-03    -2.631    -2.759   -0.128
   KSO4-                7.359e-07   5.479e-07    -6.133    -6.261   -0.128
   KOH                  1.758e-10   1.758e-10    -9.755    -9.755    0.000
Mg                1.320e-03
   Mg+2                 1.292e-03   3.973e-04    -2.889    -3.401   -0.512
   MgHCO3+              2.203e-05   1.641e-05    -4.657    -4.785   -0.128
   MgSO4                4.141e-06   4.141e-06    -5.383    -5.383    0.000
   MgCO3                1.840e-06   1.840e-06    -5.735    -5.735    0.000
   MgOH+                5.641e-08   4.201e-08    -7.249    -7.377   -0.128
   MgSiO(OH)3+          1.356e-08   1.010e-08    -7.868    -7.996   -0.128
   MgSiO2(OH)2          2.195e-10   2.195e-10    -9.658    -9.658    0.000
Na                1.977e-01
   Na+                  1.974e-01   1.470e-01    -0.705    -0.833   -0.128
   NaHCO3               2.917e-04   2.917e-04    -3.535    -3.535    0.000
   NaSO4-               4.398e-05   3.275e-05    -4.357    -4.485   -0.128
   NaCO3-               1.783e-05   1.328e-05    -4.749    -4.877   -0.128
   NaOH                 2.828e-08   2.828e-08    -7.549    -7.549    0.000
O(0)              0.000e+00
   O2                   0.000e+00   0.000e+00   -69.795   -69.795    0.000
S(-2)             5.166e-11
   HS-                  4.139e-11   3.082e-11   -10.383   -10.511   -0.128
   H2S                  1.027e-11   1.027e-11   -10.988   -10.988    0.000
   S-2                  2.940e-22   9.038e-23   -21.532   -22.044   -0.512
S(2)              6.463e-18
   S2O3-2               3.231e-18   9.934e-19   -17.491   -18.003   -0.512
S(4)              5.736e-16
   SO3-2                4.650e-16   1.429e-16   -15.333   -15.845   -0.512
   HSO3-                1.087e-16   8.092e-17   -15.964   -16.092   -0.128
S(6)              2.000e-04
   SO4-2                1.446e-04   4.447e-05    -3.840    -4.352   -0.512
   NaSO4-               4.398e-05   3.275e-05    -4.357    -4.485   -0.128
   CaSO4                6.055e-06   6.055e-06    -5.218    -5.218    0.000
   MgSO4                4.141e-06   4.141e-06    -5.383    -5.383    0.000
   KSO4-                7.359e-07   5.479e-07    -6.133    -6.261   -0.128
   SrSO4                4.198e-07   4.198e-07    -6.377    -6.377    0.000
   FeSO4                2.098e-08   2.098e-08    -7.678    -7.678    0.000
   HSO4-                1.980e-10   1.474e-10    -9.703    -9.831   -0.128
   FeHSO4+              6.320e-15   4.706e-15   -14.199   -14.327   -0.128
   FeSO4+               6.338e-23   4.719e-23   -22.198   -22.326   -0.128
   Fe(SO4)2-            6.166e-26   4.591e-26   -25.210   -25.338   -0.128
   FeHSO4+2             1.402e-29   4.312e-30   -28.853   -29.365   -0.512
Si                1.781e-04
   Si(OH)4              1.770e-04   1.770e-04    -3.752    -3.752    0.000
   SiO(OH)3-            1.080e-06   8.038e-07    -5.967    -6.095   -0.128
   MgSiO(OH)3+          1.356e-08   1.010e-08    -7.868    -7.996   -0.128
   CaSiO(OH)3+          1.168e-08   8.694e-09    -7.933    -8.061   -0.128
   MgSiO2(OH)2          2.195e-10   2.195e-10    -9.658    -9.658    0.000
   CaSiO2(OH)2          2.996e-11   2.996e-11   -10.524   -10.524    0.000
   SiO2(OH)2-2          3.587e-12   1.103e-12   -11.445   -11.958   -0.512
   FeSiO(OH)3+2         1.269e-18   3.900e-19   -17.897   -18.409   -0.512
Sr                1.616e-04
   Sr+2                 1.575e-04   4.842e-05    -3.803    -4.315   -0.512
   SrHCO3+              3.511e-06   2.614e-06    -5.455    -5.583   -0.128
   SrSO4                4.198e-07   4.198e-07    -6.377    -6.377    0.000
   SrCO3                1.500e-07   1.500e-07    -6.824    -6.824    0.000
```

```
        SrOH+                    9.712e-11   7.232e-11   -10.013   -10.141    -0.128

----------------------------Saturation indices----------------------------

            Phase            SI  log IAP   log KT

            Anhydrite      -3.16   -7.52   -4.36  CaSO4
            Aragonite      -0.14    1.85    1.99  CaCO3
            Brucite        -5.31   11.53   16.84  Mg(OH)2
            Calcite         0.00    1.85    1.85  CaCO3
            Celestite      -2.04   -8.67   -6.63  SrSO4
            CH4(g)        -11.60  -14.46   -2.86  CH4
            CO2(g)         -2.10   -9.92   -7.82  CO2
            Dolomite(dis)  -0.65    3.46    4.12  CaMg(CO3)2
            Dolomite(ord)  -0.10    3.46    3.57  CaMg(CO3)2
            Fe(cr)        -12.56    1.26   13.82  Fe
            Fe(OH)3(am)    -4.62    0.38    5.00  Fe(OH)3
            Fe(OH)3(mic)   -2.62    0.38    3.00  Fe(OH)3
            FeCO3(pr)      -0.44   -0.56   -0.12  FeCO3
            Goethite        1.38    0.38   -1.00  FeOOH
            Graphite       -4.29  -26.11  -21.82  C
            Gypsum         -2.94   -7.52   -4.58  CaSO4:2H2O
            H2(g)          -8.10  -11.20   -3.11  H2
            H2S(g)         -9.97  -17.98   -8.01  H2S
            Hematite       -0.35    0.77    1.12  Fe2O3
            Magnesite      -0.43    1.61    2.04  MgCO3
            Magnetite       0.10   10.12   10.02  Fe3O4
            Melanterite    -7.74   -9.95   -2.21  FeSO4:7H2O
            O2(g)         -66.90  -69.80   -2.89  O2
            Portlandite   -11.04   11.76   22.80  Ca(OH)2
            Pyrite          0.00  -18.50  -18.50  FeS2
            Quartz          0.00   -3.75   -3.75  SiO2
            S(rhomb)       -7.74   -9.88   -2.14  S
            Siderite        0.00   -0.56   -0.56  FeCO3
            SiO2(am)       -1.03   -3.75   -2.71  SiO2
            Strontianite   -0.36    0.70    1.06  SrCO3
            Troilite       -3.31   -8.62   -5.31  FeS
```

Appendix 2 – High-P$_{CO2}$ / low-pH variant (Helvetic marls)

Listing of part of the Phreeqc output file giving a full description of the solution, aqueous speciation and mineral saturation indices. Select values are given in Table 6-2 (column "High-P$_{CO2}$").

```
--------------------------Description of solution--------------------------
                                   pH  =   7.012    Charge balance
                                   pe  =  -2.897    Adjusted to redox equilibrium
                   Activity of water  =   0.993
                      Ionic strength  =   2.192e-01
                  Mass of water (kg)  =   1.000e+00
             Total alkalinity (eq/kg) =   1.381e-02
               Total CO2 (mol/kg)     =   1.586e-02
               Temperature (deg C)    =  25.000
             Electrical balance (eq)  =  -4.380e-12
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                          Iterations  =  12
                             Total H  = 1.110322e+02
                             Total O  = 5.555587e+01

--------------------------Distribution of species--------------------------

                                              Log       Log       Log
     Species          Molality    Activity  Molality  Activity   Gamma

     OH-             1.374e-07   1.021e-07   -6.862    -6.991    -0.129
     H+              1.309e-07   9.730e-08   -6.883    -7.012    -0.129
     H2O             5.551e+01   9.927e-01    1.744    -0.003     0.000
C(-4)         7.954e-15
     CH4             7.954e-15   7.954e-15  -14.099   -14.099     0.000
C(4)          1.586e-02
     HCO3-           1.273e-02   9.459e-03   -1.895    -2.024    -0.129
     CO2             2.085e-03   2.085e-03   -2.681    -2.681     0.000
     NaHCO3          8.087e-04   8.087e-04   -3.092    -3.092     0.000
     CaHCO3+         1.180e-04   8.767e-05   -3.928    -4.057    -0.129
     MgHCO3+         6.311e-05   4.690e-05   -4.200    -4.329    -0.129
     NaCO3-          1.736e-05   1.290e-05   -4.760    -4.889    -0.129
     CO3-2           1.494e-05   4.558e-06   -4.826    -5.341    -0.516
     SrHCO3+         1.004e-05   7.458e-06   -4.998    -5.127    -0.129
     CaCO3           5.549e-06   5.549e-06   -5.256    -5.256     0.000
     FeHCO3+         3.596e-06   2.673e-06   -5.444    -5.573    -0.129
     MgCO3           1.843e-06   1.843e-06   -5.734    -5.734     0.000
     FeCO3           3.089e-07   3.089e-07   -6.510    -6.510     0.000
     SrCO3           1.500e-07   1.500e-07   -6.824    -6.824     0.000
Ca            2.512e-03
     Ca+2            2.382e-03   7.266e-04   -2.623    -3.139    -0.516
     CaHCO3+         1.180e-04   8.767e-05   -3.928    -4.057    -0.129
     CaSO4           6.336e-06   6.336e-06   -5.198    -5.198     0.000
     CaCO3           5.549e-06   5.549e-06   -5.256    -5.256     0.000
     CaSiO(OH)3+     4.362e-09   3.242e-09   -8.360    -8.489    -0.129
     CaOH+           1.655e-09   1.230e-09   -8.781    -8.910    -0.129
     CaSiO2(OH)2     3.914e-12   3.914e-12  -11.407   -11.407     0.000
Cl            2.020e-01
     Cl-             2.020e-01   1.501e-01   -0.695    -0.824    -0.129
     FeCl+           7.878e-07   5.855e-07   -6.104    -6.232    -0.129
     FeCl+2          5.089e-21   1.552e-21  -20.293   -20.809    -0.516
     FeCl2+          1.400e-21   1.041e-21  -20.854   -20.983    -0.129
     FeCl3           1.562e-23   1.562e-23  -22.806   -22.806     0.000
Fe(2)         1.399e-05
     Fe+2            9.263e-06   2.825e-06   -5.033    -5.549    -0.516
     FeHCO3+         3.596e-06   2.673e-06   -5.444    -5.573    -0.129
     FeCl+           7.878e-07   5.855e-07   -6.104    -6.232    -0.129
     FeCO3           3.089e-07   3.089e-07   -6.510    -6.510     0.000
     FeSO4           2.196e-08   2.196e-08   -7.658    -7.658     0.000
     FeOH+           1.227e-08   9.116e-09   -7.911    -8.040    -0.129
     FeHSO4+         1.891e-14   1.405e-14  -13.723   -13.852    -0.129
```

```
Fe(3)              2.040e-13
    Fe(OH)2+            1.025e-13   7.619e-14   -12.989   -13.118   -0.129
    Fe(OH)3            1.001e-13   1.001e-13   -12.999   -12.999    0.000
    Fe(OH)4-           1.254e-15   9.317e-16   -14.902   -15.031   -0.129
    FeOH+2             7.394e-17   2.255e-17   -16.131   -16.647   -0.516
    FeSiO(OH)3+2       1.584e-18   4.831e-19   -17.800   -18.316   -0.516
    FeCl+2             5.089e-21   1.552e-21   -20.293   -20.809   -0.516
    Fe+3              4.952e-21   3.424e-22   -20.305   -21.466   -1.160
    FeCl2+             1.400e-21   1.041e-21   -20.854   -20.983   -0.129
    FeSO4+             2.208e-22   1.641e-22   -21.656   -21.785   -0.129
    FeCl3             1.562e-23   1.562e-23   -22.806   -22.806    0.000
    Fe(SO4)2-          2.111e-25   1.569e-25   -24.675   -24.804   -0.129
    FeHSO4+2           1.402e-28   4.277e-29   -27.853   -28.369   -0.516
    Fe2(OH)2+4         1.582e-30   1.369e-32   -29.801   -31.864   -2.063
    Fe3(OH)4+5         3.641e-40   0.000e+00   -39.439   -42.662   -3.223
H(0)               9.225e-12
    H2                4.613e-12   4.613e-12   -11.336   -11.336    0.000
K                  2.420e-03
    K+                2.419e-03   1.798e-03   -2.616    -2.745    -0.129
    KSO4-             7.486e-07   5.563e-07   -6.126    -6.255    -0.129
    KOH               6.360e-11   6.360e-11   -10.197   -10.197    0.000
Mg                 1.459e-03
    Mg+2              1.389e-03   4.237e-04   -2.857    -3.373    -0.516
    MgHCO3+            6.311e-05   4.690e-05   -4.200    -4.329    -0.129
    MgSO4             4.342e-06   4.342e-06   -5.362    -5.362     0.000
    MgCO3             1.843e-06   1.843e-06   -5.734    -5.734     0.000
    MgOH+             2.112e-08   1.570e-08   -7.675    -7.804    -0.129
    MgSiO(OH)3+        5.076e-09   3.772e-09   -8.294    -8.423    -0.129
    MgSiO2(OH)2        2.874e-11   2.874e-11   -10.542   -10.542    0.000
Na                 2.055e-01
    Na+               2.046e-01   1.520e-01   -0.689    -0.818    -0.129
    NaHCO3            8.087e-04   8.087e-04   -3.092    -3.092     0.000
    NaSO4-            4.482e-05   3.331e-05   -4.349    -4.477    -0.129
    NaCO3-            1.736e-05   1.290e-05   -4.760    -4.889    -0.129
    NaOH              1.025e-08   1.025e-08   -7.989    -7.989     0.000
O(0)               0.000e+00
    O2                0.000e+00   0.000e+00   -69.531   -69.531    0.000
S(-2)              5.892e-11
    HS-               3.452e-11   2.566e-11   -10.462   -10.591   -0.129
    H2S               2.440e-11   2.440e-11   -10.613   -10.613    0.000
    S-2               8.644e-23   2.637e-23   -22.063   -22.579   -0.516
S(2)               1.521e-17
    S2O3-2            7.607e-18   2.320e-18   -17.119   -17.634   -0.516
S(4)               5.654e-16
    SO3-2             3.400e-16   1.037e-16   -15.469   -15.984   -0.516
    HSO3-             2.254e-16   1.675e-16   -15.647   -15.776   -0.129
S(6)               2.000e-04
    SO4-2             1.433e-04   4.371e-05   -3.844    -4.359    -0.516
    NaSO4-            4.482e-05   3.331e-05   -4.349    -4.477    -0.129
    CaSO4             6.336e-06   6.336e-06   -5.198    -5.198     0.000
    MgSO4             4.342e-06   4.342e-06   -5.362    -5.362     0.000
    KSO4-             7.486e-07   5.563e-07   -6.126    -6.255    -0.129
    SrSO4             4.393e-07   4.393e-07   -6.357    -6.357     0.000
    FeSO4             2.196e-08   2.196e-08   -7.658    -7.658     0.000
    HSO4-             5.564e-10   4.135e-10   -9.255    -9.384    -0.129
    FeHSO4+            1.891e-14   1.405e-14   -13.723   -13.852   -0.129
    FeSO4+            2.208e-22   1.641e-22   -21.656   -21.785   -0.129
    Fe(SO4)2-         2.111e-25   1.569e-25   -24.675   -24.804   -0.129
    FeHSO4+2          1.402e-28   4.277e-29   -27.853   -28.369   -0.516
Si                 1.773e-04
    Si(OH)4           1.769e-04   1.769e-04   -3.752    -3.752     0.000
    SiO(OH)3-         3.788e-07   2.815e-07   -6.422    -6.550    -0.129
    MgSiO(OH)3+        5.076e-09   3.772e-09   -8.294    -8.423    -0.129
    CaSiO(OH)3+        4.362e-09   3.242e-09   -8.360    -8.489    -0.129
    MgSiO2(OH)2        2.874e-11   2.874e-11   -10.542   -10.542    0.000
    CaSiO2(OH)2        3.914e-12   3.914e-12   -11.407   -11.407    0.000
    SiO2(OH)2-2        4.437e-13   1.353e-13   -12.353   -12.869   -0.516
    FeSiO(OH)3+2       1.584e-18   4.831e-19   -17.800   -18.316   -0.516
Sr                 1.796e-04
    Sr+2              1.690e-04   5.155e-05   -3.772    -4.288    -0.516
    SrHCO3+            1.004e-05   7.458e-06   -4.998    -5.127    -0.129
    SrSO4             4.393e-07   4.393e-07   -6.357    -6.357     0.000
    SrCO3             1.500e-07   1.500e-07   -6.824    -6.824     0.000
```

```
      SrOH+                     3.629e-11   2.697e-11   -10.440   -10.569    -0.129

-----------------------------Saturation indices-----------------------------

              Phase          SI  log IAP  log KT

              Anhydrite      -3.14    -7.50    -4.36  CaSO4
              Aragonite      -0.14     1.85     1.99  CaCO3
              Brucite        -6.20    10.64    16.84  Mg(OH)2
              Calcite         0.00     1.85     1.85  CaCO3
              Celestite      -2.02    -8.65    -6.63  SrSO4
              CH4(g)        -11.24   -14.10    -2.86  CH4
              CO2(g)         -1.21    -9.03    -7.82  CO2
              Dolomite(dis)  -0.65     3.46     4.12  CaMg(CO3)2
              Dolomite(ord)  -0.10     3.46     3.57  CaMg(CO3)2
              Fe(cr)        -13.58     0.24    13.82  Fe
              Fe(OH)3(am)    -5.44    -0.44     5.00  Fe(OH)3
              Fe(OH)3(mic)   -3.44    -0.44     3.00  Fe(OH)3
              FeCO3(pr)      -0.44    -0.56    -0.12  FeCO3
              Goethite        0.56    -0.44    -1.00  FeOOH
              Graphite       -3.67   -25.49   -21.82  C
              Gypsum         -2.92    -7.50    -4.58  CaSO4:2H2O
              H2(g)          -8.23   -11.34    -3.11  H2
              H2S(g)         -9.59   -17.60    -8.01  H2S
              Hematite       -1.99    -0.87     1.12  Fe2O3
              Magnesite      -0.43     1.61     2.04  MgCO3
              Magnetite      -2.42     7.60    10.02  Fe3O4
              Melanterite    -7.72    -9.93    -2.21  FeSO4:7H2O
              O2(g)         -66.64   -69.53    -2.89  O2
              Portlandite   -11.92    10.88    22.80  Ca(OH)2
              Pyrite         -0.00   -18.50   -18.50  FeS2
              Quartz         -0.00    -3.75    -3.75  SiO2
              S(rhomb)       -7.23    -9.37    -2.14  S
              Siderite       -0.00    -0.56    -0.56  FeCO3
              SiO2(am)       -1.03    -3.75    -2.71  SiO2
              Strontianite   -0.36     0.70     1.06  SrCO3
              Troilite       -3.82    -9.13    -5.31  FeS
```

Appendix 3 – Low-P$_{CO2}$ variant (Helvetic marls)

Listing of part of the Phreeqc output file giving a full description of the solution, aqueous speciation and mineral saturation indices. Select values are given in Table 6-2 (column "Low-P$_{CO2}$").

```
--------------------------Description of solution--------------------------

                                 pH  =   7.948      Charge balance
                                 pe  =  -3.968      Adjusted to redox equilibrium
                   Activity of water =   0.993
                       Ionic strength =   2.077e-01
                   Mass of water (kg) =   1.000e+00
             Total alkalinity (eq/kg) =   1.815e-03
                 Total CO2 (mol/kg) =   1.799e-03
                Temperature (deg C) =  25.000
             Electrical balance (eq) =   2.508e-15
 Percent error, 100*(Cat-|An|)/(Cat+|An|) =   0.00
                          Iterations =  12
                             Total H = 1.110199e+02
                             Total O = 5.551564e+01

--------------------------Distribution of species--------------------------

                                              Log       Log       Log
     Species              Molality  Activity Molality Activity  Gamma

     OH-                  1.183e-06 8.818e-07  -5.927   -6.055   -0.128
     H+                   1.513e-08 1.128e-08  -7.820   -7.948   -0.128
     H2O                  5.551e+01 9.931e-01   1.744   -0.003    0.000
C(-4)        1.402e-15
     CH4                  1.402e-15 1.402e-15 -14.853  -14.853    0.000
C(4)         1.799e-03
     HCO3-                1.606e-03 1.197e-03  -2.794   -2.922   -0.128
     NaHCO3               9.758e-06 9.758e-06  -4.011   -4.011    0.000
     CO2                  3.056e-05 3.056e-05  -4.515   -4.515    0.000
     NaCO3-               1.803e-05 1.343e-05  -4.744   -4.872   -0.128
     CO3-2                1.614e-05 4.978e-06  -4.792   -5.303   -0.511
     CaHCO3+              1.363e-05 1.016e-05  -4.865   -4.993   -0.128
     MgHCO3+              7.275e-06 5.421e-06  -5.138   -5.266   -0.128
     CaCO3                5.549e-06 5.549e-06  -5.256   -5.256    0.000
     MgCO3                1.839e-06 1.839e-06  -5.735   -5.735    0.000
     SrHCO3+              1.160e-06 8.646e-07  -5.935   -6.063   -0.128
     FeHCO3+              4.156e-07 3.097e-07  -6.381   -6.509   -0.128
     FeCO3                3.089e-07 3.089e-07  -6.510   -6.510    0.000
     SrCO3                1.501e-07 1.501e-07  -6.824   -6.824    0.000
Ca           2.182e-03
     Ca+2                 2.157e-03 6.653e-04  -2.666   -3.177   -0.511
     CaHCO3+              1.363e-05 1.016e-05  -4.865   -4.993   -0.128
     CaSO4                5.944e-06 5.944e-06  -5.226   -5.226    0.000
     CaCO3                5.549e-06 5.549e-06  -5.256   -5.256    0.000
     CaSiO(OH)3+          3.440e-08 2.564e-08  -7.463   -7.591   -0.128
     CaOH+                1.305e-08 9.725e-09  -7.884   -8.012   -0.128
     CaSiO2(OH)2          2.671e-10 2.671e-10  -9.573   -9.573    0.000
Cl           2.020e-01
     Cl-                  2.020e-01 1.505e-01  -0.695   -0.822   -0.128
     FeCl+                7.214e-07 5.376e-07  -6.142   -6.270   -0.128
     FeCl+2               3.924e-22 1.210e-22 -21.406  -21.917   -0.511
     FeCl2+               1.092e-22 8.138e-23 -21.962  -22.090   -0.128
     FeCl3                1.225e-24 1.225e-24 -23.912  -23.912    0.000
Fe(2)        9.952e-06
     Fe+2                 8.389e-06 2.587e-06  -5.076   -5.587   -0.511
     FeCl+                7.214e-07 5.376e-07  -6.142   -6.270   -0.128
     FeHCO3+              4.156e-07 3.097e-07  -6.381   -6.509   -0.128
     FeCO3                3.089e-07 3.089e-07  -6.510   -6.510    0.000
     FeOH+                9.669e-08 7.206e-08  -7.015   -7.142   -0.128
     FeSO4                2.060e-08 2.060e-08  -7.686   -7.686    0.000
     FeHSO4+              2.050e-15 1.528e-15 -14.688  -14.816   -0.128
```

```
Fe(3)              6.142e-12
   Fe(OH)3            5.009e-12   5.009e-12   -11.300   -11.300    0.000
   Fe(OH)2+           5.924e-13   4.415e-13   -12.227   -12.355   -0.128
   Fe(OH)4-           5.399e-13   4.024e-13   -12.268   -12.395   -0.128
   FeOH+2             4.908e-17   1.514e-17   -16.309   -16.820   -0.511
   FeSiO(OH)3+2       1.052e-18   3.244e-19   -17.978   -18.489   -0.511
   FeCl+2             3.924e-22   1.210e-22   -21.406   -21.917   -0.511
   Fe+3               3.755e-22   2.662e-23   -21.425   -22.575   -1.149
   FeCl2+             1.092e-22   8.138e-23   -21.962   -22.090   -0.128
   FeSO4+             1.754e-23   1.307e-23   -22.756   -22.884   -0.128
   FeCl3              1.225e-24   1.225e-24   -23.912   -23.912    0.000
   Fe(SO4)2-          1.718e-26   1.280e-26   -25.765   -25.893   -0.128
   FeHSO4+2           1.280e-30   3.948e-31   -29.893   -30.404   -0.511
   Fe2(OH)2+4         6.816e-31   6.168e-33   -30.166   -32.210   -2.043
   Fe3(OH)4+5         8.869e-40   0.000e+00   -39.052   -42.245   -3.193
H(0)               1.718e-11
   H2                8.591e-12   8.591e-12   -11.066   -11.066    0.000
K                  2.306e-03
   K+                2.305e-03   1.718e-03    -2.637    -2.765   -0.128
   KSO4-             7.308e-07   5.446e-07    -6.136    -6.264   -0.128
   KOH               5.246e-10   5.246e-10    -9.280    -9.280    0.000
Mg                 1.268e-03
   Mg+2              1.255e-03   3.871e-04    -2.901    -3.412   -0.511
   MgHCO3+           7.275e-06   5.421e-06    -5.138    -5.266   -0.128
   MgSO4             4.063e-06   4.063e-06    -5.391    -5.391    0.000
   MgCO3             1.839e-06   1.839e-06    -5.735    -5.735    0.000
   MgOH+             1.661e-07   1.238e-07    -6.780    -6.907   -0.128
   MgSiO(OH)3+       3.994e-08   2.976e-08    -7.399    -7.526   -0.128
   MgSiO2(OH)2       1.957e-09   1.957e-09    -8.708    -8.708    0.000
Na                 1.947e-01
   Na+               1.945e-01   1.450e-01    -0.711    -0.839   -0.128
   NaHCO3            9.758e-05   9.758e-05    -4.011    -4.011    0.000
   NaSO4-            4.365e-05   3.253e-05    -4.360    -4.488   -0.128
   NaCO3-            1.803e-05   1.343e-05    -4.744    -4.872   -0.128
   NaOH              8.435e-08   8.435e-08    -7.074    -7.074    0.000
O(0)               0.000e+00
   O2                0.000e+00   0.000e+00   -70.071   -70.071    0.000
S(-2)              5.313e-11
   HS-               4.910e-11   3.659e-11   -10.309   -10.437   -0.128
   H2S               4.032e-12   4.032e-12   -11.394   -11.394    0.000
   S-2               1.052e-21   3.245e-22   -20.978   -21.489   -0.511
S(2)               2.546e-18
   S2O3-2            1.273e-18   3.927e-19   -17.895   -18.406   -0.511
S(4)               6.910e-16
   SO3-2             6.413e-16   1.978e-16   -15.193   -15.704   -0.511
   HSO3-             4.969e-17   3.703e-17   -16.304   -16.431   -0.128
S(6)               2.000e-04
   SO4-2             1.452e-04   4.478e-05    -3.838    -4.349   -0.511
   NaSO4-            4.365e-05   3.253e-05    -4.360    -4.488   -0.128
   CaSO4             5.944e-06   5.944e-06    -5.226    -5.226    0.000
   MgSO4             4.063e-06   4.063e-06    -5.391    -5.391    0.000
   KSO4-             7.308e-07   5.446e-07    -6.136    -6.264   -0.128
   SrSO4             4.122e-07   4.122e-07    -6.385    -6.385    0.000
   FeSO4             2.060e-08   2.060e-08    -7.686    -7.686    0.000
   HSO4-             6.587e-11   4.909e-11   -10.181   -10.309   -0.128
   FeHSO4+           2.050e-15   1.528e-15   -14.688   -14.816   -0.128
   FeSO4+            1.754e-23   1.307e-23   -22.756   -22.884   -0.128
   Fe(SO4)2-         1.718e-26   1.280e-26   -25.765   -25.893   -0.128
   FeHSO4+2          1.280e-30   3.948e-31   -29.893   -30.404   -0.511
Si                 1.804e-04
   Si(OH)4           1.770e-04   1.770e-04    -3.752    -3.752    0.000
   SiO(OH)3-         3.263e-06   2.431e-06    -5.486    -5.614   -0.128
   MgSiO(OH)3+       3.994e-08   2.976e-08    -7.399    -7.526   -0.128
   CaSiO(OH)3+       3.440e-08   2.564e-08    -7.463    -7.591   -0.128
   MgSiO2(OH)2       1.957e-09   1.957e-09    -8.708    -8.708    0.000
   CaSiO2(OH)2       2.671e-10   2.671e-10    -9.573    -9.573    0.000
   SiO2(OH)2-2       3.270e-11   1.009e-11   -10.485   -10.996   -0.511
   FeSiO(OH)3+2      1.052e-18   3.244e-19   -17.978   -18.489   -0.511
Sr                 1.548e-04
   Sr+2              1.531e-04   4.722e-05    -3.815    -4.326   -0.511
   SrHCO3+           1.160e-06   8.646e-07    -5.935    -6.063   -0.128
   SrSO4             4.122e-07   4.122e-07    -6.385    -6.385    0.000
   SrCO3             1.501e-07   1.501e-07    -6.824    -6.824    0.000
```

```
    SrOH+                        2.862e-10   2.133e-10   -9.543    -9.671    -0.128

----------------------------Saturation indices----------------------------

              Phase            SI log IAP  log KT

              Anhydrite      -3.17   -7.53   -4.36  CaSO4
              Aragonite      -0.14    1.85    1.99  CaCO3
              Brucite        -4.36   12.48   16.84  Mg(OH)2
              Calcite         0.00    1.85    1.85  CaCO3
              Celestite      -2.04   -8.67   -6.63  SrSO4
              CH4(g)        -12.00  -14.85   -2.86  CH4
              CO2(g)         -3.05  -10.87   -7.82  CO2
              Dolomite(dis)  -0.66    3.46    4.12  CaMg(CO3)2
              Dolomite(ord)  -0.11    3.46    3.57  CaMg(CO3)2
              Fe(cr)        -11.47    2.35   13.82  Fe
              Fe(OH)3(am)    -3.74    1.26    5.00  Fe(OH)3
              Fe(OH)3(mic)   -1.74    1.26    3.00  Fe(OH)3
              FeCO3(pr)      -0.44   -0.56   -0.12  FeCO3
              Goethite        2.26    1.26   -1.00  FeOOH
              Graphite       -4.96  -26.78  -21.82  C
              Gypsum         -2.95   -7.53   -4.58  CaSO4:2H2O
              H2(g)          -7.96  -11.07   -3.11  H2
              H2S(g)        -10.37  -18.38   -8.01  H2S
              Hematite        1.41    2.53    1.12  Fe2O3
              Magnesite      -0.43    1.61    2.04  MgCO3
              Magnetite       2.81   12.83   10.02  Fe3O4
              Melanterite    -7.75   -9.96   -2.21  FeSO4:7H2O
              O2(g)         -67.18  -70.07   -2.89  O2
              Portlandite   -10.09   12.71   22.80  Ca(OH)2
              Pyrite          0.00  -18.50  -18.50  FeS2
              Quartz          0.00   -3.75   -3.75  SiO2
              S(rhomb)       -8.28  -10.42   -2.14  S
              Siderite       -0.00   -0.56   -0.56  FeCO3
              SiO2(am)       -1.03   -3.75   -2.71  SiO2
              Strontianite   -0.36    0.70    1.06  SrCO3
              Troilite       -2.77   -8.08   -5.31  FeS
```

Appendix 4 – Low-pε variant (Helvetic marls)

Listing of part of the Phreeqc output file giving a full description of the solution, aqueous speciation and mineral saturation indices. Select values are given in Table 6-2 (column "Low-pε").

```
--------------------------Description of solution--------------------------

                                  pH  =   7.456      Charge balance
                                  pe  =  -4.841      Adjusted to redox equilibrium
                    Activity of water =   0.993
                       Ionic strength =   2.108e-01
                     Mass of water (kg) =  1.000e+00
                Total alkalinity (eq/kg) =   5.473e-03
                    Total CO2 (mol/kg) =   5.558e-03
                   Temperature (deg C) =  25.000
               Electrical balance (eq) =  -2.121e-14
  Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                           Iterations =  14
                              Total H = 1.110281e+02
                              Total O = 5.552585e+01

---------------------------Distribution of species--------------------------

                                             Log      Log       Log
     Species           Molality    Activity  Molality Activity  Gamma

     OH-               3.817e-07   2.842e-07   -6.418   -6.546   -0.128
     H+                4.697e-08   3.498e-08   -7.328   -7.456   -0.128
     H2O               5.551e+01   9.930e-01    1.744   -0.003    0.000
C(-4)          1.105e-03
     CH4               1.105e-03   1.105e-03   -2.957   -2.957    0.000
C(4)           5.558e-03
     HCO3-             4.862e-03   3.621e-03   -2.313   -2.441   -0.128
     NaHCO3            2.992e-04   2.992e-04   -3.524   -3.524    0.000
     CO2               2.868e-04   2.868e-04   -3.542   -3.542    0.000
     CaHCO3+           4.232e-05   3.152e-05   -4.373   -4.501   -0.128
     MgHCO3+           2.260e-05   1.683e-05   -4.646   -4.774   -0.128
     NaCO3-            1.783e-05   1.328e-05   -4.749   -4.877   -0.128
     CO3-2             1.579e-05   4.854e-06   -4.802   -5.314   -0.512
     CaCO3             5.549e-06   5.549e-06   -5.256   -5.256    0.000
     SrHCO3+           3.601e-06   2.682e-06   -5.444   -5.572   -0.128
     MgCO3             1.840e-06   1.840e-06   -5.735   -5.735    0.000
     SrCO3             1.500e-07   1.500e-07   -6.824   -6.824    0.000
     FeHCO3+           6.434e-17   4.791e-17  -16.192  -16.320   -0.128
     FeCO3             1.540e-17   1.540e-17  -16.812  -16.812    0.000
Ca             2.267e-03
     Ca+2              2.219e-03   6.823e-04   -2.654   -3.166   -0.512
     CaHCO3+           4.232e-05   3.152e-05   -4.373   -4.501   -0.128
     CaCO3             5.549e-06   5.549e-06   -5.256   -5.256    0.000
     CaSiO(OH)3+       1.138e-08   8.474e-09   -7.944   -8.072   -0.128
     CaOH+             4.317e-09   3.215e-09   -8.365   -8.493   -0.128
     CaSO4             7.587e-11   7.587e-11  -10.120  -10.120    0.000
     CaSiO2(OH)2       2.846e-11   2.846e-11  -10.546  -10.546    0.000
Cl             2.020e-01
     Cl-               2.020e-01   1.504e-01   -0.695   -0.823   -0.128
     FeCl+             3.689e-17   2.747e-17  -16.433  -16.561   -0.128
     FeCl+2            2.689e-33   8.269e-34  -32.570  -33.083   -0.512
     FeCl2+            7.461e-34   5.556e-34  -33.127  -33.255   -0.128
     FeCl3             8.357e-36   8.357e-36  -35.078  -35.078    0.000
Fe(2)          5.485e-16
     Fe+2              4.303e-16   1.323e-16  -15.366  -15.878   -0.512
     FeHCO3+           6.434e-17   4.791e-17  -16.192  -16.320   -0.128
     FeCl+             3.689e-17   2.747e-17  -16.433  -16.561   -0.128
     FeCO3             1.540e-17   1.540e-17  -16.812  -16.812    0.000
     FeOH+             1.595e-18   1.188e-18  -17.797  -17.925   -0.128
     FeSO4             1.311e-23   1.311e-23  -22.882  -22.882    0.000
     FeHSO4+           4.051e-30   3.016e-30  -29.392  -29.521   -0.128
```

```
Fe(3)           1.608e-24
    Fe(OH)3           1.147e-24   1.147e-24   -23.940   -23.940    0.000
    Fe(OH)2+          4.211e-25   3.136e-25   -24.376   -24.504   -0.128
    Fe(OH)4-          3.987e-26   2.969e-26   -25.399   -25.527   -0.128
    FeOH+2            1.085e-28   3.336e-29   -27.965   -28.477   -0.512
    FeSiO(OH)3+2      2.325e-30   7.148e-31   -29.634   -30.146   -0.512
    FeCl+2            2.689e-33   8.269e-34   -32.570   -33.083   -0.512
    Fe+3             2.585e-33   1.820e-34   -32.587   -33.740   -1.152
    FeCl2+            7.461e-34   5.556e-34   -33.127   -33.255   -0.128
    FeCl3            8.357e-36   8.357e-36   -35.078   -35.078    0.000
    FeSO4+            1.494e-39   1.112e-39   -38.826   -38.954   -0.128
    FeHSO4+2         0.000e+00   0.000e+00   -45.470   -45.982   -0.512
    Fe(SO4)2-        0.000e+00   0.000e+00   -46.740   -46.868   -0.128
    Fe2(OH)2+4       0.000e+00   0.000e+00   -53.475   -55.523   -2.049
    Fe3(OH)4+5       0.000e+00   0.000e+00   -74.506   -77.707   -3.201
H(0)            9.250e-09
    H2               4.625e-09   4.625e-09    -8.335    -8.335    0.000
K               2.337e-03
    K+               2.337e-03   1.740e-03    -2.631    -2.759   -0.128
    KOH              1.713e-10   1.713e-10    -9.766    -9.766    0.000
    KSO4-            9.221e-12   6.866e-12   -11.035   -11.163   -0.128
Mg              1.316e-03
    Mg+2             1.292e-03   3.972e-04    -2.889    -3.401   -0.512
    MgHCO3+          2.260e-05   1.683e-05    -4.646    -4.774   -0.128
    MgCO3            1.840e-06   1.840e-06    -5.735    -5.735    0.000
    MgOH+            5.498e-08   4.094e-08    -7.260    -7.388   -0.128
    MgSiO(OH)3+      1.322e-08   9.842e-09    -7.879    -8.007   -0.128
    MgSiO2(OH)2      2.086e-10   2.086e-10    -9.681    -9.681    0.000
    MgSO4            5.189e-11   5.189e-11   -10.285   -10.285    0.000
Na              1.976e-01
    Na+              1.973e-01   1.469e-01    -0.705    -0.833   -0.128
    NaHCO3           2.992e-04   2.992e-04    -3.524    -3.524    0.000
    NaCO3-           1.783e-05   1.328e-05    -4.749    -4.877   -0.128
    NaOH             2.756e-08   2.756e-08    -7.560    -7.560    0.000
    NaSO4-           5.511e-10   4.104e-10    -9.259    -9.387   -0.128
O(0)            0.000e+00
    O2               0.000e+00   0.000e+00   -75.534   -75.534    0.000
S(-2)           2.000e-04
    HS-              1.594e-04   1.187e-04    -3.797    -3.926   -0.128
    H2S              4.058e-05   4.058e-05    -4.392    -4.392    0.000
    S-2              1.104e-15   3.394e-16   -14.957   -15.469   -0.512
S(2)            3.200e-16
    S2O3-2           1.600e-16   4.920e-17   -15.796   -16.308   -0.512
S(4)            5.344e-18
    SO3-2            4.310e-18   1.325e-18   -17.366   -17.878   -0.512
    HSO3-            1.034e-18   7.697e-19   -17.986   -18.114   -0.128
S(6)            2.506e-09
    SO4-2            1.812e-09   5.573e-10    -8.742    -9.254   -0.512
    NaSO4-           5.511e-10   4.104e-10    -9.259    -9.387   -0.128
    CaSO4            7.587e-11   7.587e-11   -10.120   -10.120    0.000
    MgSO4            5.189e-11   5.189e-11   -10.285   -10.285    0.000
    KSO4-            9.221e-12   6.866e-12   -11.035   -11.163   -0.128
    SrSO4            5.261e-12   5.261e-12   -11.279   -11.279    0.000
    HSO4-            2.545e-15   1.895e-15   -14.594   -14.722   -0.128
    FeSO4            1.311e-23   1.311e-23   -22.882   -22.882    0.000
    FeHSO4+          4.051e-30   3.016e-30   -29.392   -29.521   -0.128
    FeSO4+           1.494e-39   1.112e-39   -38.826   -38.954   -0.128
    FeHSO4+2         0.000e+00   0.000e+00   -45.470   -45.982   -0.512
    Fe(SO4)2-        0.000e+00   0.000e+00   -46.740   -46.868   -0.128
Si              1.780e-04
    Si(OH)4          1.770e-04   1.770e-04    -3.752    -3.752    0.000
    SiO(OH)3-        1.052e-06   7.836e-07    -5.978    -6.106   -0.128
    MgSiO(OH)3+      1.322e-08   9.842e-09    -7.879    -8.007   -0.128
    CaSiO(OH)3+      1.138e-08   8.474e-09    -7.944    -8.072   -0.128
    MgSiO2(OH)2      2.086e-10   2.086e-10    -9.681    -9.681    0.000
    CaSiO2(OH)2      2.846e-11   2.846e-11   -10.546   -10.546    0.000
    SiO2(OH)2-2      3.407e-12   1.048e-12   -11.468   -11.980   -0.512
    FeSiO(OH)3+2     2.325e-30   7.148e-31   -29.634   -30.146   -0.512
Sr              1.612e-04
    Sr+2             1.575e-04   4.842e-05    -3.803    -4.315   -0.512
    SrHCO3+          3.601e-06   2.682e-06    -5.444    -5.572   -0.128
    SrCO3            1.500e-07   1.500e-07    -6.824    -6.824    0.000
    SrOH+            9.466e-11   7.049e-11   -10.024   -10.152   -0.128
```

```
   SrSO4                    5.261e-12   5.261e-12   -11.279   -11.279     0.000

----------------------------Saturation indices----------------------------

           Phase            SI  log IAP  log KT

           Anhydrite       -8.06   -12.42   -4.36  CaSO4
           Aragonite       -0.14     1.85    1.99  CaCO3
           Brucite         -5.33    11.51   16.84  Mg(OH)2
           Calcite          0.00     1.85    1.85  CaCO3
           Celestite       -6.94   -13.57   -6.63  SrSO4
           CH4(g)          -0.10    -2.96   -2.86  CH4
           CO2(g)          -2.07    -9.89   -7.82  CO2
           Dolomite(dis)   -0.65     3.46    4.12  CaMg(CO3)2
           Dolomite(ord)   -0.10     3.46    3.57  CaMg(CO3)2
           Fe(cr)         -20.02    -6.20   13.82  Fe
           Fe(OH)3(am)    -16.38   -11.38    5.00  Fe(OH)3
           Fe(OH)3(mic)   -14.38   -11.38    3.00  Fe(OH)3
           FeCO3(pr)      -10.74   -10.86   -0.12  FeCO3
           Goethite       -10.38   -11.38   -1.00  FeOOH
           Graphite         1.47   -20.35  -21.82  C
           Gypsum          -7.85   -12.43   -4.58  CaSO4:2H2O
           H2(g)           -5.23    -8.33   -3.11  H2
           H2S(g)          -3.37   -11.38   -8.01  H2S
           Hematite       -23.87   -22.75    1.12  Fe2O3
           Magnesite       -0.43     1.61    2.04  MgCO3
           Magnetite      -33.74   -23.72   10.02  Fe3O4
           Melanterite    -22.94   -25.15   -2.21  FeSO4:7H2O
           O2(g)          -72.64   -75.53   -2.89  O2
           Portlandite    -11.06    11.74   22.80  Ca(OH)2
           Pyrite           0.00   -18.50  -18.50  FeS2
           Quartz           0.00    -3.75   -3.75  SiO2
           S(rhomb)        -4.01    -6.15   -2.14  S
           Siderite       -10.30   -10.86   -0.56  FeCO3
           SiO2(am)        -1.03    -3.75   -2.71  SiO2
           Strontianite    -0.36     0.70    1.06  SrCO3
           Troilite        -7.04   -12.35   -5.31  FeS
```

Appendix 5 – High Na-Cl variant (Helvetic marls)

Listing of part of the Phreeqc output file giving a full description of the solution, aqueous speciation and mineral saturation indices. Select values are given in Table 6-3.

```
--------------------------Description of solution--------------------------

                                pH  =   7.156     Charge balance
                                pe  =  -2.995     Adjusted to redox equilibrium
                  Activity of water =   0.983
                     Ionic strength =   5.214e-01
                 Mass of water (kg) =   1.000e+00
             Total alkalinity (eq/kg) =   2.569e-03
                 Total CO2 (mol/kg) =   2.794e-03
                Temperature (deg C) =  25.000
            Electrical balance (eq) =  -2.150e-13
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                         Iterations =  11
                            Total H = 1.110209e+02
                            Total O = 5.551929e+01

--------------------------Distribution of species--------------------------

                                           Log       Log       Log
    Species              Molality  Activity Molality  Activity   Gamma

    OH-                  1.917e-07 1.408e-07  -6.717    -6.851   -0.134
    H+                   9.513e-08 6.990e-08  -7.022    -7.156   -0.134
    H2O                  5.551e+01 9.832e-01   1.744    -0.007    0.000
C(-4)           4.150e-16
    CH4                  4.150e-16 4.150e-16 -15.382   -15.382    0.000
C(4)            2.794e-03
    HCO3-                2.092e-03 1.537e-03  -2.679    -2.813   -0.134
    NaHCO3               2.922e-04 2.922e-04  -3.534    -3.534    0.000
    CO2                  2.457e-04 2.457e-04  -3.610    -3.610    0.000
    CaHCO3+              8.571e-05 6.297e-05  -4.067    -4.201   -0.134
    MgHCO3+              4.825e-05 3.545e-05  -4.317    -4.450   -0.134
    NaCO3-               8.832e-06 6.489e-06  -5.054    -5.188   -0.134
    SrHCO3+              7.183e-06 5.277e-06  -5.144    -5.278   -0.134
    CaCO3                5.549e-06 5.549e-06  -5.256    -5.256    0.000
    CO3-2                3.539e-06 1.031e-06  -5.451    -5.987   -0.536
    FeHCO3+              2.613e-06 1.920e-06  -5.583    -5.717   -0.134
    MgCO3                1.940e-06 1.940e-06  -5.712    -5.712    0.000
    FeCO3                3.089e-07 3.089e-07  -6.510    -6.510    0.000
    SrCO3                1.478e-07 1.478e-07  -6.830    -6.830    0.000
Ca              1.115e-02
    Ca+2                 1.102e-02 3.212e-03  -1.958    -2.493   -0.536
    CaHCO3+              8.571e-05 6.297e-05  -4.067    -4.201   -0.134
    CaSO4                3.703e-05 3.703e-05  -4.431    -4.431    0.000
    CaCO3                5.549e-06 5.549e-06  -5.256    -5.256    0.000
    CaSiO(OH)3+          2.664e-08 1.957e-08  -7.574    -7.708   -0.134
    CaOH+                1.021e-08 7.499e-09  -7.991    -8.125   -0.134
    CaSiO2(OH)2          3.290e-11 3.290e-11 -10.483   -10.483    0.000
Cl              5.000e-01
    Cl-                  5.000e-01 3.673e-01  -0.301    -0.435   -0.134
    FeCl+                8.621e-06 6.334e-06  -5.064    -5.198   -0.134
    FeCl+2               4.594e-20 1.339e-20 -19.338   -19.873   -0.536
    FeCl2+               2.990e-20 2.197e-20 -19.524   -19.658   -0.134
    FeCl3                8.069e-22 8.069e-22 -21.093   -21.093    0.000
Fe(2)           5.462e-05
    Fe+2                 4.287e-05 1.249e-05  -4.368    -4.903   -0.536
    FeCl+                8.621e-06 6.334e-06  -5.064    -5.198   -0.134
    FeHCO3+              2.613e-06 1.920e-06  -5.583    -5.717   -0.134
    FeCO3                3.089e-07 3.089e-07  -6.510    -6.510    0.000
    FeSO4                1.283e-07 1.283e-07  -6.892    -6.892    0.000
    FeOH+                7.563e-08 5.556e-08  -7.121    -7.255   -0.134
    FeHSO4+              8.029e-14 5.899e-14 -13.095   -13.229   -0.134
Fe(3)           1.637e-12
```

```
        Fe(OH)3              9.251e-13   9.251e-13   -12.034   -12.034    0.000
        Fe(OH)2+             6.948e-13   5.105e-13   -12.158   -12.292   -0.134
        Fe(OH)4-             1.615e-14   1.187e-14   -13.792   -13.926   -0.134
        FeOH+2               3.761e-16   1.096e-16   -15.425   -15.960   -0.536
        FeSiO(OH)3+2         7.980e-18   2.325e-18   -17.098   -17.634   -0.536
        FeCl+2               4.594e-20   1.339e-20   -19.338   -19.873   -0.536
        FeCl2+               2.990e-20   2.197e-20   -19.524   -19.658   -0.134
        Fe+3                 1.935e-20   1.207e-21   -19.713   -20.918   -1.205
        FeSO4+               1.040e-21   7.644e-22   -20.983   -21.117   -0.134
        FeCl3                8.069e-22   8.069e-22   -21.093   -21.093    0.000
        Fe(SO4)2-            1.315e-24   9.662e-25   -23.881   -24.015   -0.134
        FeHSO4+2             4.913e-28   1.431e-28   -27.309   -27.844   -0.536
        Fe2(OH)2+4           4.485e-29   3.233e-31   -28.348   -30.490   -2.142
        Fe3(OH)4+5           7.670e-38   0.000e+00   -37.115   -40.462   -3.347
H(0)            7.489e-12
        H2                   3.744e-12   3.744e-12   -11.427   -11.427    0.000
K              5.155e-03
        K+                   5.153e-03   3.786e-03    -2.288    -2.422   -0.134
        KSO4-                2.108e-06   1.549e-06    -5.676    -5.810   -0.134
        KOH                  1.847e-10   1.847e-10    -9.734    -9.734    0.000
Mg             6.843e-03
        Mg+2                 6.765e-03   1.971e-03    -2.170    -2.705   -0.536
        MgHCO3+              4.825e-05   3.545e-05    -4.317    -4.450   -0.134
        MgSO4                2.670e-05   2.670e-05    -4.574    -4.574    0.000
        MgCO3                1.940e-06   1.940e-06    -5.712    -5.712    0.000
        MgOH+                1.370e-07   1.007e-07    -6.863    -6.997   -0.134
        MgSiO(OH)3+          3.262e-08   2.397e-08    -7.487    -7.620   -0.134
        MgSiO2(OH)2          2.542e-10   2.542e-10    -9.595    -9.595    0.000
Na             4.606e-01
        Na+                  4.601e-01   3.381e-01    -0.337    -0.471   -0.134
        NaHCO3               2.922e-04   2.922e-04    -3.534    -3.534    0.000
        NaSO4-               1.332e-04   9.789e-05    -3.875    -4.009   -0.134
        NaCO3-               8.832e-06   6.489e-06    -5.054    -5.188   -0.134
        NaOH                 3.142e-08   3.142e-08    -7.503    -7.503    0.000
O(0)           0.000e+00
        O2                   0.000e+00   0.000e+00   -69.359   -69.359    0.000
S(-2)          2.247e-11
        HS-                  1.496e-11   1.099e-11   -10.825   -10.959   -0.134
        H2S                  7.509e-12   7.509e-12   -11.124   -11.124    0.000
        S-2                  5.398e-23   1.573e-23   -22.268   -22.803   -0.536
S(2)           6.543e-18
        S2O3-2               3.271e-18   9.532e-19   -17.485   -18.021   -0.536
S(4)           5.631e-16
        SO3-2                3.856e-16   1.123e-16   -15.414   -15.949   -0.536
        HSO3-                1.775e-16   1.304e-16   -15.751   -15.885   -0.134
S(6)           4.000e-04
        SO4-2                1.983e-04   5.777e-05    -3.703    -4.238   -0.536
        NaSO4-               1.332e-04   9.789e-05    -3.875    -4.009   -0.134
        CaSO4                3.703e-05   3.703e-05    -4.431    -4.431    0.000
        MgSO4                2.670e-05   2.670e-05    -4.574    -4.574    0.000
        SrSO4                2.529e-06   2.529e-06    -5.597    -5.597    0.000
        KSO4-                2.108e-06   1.549e-06    -5.676    -5.810   -0.134
        FeSO4                1.283e-07   1.283e-07    -6.892    -6.892    0.000
        HSO4-                5.344e-10   3.926e-10    -9.272    -9.406   -0.134
        FeHSO4+              8.029e-14   5.899e-14   -13.095   -13.229   -0.134
        FeSO4+               1.040e-21   7.644e-22   -20.983   -21.117   -0.134
        Fe(SO4)2-            1.315e-24   9.662e-25   -23.881   -24.015   -0.134
        FeHSO4+2             4.913e-28   1.431e-28   -27.309   -27.844   -0.536
Si             1.741e-04
        Si(OH)4              1.735e-04   1.735e-04    -3.761    -3.761    0.000
        SiO(OH)3-            5.233e-07   3.845e-07    -6.281    -6.415   -0.134
        MgSiO(OH)3+          3.262e-08   2.397e-08    -7.487    -7.620   -0.134
        CaSiO(OH)3+          2.664e-08   1.957e-08    -7.574    -7.708   -0.134
        MgSiO2(OH)2          2.542e-10   2.542e-10    -9.595    -9.595    0.000
        CaSiO2(OH)2          3.290e-11   3.290e-11   -10.483   -10.483    0.000
        SiO2(OH)2-2          8.830e-13   2.573e-13   -12.054   -12.590   -0.536
        FeSiO(OH)3+2         7.980e-18   2.325e-18   -17.098   -17.634   -0.536
Sr             7.802e-04
        Sr+2                 7.704e-04   2.245e-04    -3.113    -3.649   -0.536
        SrHCO3+              7.183e-06   5.277e-06    -5.144    -5.278   -0.134
        SrSO4                2.529e-06   2.529e-06    -5.597    -5.597    0.000
        SrCO3                1.478e-07   1.478e-07    -6.830    -6.830    0.000
        SrOH+                2.204e-10   1.619e-10    -9.657    -9.791   -0.134
```

```
----------------------------Saturation indices-----------------------------

        Phase            SI log IAP  log KT

        Anhydrite      -2.37   -6.73   -4.36  CaSO4
        Aragonite      -0.14    1.85    1.99  CaCO3
        Brucite        -5.25   11.59   16.84  Mg(OH)2
        Calcite        -0.00    1.85    1.85  CaCO3
        Celestite      -1.26   -7.89   -6.63  SrSO4
        CH4(g)        -12.53  -15.38   -2.86  CH4
        CO2(g)         -2.14   -9.96   -7.82  CO2
        Dolomite(dis)  -0.63    3.49    4.12  CaMg(CO3)2
        Dolomite(ord)  -0.08    3.49    3.57  CaMg(CO3)2
        Fe(cr)        -12.74    1.09   13.82  Fe
        Fe(OH)3(am)    -4.47    0.53    5.00  Fe(OH)3
        Fe(OH)3(mic)   -2.47    0.53    3.00  Fe(OH)3
        FeCO3(pr)      -0.44   -0.56   -0.12  FeCO3
        Goethite        1.53    0.53   -1.00  FeOOH
        Graphite       -4.77  -26.59  -21.82  C
        Gypsum         -2.17   -6.75   -4.58  CaSO4:2H2O
        H2(g)          -8.32  -11.43   -3.11  H2
        H2S(g)        -10.10  -18.11   -8.01  H2S
        Hematite       -0.05    1.07    1.12  Fe2O3
        Magnesite      -0.40    1.64    2.04  MgCO3
        Magnetite       0.45   10.47   10.02  Fe3O4
        Melanterite    -6.98   -9.19   -2.21  FeSO4:7H2O
        O2(g)         -66.46  -69.36   -2.89  O2
        Portlandite   -11.00   11.80   22.80  Ca(OH)2
        Pyrite          0.00  -18.50  -18.50  FeS2
        Quartz          0.00   -3.75   -3.75  SiO2
        S(rhomb)       -7.65   -9.79   -2.14  S
        Siderite       -0.00   -0.56   -0.56  FeCO3
        SiO2(am)       -1.03   -3.75   -2.71  SiO2
        Strontianite   -0.36    0.69    1.06  SrCO3
        Troilite       -3.40   -8.71   -5.31  FeS
```