

Arbeitsbericht NAB 09-14

**Reference pore water for the
Opalinus Clay and "Brown
Dogger" for the provisional
safety-analysis in the framework
of the sectoral plan -
interim results (SGT-ZE)**

October 2009

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University of Bern

Nationale Genossenschaft
für die Lagerung
radioaktiver Abfälle

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KEYWORDS

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1 Summary

A single composition for a reference pore water for both the Opalinus Clay and “Brown Dogger” is proposed for all siting regions (Table 6-2). This reference pore water is very similar to that developed by Nagra (2002) for Benken. The uncertainty range (for Opalinus Clay) in the constraining $P(\text{CO}_2)$ is significantly reduced compared to 2002, resulting in a much reduced range in pH and alkalinity (Table 6-4).

To account for the possibility that salinities as high as encountered at Mont Russelin (chlorinity of slightly more than modern sea water, 22 g/L), a high-salinity variant is also defined (Table 6-3).

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 Opalinus Clay and "Brown Dogger" 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 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 "Brown Dogger" is used for clayey strata that are stratigraphically located between the underlying Opalinus Clay Formation (lower Dogger) and calcareous marls of the lower Malm (Effingen Member).

3 Introduction

The Opalinus Clay Formation (Opalinuston) was proposed by Nagra (2008) as a potential host rock for high-level (HAA) and low/intermediate-level radioactive waste (SMA) in several siting regions. The claystone sequence named "Brown Dogger" (overlying Opalinus Clay) was proposed for low/intermediate-level radioactive waste (SMA) in the regions "Zürcher Weinland" and "Nördliche Lägern".

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, 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. A prime example of such an approach is that developed for Opalinus Clay at the Mont Terri Rock Laboratory (Pearson et al. 2003).

The efforts (tens of man-years) undertaken for the case of Opalinus Clay comprised numerous laboratory and in-situ experiments as well as geochemical modelling and synthesis work. The result was a robust and defensible geochemical model for the pore water composition and its controls via mineral-water interaction and ion exchange processes. Despite this effort, a number of open issues - or lack of accurate constraints on some parameters - are still persisting and are the subject of on-going research (Wersin et al. 2009).

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. This is not the case for the "Brown Dogger". For the latter, the same pore water composition is suggested based on similarity in mineralogy and hydraulic properties, stratigraphic continuity, continuity in formation-scale pore water diffusion profiles (chloride, stable isotopes) and in the absence of direct investigations on which to base a rock-specific model.

5 Regions of interest and knowledge base

Figure 5-1 shows an overview map of all proposed siting regions (Nagra 2008). The following regions include Opalinus Clay (OPA) and/or "Brown Dogger" (BD) as proposed host rocks, for either a HAA (high-level waste) or SMA (low/intermediate-level waste) (or both) repository. The regions "Zürcher Weinland", "Nördliche Lägern" and "Bözberg" bear the potential for a combined SMA-HAA repository in Opalinus Clay.

Zürcher Weinland:	OPA (SMA, HAA)	BD (SMA)
Südliches Schaffhausen:	OPA (SMA)	
Nördliche Lägern:	OPA (SMA, HAA)	BD (SMA)
Bözberg:	OPA (SMA, HAA)	
Jura Südfuss:	OPA (SMA)	

The different depth criteria applied (Nagra 2008) foresee a depth >400 m below surface for a HAA repository, and >200 m for a SMA repository, with some permissible or required deviations depending on the local geological situation.

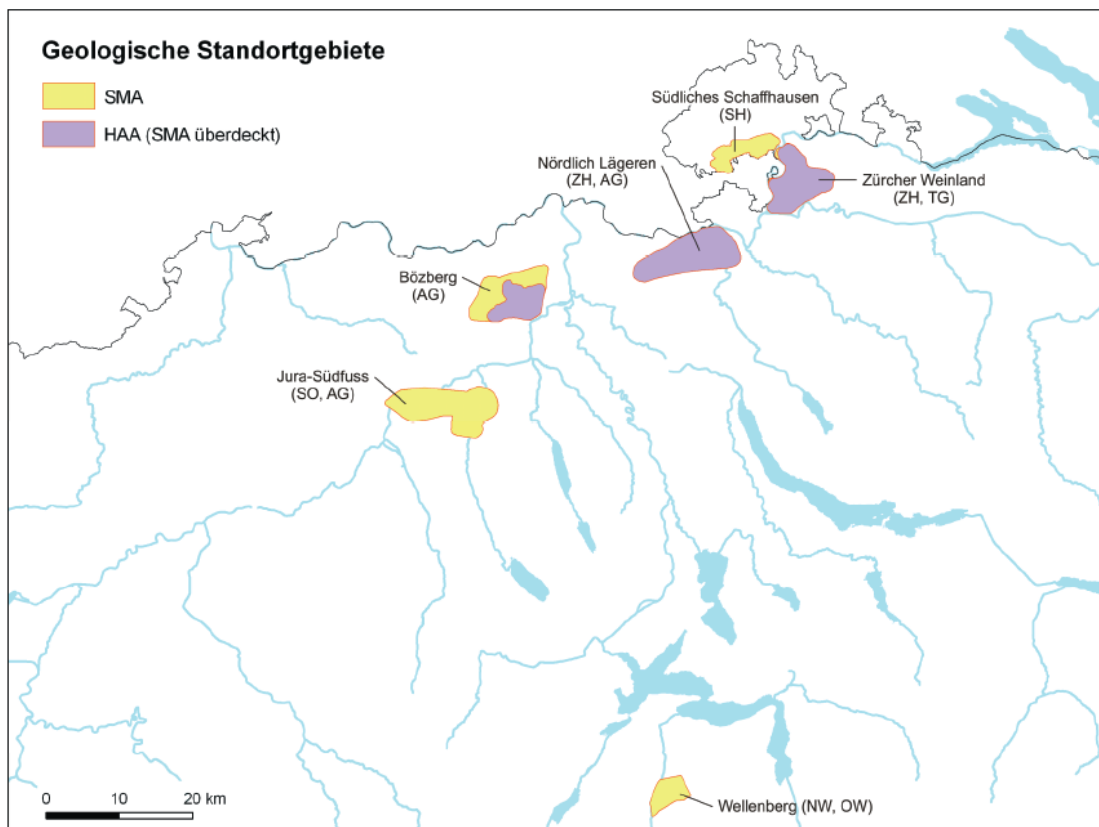


Fig. 5-1: Suggested siting regions for a SMA and HAA repository. The regions "Zürcher Weinland", "Nördliche Lägern" and "Bözberg" bear the potential for a combined SMA-HAA repository.

(Fig. 6.1-1 from Nagra 2008)

Nearest locations from where relevant geological data about the Opalinus Clay is available are listed below. The names relate to borehole locations of Nagra's scientific deep drilling program unless otherwise stated. Indicated is also the likely thickness of the Opalinus Clay in the siting region.

Südliches Schaffhausen: Benken (5 km SE), Weiach (10 km W), some relevant surface outcrops and boreholes in Klettgau and Wutach area (Nagra 2008, Beilage 5.2-1 and 5.2-2). OPA thickness: 90-110 m. Further details: Nagra (2008), Section 5.5.1.1.

Zürcher Weinland: Benken (within region), Weiach (11 km SW), additional boreholes and relevant surface outcrops in adjacent regions (Nagra 2008, Beilage 5.2-1, 5.2-2). OPA thickness: 110 m. Further details: Nagra (2008), Section 5.5.1.2.

Nördliche Lägern: Weiach (within region), Benken (12 km NE), Riniken (12 km W), additional boreholes and relevant surface outcrops in adjacent regions (Nagra 2008, Beilage 5.2-1, 5.2-2). OPA thickness: 110 m. Further details: Nagra (2008), Section 5.5.1.3.

Bözberg: Riniken (at margin of region), Weiach (20 km E), Schafisheim (11 km S), additional boreholes and relevant surface outcrops in adjacent regions (Nagra 2008, Beilage 5.2-1, 5.2-2). OPA thickness: 100-120 m. Further details: Nagra (2008), Section 5.5.1.4.

Jura Südfuss: Schafisheim (4 km E), EWS¹ boreholes Küttigen (5 km SW), EWS borehole Oftringen (4 km N), additional boreholes and relevant surface outcrops in adjacent regions (Nagra 2008, Beilage 5.2-1, 5.2-2). OPA thickness: 80-100 m. Further details: Nagra (2008), Section 5.5.1.5.

The unofficial term "Brown Dogger" is used by Nagra (2008) for a clayey sequence of strata located between Opalinus Clay and Malm. These strata stretch from the Plateau Jura East of Aar river to the area of Zürcher Weinland-Schaffhausen. The "Brown Dogger" is the host rock *sensu stricto*, but also comprises the underlying Opalinus Clay and overlying Effingen Member as a combined rock package effective for waste confinement.

Geological information for the "Brown Dogger" is available as indicated above for the Opalinus Clay. The thickness of the clayey sequence is:

Zürcher Weinland: 90 m

Nördliche Lägern: 80 m

The deep borehole at Benken (Zürcher Weinland) also comprised a detailed sampling and analytical program for the "Brown Dogger" yielding a data base of comparable quality to that for Opalinus Clay.

Formation-scale geochemical profiles, chloride content and isotopic composition in particular, were examined and interpreted for Mont Terri (Pearson et al. 2003, Mazurek et al. 2009), Mont Russelin (Mazurek et al. 2009) and Benken (Nagra 2002, Gimmi and Waber 2004, Mazurek et al. 2009), including data for the middle and upper Dogger. While the profiles are continuous across Opalinus Clay and middle/upper Dogger ("Brown Dogger") at Benken, the boundary located stratigraphically above Opalinus Clay is a low-salinity aquifer boundary in the case of Mont Terri and Mont Russelin (located West of the regional extent of "Brown Dogger").

¹ EWS: Erdwärmesonde (geothermal well)

Information on mineralogy for the "Brown Dogger", including clay mineralogy, carbon and sulphur contents, from boreholes Benken and Weiach are newly compiled by Mazurek (in prep.) for all relevant strata, along with some petrophysical properties (porosities, densities). Some additional data is presently being generated from a re-sampling of existing core material from the Nagra scientific drilling program (University of Bern, work in progress).

The regional hydro-geochemical situation is described and interpreted in detail in Nagra (2002, Section 3.7). Interpretation includes estimation of residence time, infiltration areas and infiltration age, groundwater flow, and groundwater evolution. Information on the groundwater composition of the regional Malm (overlying) and Upper Muschelkalk (underlying) aquifers is available from boreholes Leuggern, Böttstein, Weiach, Riniken, Schafisheim (Pearson et al. 1989), and Benken (Gimmi and Waber 2004). Groundwater composition for the local underlying Keuper aquifer is available from Riniken (Pearson et al. 1989) and Benken (Gimmi and Waber 2004). Chloride concentrations and sulphate concentrations are listed in Table 5-1. Information from springs, wells, and other boreholes from the Malm, Keuper and Muschelkalk aquifers is detailed in Nagra (2002, Section 3.7). In the absence of data from the Malm aquifer in the Schafisheim borehole, a sample from the overlying Untere Süsswassermolasse (USM) is given.

Tab. 5-1: Chloride and sulphate concentrations from groundwaters sampled in the Nagra deep boreholes.

Borehole	Aquifer	Depth	Chloride [mg/l]	Sulphate [mg/l]
Leuggern	Muschelkalk	54-96	34	540
Böttstein	Muschelkalk	123-202	1300	2600
Riniken	Keuper	501-530	2800	7300
	Muschelkalk	617-696	6000	3000
Schafisheim	USM	553-563	5200	5
	Muschelkalk	1228-1239	6400	2800
	Muschelkalk	1241-1262	6700	2850
Weiach	Malm	243-267	3800	33
	Muschelkalk	822-869	53	2000
Benken	Malm	380-395	4550	1450
	Keuper	698-739	520	5900
	Muschelkalk	813-826	75	1300

Data rounded from Pearson et al. (1989) and Gimmi and Waber (2004). USM = Untere Süsswassermolasse.

Despite the complexity (details in Nagra 2002), the underlying Muschelkalk aquifer is characterized by relatively sulphatic waters with low chloride contents in the Eastern siting regions Nördliche Lägern, Zürcher Weinland and Südliches Schaffhausen (Weiach and Benken, Table 5-1), and by much higher mineralized Cl-SO₄ waters in the Western regions Bözberg and Jura Südfuss (Riniken and Schafisheim, Table 5-1), freshening up towards the North (Böttstein, Leuggern).

The underlying Keuper aquifer is of local character and showed only sufficient yield for sampling at Riniken and Benken, and the waters are sulphatic in composition. At Benken, the Muschelkalk aquifer is much less mineralized than the Keuper aquifer above it.

The situation in the Malm aquifer is very complex (Nagra 2002). Weiach and Benken show chlorinities of 3800-4500 mg/l, with Benken being relatively more sulphatic and displaying relatively low hydraulic conductivities. At Schafisheim, the USM aquifer contains 5200 mg/l of chloride and no sulphate. Towards the North, the Malm aquifer is freshening up and is tapped locally for drinking water at shallower depths.

6 Reference porewater for Opalinus Clay

6.1 Existing data on pore water composition

The existing data base of field and laboratory data relevant for constraining the pore water composition is largely related to work performed at the Mont Terri Rock Laboratory, Nagra's scientific deep borehole at Benken, and the Mont Russelin Gallery (freeway tunnel just East of Mont Terri tunnel). All data is summarized in Pearson et al. (2003), Nagra (2002), and most recently reviewed and updated in Wersin et al. (2009). Data from the Mont Russelin profile is summarized in Mazurek et al. (2009) and reported in detail in Koroleva and Mazurek (2009). The data base for these localities is excellent and remaining uncertainties reflect difficulties inherent to the claystone medium itself rather than omissions in scientific investigations. The Mont Russelin region is less studied compared to the others, but did yield the highest salinities (ca. 23 g/l) so far encountered in Opalinus Clay.

Only very limited relevant geochemical information is available from the older deep Nagra boreholes. There is an unpublished chloride profile from leaching data from the Weiach borehole, but interpretation in terms of pore water chlorinity is hampered by poorly constrained and inconsistent porosity data. Only a single chloride leaching analysis had been performed in each of the boreholes Riniken and Schafisheim (unpublished), that are difficult to interpret for lack of reliable porosity data. There are efforts under way to re-examine old drill core from these boreholes and supplement additional information (University of Bern, work in progress).

Unpublished data from the OPA section of the Weiach borehole (H.N. Waber, pers. comm.) show discrepancies in data between total porosity (He-pycnometry) obtained by two different laboratories. The porosities obtained by University of Leeds are on average smaller than those derived at University of Bern. Assuming a 50 % anion-accessible porosity, the calculated pore water chlorinities range from 5000-9900 mg/l (Leeds) or from 4600-6800 mg/l (Bern). There is no curved chlorinity profile with depth apparent, but uncertainties are so large that the absence of a curved profile cannot be assumed. While this data is rather poorly constrained compared to other data, it suggests that chlorinities in OPA in the Weiach borehole are similar to those found in Benken, and do not exceed the maximum chlorinities observed at Mont Terri (13000 mg/l).

There are no constraints on the composition of the bounding aquifers below and above the Opalinus Clay / "Brown Dogger" strata available from the deep boreholes Weiach, Riniken and Schafisheim. Accordingly, there are only few local constraints on the overall hydro-geochemical evolution other than from the Benken borehole, where the focus was specifically on Opalinus Clay and its hydrogeochemical context.

The highest reported chlorinities (derived from squeezing and/or aqueous extracts and recalculated to the anion-accessible porosity) differ by a factor of three between Mont Russelin (highest) and Benken (lowest) with Mont Terri showing in-between values. All three localities yielded formation-scale curved profiles of chlorinity with highest values present near the centre of the formation, falling off towards the lower and upper bounding aquifers (the upper bounding aquifer is above the "Brown Dogger" in the case of Benken). In absolute terms, the chlorinities in the centre of the formation range from near present-day sea water (Mont Russelin, 22 g/l) to ca. 7 g/l (Benken).

The Benken chloride and isotopic profiles display no chemical or isotopic discontinuity across the Opalinus Clay - "Brown Dogger" boundary, and show highest chloride concentrations in the region of this boundary (Nagra 2002, Mazurek et al. 2009). The overall profile is distinctly

asymmetric towards very low chlorinities at the lower bounding aquifer (Keuper, ca. 500 mg/l), and much higher chlorinities of ca. 4600 mg/l towards the overlying Malm aquifer.

The SO_4/Cl molal ratios are near that of present-day sea water at Mont Terri and Mont Russelin (ca. 0.05), but are distinctly higher at Benken (ca. 0.15).

The data from Mont Russelin just became available (Koroleva and Mazurek 2009), and consist of mineralogical and physical parameters, aqueous leaching data (Cl, Br), pore water squeezing data (full analyses), and isotopic data (stable isotopes and He). The shape of the Cl and isotopic profile have been interpreted also by Mazurek et al. (2009), but the pore water compositions have not yet been interpreted in detail. The striking feature is that salinities up to just above modern sea water are reached in the Mont Russelin anticline, dropping off towards the Dogger aquifer.

The anion-accessible porosity is well constrained to 50-60 % of the water-loss porosity at Mont Terri (Pearson et al. 2003, Nagra 2002) by multiple lines of evidence, and it is slightly smaller at Benken. A value of 48 % is quoted in Nagra (2002, Table 5.4-7). Here, we suggest a value of 50 % for the proposed siting regions.

6.2 Existing models for pore water composition

Thermodynamic models for the pore water composition of Opalinus Clay were first developed for the Mont Terri locality (Pearson et al. 2003, Bradbury and Baeyens 1997/1998) and then adapted to the Benken locality (Nagra 2002) for Nagra's Safety Case. Most recent developments and a complete review of all existing model variants are detailed in Wersin et al. (2009). All models use a combination of directly measured concentrations, mineral saturation constraints, constraints from the exchangeable cation population and possibly some assumed fixed parameters. The models have evolved from using several arbitrary constraints (e.g., a fixed partial pressure of CO_2 , a fixed SO_4/Cl ratio) to models that are fully constrained by mineral saturation equilibria and ion exchange equilibria (reviewed in Wersin et al. 2009).

The original model for the reference pore water for the Benken locality (Nagra 2002, Table 5.12-2) is listed below (Table 6-1) including the parameters relevant for this report. Omitted were the components Al and F, as well as Mn and U, that were fixed by mineral saturation constraints (kaolinite, fluorite, UO_2 , rhodochrosite). More details and discussion of the model is given in Pearson (2002). Mg concentration may equally well be constrained by ion exchange instead of dolomite saturation. If this is done, the resultant solution composition should be near dolomite saturation.

Tab. 6-1: Model for OPA reference porewater for Benken (adapted from Nagra 2002)

Parameter	Data origin	Modelling constraint	Input value / output value
Temperature	Required by thermodynamic data base	Fixed	25 °C
Cl(total)	Squeezing, aqueous extracts	Fixed concentration	0.16 (+0.04/-0.08) mol/l
S ^{VI} (total)	SO ₄ /Cl from aqueous extracts	Fixed concentration	Cl-0.15 (+0.05/-0.1) mol/l 2310 mg/kg _{H2O} (as SO ₄)
Log[P(CO ₂)]	Experimental, Mont Terri	Fixed partial pressure	-2.2 (+0.07/-1.3) bar
pH	Thermodynamics	Charge balance	7.24
C ^{IV} -species	Thermodynamics	Speciation equilibria	32.4 mg/kg _{H2O} (as C) 153 mg/kg _{H2O} (as HCO ₃)
Ca ²⁺	Thermodynamics, geology	Calcite saturation	420 mg/kg _{H2O}
Mg ²⁺	Thermodynamics, geology	Dolomite saturation	182 mg/kg _{H2O}
Na ⁺ K ⁺ Sr ²⁺	Measured occupancy and selectivity on exchanger	[CaX ₂]/[NaX] ² , K _{Na/Ca} [NaX]/[KX], K _{Na/K} [SrX]/[NaX] ² , K _{Na/Sr}	3880 mg/kg _{H2O} 221 mg/kg _{H2O} 26.6 mg/kg _{H2O}
Si	Thermodynamics, geology	Quartz saturation	10.7 mg/kg _{H2O} (as SiO ₂)
Fe ²⁺	Thermodynamics, geology	Siderite saturation	2.4 mg/kg _{H2O}
S ^{-II}	Thermodynamics, geology	Pyrite saturation	4.7·10 ⁻⁷ mg/kg _{H2O} (as H ₂ S)
Eh, pe	Thermodynamics, geology	S ^{VI} /S ^{-II} activity ratio (pyrite, siderite sat.)	-0.17 V, -2.83

Components Al, F, U and Mn were omitted compared to Table 5.12-2 of Nagra (2002). X denotes the exchange site, and K are the equilibrium constants between the cation in solution and on the exchanger. The calculations are performed with the Nagra-PSI thermodynamic data base, the Gaines-Thomas convention for activities on the exchanger, and the Davies equation for activity coefficients of aqueous species.

Nagra (2002) performed sensitivity calculations based on the estimated uncertainty range as indicated in Table 6-1 for the input parameters chloride, sulphate and P_{CO2}. They modelled a low-salinity and high-salinity case, each with a low-P_{CO2} and high-P_{CO2} sub-case. The resultant range in some of the critical parameters were (Nagra 2002, Table 5-12.3): 6.80-8.17 for pH, and 7.0-79 mg/kg_{H2O} for total carbon (C^{IV}). This rather large range is mainly due to the large range in the partial pressure of CO₂ (two orders of magnitude) and much less due to differences in ionic strength (salinity).

BRGM further developed a pore water model (THERMOAR, Gaucher et al. 2009) at the Bure site for Callovian-Oxfordian claystone and also applied it to Opalinus Clay. The main thrust of this model is to constrain all pore water components by mineral saturation equilibria and ion exchange equilibria. This model is discussed and compared to the others in Wersin et al. (2009), and the key differences to the model above are as follows.

- Sulphate concentration is linked to celestite saturation (and Sr²⁺ is linked to ion exchange).

- Potassium concentration is linked to illite saturation and ion exchange. A model is used to describe the observed dependence of the ion exchange "equilibrium constant" on potassium concentration. This latter model avoids the discrepancy observed between potassium values calculated with generic distribution coefficients and measured solution compositions from long-term sampling boreholes at Mont Terri (Pearson et al. 2003). This discrepancy was up to a factor of 10 with modelled values being too large.
- Aluminium concentrations are linked to chlorite equilibrium, rather than kaolinite saturation.
- Dolomite saturation is not used as a constraint.
- There is no need to assume a partial pressure of CO₂ due to the larger number of mineral saturation constraints that result in a determined pH and carbonate system.

The corollary of such an uniquely constrained pore water model is that all compositions are buffered by mineral reactions, and therefore differences in concentrations across a formation can only be induced by differences in salinity and/or ion exchange population. Especially the carbonate system is fully buffered along with pH, and therefore variations in P_{CO2} ought to be minimal across the formation. While there are many good arguments for such a model, not all details are yet established with respect to its application to Opalinus Clay at Mont Terri. Specifically, the ubiquitous occurrence of celestite (that fixes sulphate concentration) is not yet established for the Benken samples, and the model relies on some site-specific mineral compositions (illite) and therefore also site-specific thermodynamic properties which have not yet been established for the Opalinus Clay sites. There is also some discussion as to if and how one should include proton exchange due to the general lack of reliable constraining data.

An important improvement since the summary work for Mont Terri (Pearson et al. 2003) and Benken (Nagra 2002) is that the partial pressure of CO₂ is now much better established for the Mont Terri locality by experimental work primarily carried out by ANDRA (data and references in Wersin et al. 2009). It is quite certain that the partial pressure is near 10⁻² bar and that the earlier obtained pressures of ca. 10⁻³ bar (and below) were subject to artefacts. From this point of view, the choice of 10^{-2.2} bars made by Nagra (2002, see Table 6-1) was correct, but the uncertainty range can be significantly decreased, to approximately 10^{-1.8} - 10^{-2.5} (for Mont Terri). This will significantly reduce the range in pH values and total inorganic carbon using the model shown in Table 6-1.

It can be argued that with the THERMOAR approach and its implied full buffering by minerals, the partial pressure of CO₂ and its reduced uncertainty range should also apply to other OPA localities based on the identical mineralogical composition. Differences in salinity are less critical because the dependence of the model pore water composition on ionic strength is not so pronounced for the carbonate system and pH. These new aspects have not yet been fully explored, and the uncertainty range for P_{CO2} to be used for the Benken locality is not firmly established, but will likely not exceed one order of magnitude. De Cannière et al. (2008) argue along similar lines of argument and state: "Now, it is generally agreed that P_{CO2} through the formation is likely to be of the order of 10⁻² bar and independent of chloride concentration because of the very similar mineralogy throughout the formation ...".

One should keep in mind that the above arguments are based on a fairly static view of the geochemistry of pore waters in claystone. Once processes are addressed such as man-induced disturbances or long-term evolutions related to changing boundary conditions, kinetic factors may also become important. This may influence the solubility controls exerted by slowly reacting minerals versus rapidly reacting minerals. The choice of which minerals are controlling

pore water composition may not have a unique answer in all situations, or may indeed require a more holistic kinetic modelling approach. In this respect, the THERMOAR approach bears a certain element of arbitrariness in choosing the controlling mineral phases, and omitting others. In the case of the Callovian-Oxfordian claystone at Bure, the choice was based on what fitted best all available data. While this makes sense for well-studied formations, it is not a feasible approach for formations lacking such data (e.g. "Brown Dogger").

6.3 Reference pore water for Opalinus Clay for all siting regions

For all five regions proposed (Figure 5-1), it is suggested that a single pore water composition - constrained by data from the Benken locality - be used to represent the relatively high-salinity centre of the Opalinus Clay Formation. The available data suggests that at least the localities Benken (Zürcher Weinland) and Weiach (Nördliche Lägern) show comparable salinities that are below the maximum salinities observed at Mont Terri (13 g/l), and certainly below those of Mont Russelin (23 g/l). This hypothesis is defensible as long as there is no evidence for higher-salinity pore waters from one of the proposed siting regions.

The close proximity of Mont Russelin and Mont Terri and the marked difference in chlorinity between them is as yet not completely understood. This fact does allow for the possibility that also elsewhere in the Opalinus Clay Formation substantial lateral gradients in chlorinity may be present. Such large gradients would be caused by contrasting geochemical groundwater evolutions in the bounding aquifers below and above the low-transmissivity rocks (OPA and "Brown Dogger"), and likely also contrasting tectonic evolution in the case of locations in the Jura fold and thrust belt.

The situation that the Opalinus Clay is overlain by clay-rich Dogger strata ("Brown Dogger") in the proposed siting regions makes it likely that, contrary to the situation at Mont Terri and Mont Russelin, there is no low-salinity aquifer present in the upper Dogger. Therefore the Opalinus Clay section is protected from geochemical disturbances from the upper boundary. Lateral variations would then largely depend on spatio-temporal variations in groundwater composition of the lower aquifer boundary, Muschelkalk and/or Keuper where present.

While this hypothesis is quite defensible for the Eastern siting regions Nördliche Lägern, Zürcher Weinland and Südliches Schaffhausen on the basis of similar conditions in the bounding aquifers, and within the formation, there is more uncertainty with respect to the Western regions Bözberg and Jura Südfuss. There is a lack of constraining data for the latter regions which does not permit a more reliable statement, and certainly not a reference pore water specific for the Western siting regions. To account for this uncertainty, a high-salinity variant, dubbed "Mont Russelin" is also defined as detailed in Section 6.4.

A preference is given to the modelling approach chosen by Nagra (2002) over that of THERMOAR due to the fact that THERMOAR is not yet fully adapted and explored for the case of Opalinus Clay at the siting regions. The differences are not expected to be significant for the purpose of calculating radionuclide sorption and solubility limits.

The model differs in the following details compared to that of Nagra (2002) based on Pearson (2002) and shown in Table 6-1. It was impossible to recreate exactly the modelled values of Pearson (2002) because the exact input values (e.g. ion exchange population) and the exact sequence of Phreeqc modelling steps were not given. The modelled composition using what was thought to be the same steps did, however, result in a composition very close to that shown in Pearson's (2002) Table 9. Starting from this, the following differences were implemented.

1. A revised equilibrium constant is used for K^+ to relate the exchangeable K^+ to that in the pore water. This revised value is compatible with observations from Mont Terri and is approximately compatible with a value according to the concentration-dependent model of Tournassat et al. (2007), as shown in Wersin et al. 2009). A log-K value of 0.95 rather than 0.7 was adopted based on a cation fractional occupancy of <0.1 for K^+ . This value is quite uncertain in this low range of K^+ -occupancy that is not well constrained by data. Pearson (2002) already mentioned this apparent discrepancy between K^+ concentrations from borehole sampling at Mont Terri and that calculated from exchanger occupancy and generic log-K. Pearson choose to adhere to the generic published exchange equilibrium constants at that time. The effect of this adjustment is fairly negligible for the overall solution composition including pH and alkalinity. It is possible that even larger log-K values of 1-1.1 might be appropriate (details in Wersin et al. 2009).
2. The same partial pressure of $10^{-2.2}$ bar for CO_2 is adopted as in Nagra (2002), but the uncertainty range is reduced from 2 to 1 order of magnitude, namely from $10^{-1.8}$ - $10^{-2.8}$ bar (see results in Section 6.4).
3. Saturation with respect to celestite was enforced. The reference water of Pearson (2002) was oversaturated (SI=0.15, his Table 10). This was avoided by constraining dissolved Sr^{2+} by celestite saturation rather than ion exchange. The initial sulphate was decreased by 0.005 moles/kg_{H₂O} to compensate the celestite that is brought into solution by equilibration. This procedure results in almost the same final sulphate content as proposed by Pearson. Enforcing celestite saturation after ion exchange would result in a decrease of sulphate by almost a factor of two. In essence, the approach chosen here puts more reliability on the sulphate concentration (from aqueous extracts performed in a glove box) than on the measured Sr^{2+} on the exchanger and the generic ion exchange equilibrium constant.
4. Mg was brought into solution by ion exchange first (priming the solution), and then dolomite saturation was enforced (resulting in some small removal of dolomite component from the solution).
5. Ca was brought into solution by ion exchange first (priming the solution), and then calcite saturation was forced (resulting in some small addition of calcite component to the solution).

Siderite and pyrite were included in the same way as in Pearson (2002) in order to calculate a redox potential. This is thought to be a relatively robust assumption even though it is not exactly known which phase or phases are controlling ferric iron.

The exchanger population of the sample from 613.48 m depth (Pearson 2002, Table 3) was used, having a CEC of 102 meq/kg_{rock}.

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.

Below is a listing of the Phreeqc input file used for modelling the reference pore water, that is in equilibrium with calcite, dolomite, celestite, quartz, siderite, pyrite, and that matches approximately the measured exchanger composition at a fixed P_{CO_2} of $10^{-2.2}$ bar. The modelled composition is listed in Table 6-2. A printout of the full speciation and other solution parameters are provided in Appendix 1.


```

DATABASE NAPSI_300401DAV.DAT
TITLE  Ref pore water for Opalinus Clay and Brown Dogger
# 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
  -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 OPA # Pearson 2002 NIB 01-13, Tab. 9
  pe  4.0 # initial value only
  redox pe
  temp 25.0
  -units  mol/kgw
  pH  7.0 charge
  Cl  0.16
  S  0.019 # 0.024-celestite(0.005) = 0.019 initial
  Na  0.198 # charge balance initial: Cl+2*SO4
EXCHANGE 1 measured exchanger # NIB 01-13, Tab 3, 613.48m
  NaX  0.520
  KX  0.084
  MgX2  0.149
  CaX2  0.237
#  SrX2  0.010 # use celestite saturation instead
EQUILIBRIUM_PHASES 1
  CO2(g)  -2.2 1.0 # range -1.8 to -2.8
  Calcite  0.0 1.0
  Dolomite(ord) 0.0 1.0
  Quartz  0.0 1.0
  Celestite  0.0 1.0
  Siderite  0.0 1.0
  Pyrite  0.0 1.0
#  Fluorite  0.0 1.0 # possibility to include fluoride
END

```

Tab. 6-2: Modelled composition and other geochemical parameters of the reference pore water for the Opalinus Clay Formation and comparison to Pearson (2002).

Parameter	Units	Value Ref. PW	Value (Pearson 2002)	Comment
Temperature	°C	25	25	
pH		7.203	7.238	
p _e		-2.781	-2.830	Siderite-pyrite equilibrium
Na (total)	mmol/kg _{H2O}	164.4	168.6	
K (total)	mmol/kg _{H2O}	2.604	5.645	
Ca (total)	mmol/kg _{H2O}	12.51	10.47	
Mg (total)	mmol/kg _{H2O}	9.625	7.477	
Sr (total)	mmol/kg _{H2O}	0.2106	0.3035	
Fe ^{II} (total)	mmol/kg _{H2O}	0.0524	0.043	
Fe ^{III} (total)	mmol/kg _{H2O}	3.31·10 ⁻⁹		
Si (total)	mmol/kg _{H2O}	0.1779	0.1778	
Cl (total)	mmol/kg _{H2O}	160.0	160.0	
S ^{VI} (total)	mmol/kg _{H2O}	24.72	24.00	
S ^{II} (total)	mmol/kg _{H2O}	12.4·10 ⁻⁹	14.1·10 ⁻⁹	
C ^{IV} (total)	mmol/kg _{H2O}	2.506	2.700	
SO ₄ /Cl	mol/mol	0.155	0.15	
Alkalinity	meq/kg _{H2O}	2.308	2.504	Total alkalinity
HCO ₃ (species)	mmol/kg _{H2O}	2.043		
P(CO ₂)	Bar	10 ^{-2.20}	10 ^{-2.20}	
Water activity		0.994		
Ionic strength	Molal	0.2299		
SI(celestite)		0.00	0.15	
SI(gypsum)		-0.28	-0.38	
SI(strontianite)		-0.98	-0.73	
Accessible porosity	% of water-loss porosity	50	50	
CEC	meq/kg(rock)	102		Clayey facies

Calculations performed with Phreeqc (version 2.15.07) and Nagra-PSI data base Version 01/01. The solutions are saturated with respect to calcite, dolomite (ordered), quartz, siderite and pyrite. Detailed speciation and solution parameters are given in Appendix 1. Saturation with respect to fluorite would add 0.153 mmol/kg fluoride to the reference pore water, but this is not included in the calculations.

The SO_4/Cl ratio of the reference pore water (and also that of Pearson 2002) is ca. 0.15 or three times higher than that of present-day sea water. The input constraints are based on data from aqueous leachates performed in a glove box environment to suppress pyrite oxidation. The slight supersaturation with respect to celestite observed by Pearson (2002) may be an indication that at least a small amount of sulphate gain did occur. The in-situ pore water may therefore contain a somewhat lower SO_4/Cl ratio, but not a higher one.

If a maximum concentration of fluoride needs to be established, saturation with respect to fluorite may be assumed, as was done by Pearson (2002). This entry in the Phreeqc input is indicated but commented out (de-activated). The value obtained is 0.153 mmol/L or 2.9 mg/L.

6.4 “Mont Russelin” variant (high-salinity) for Opalinus Clay

Although there is no evidence for pore waters in the siting regions to reach present-day sea water salinities (20 g/l), the fact that at Mont Russelin (next to Mont Terri) such pore waters were recently detected (Koroleva and Mazurek 2009), does imply that such high salinities may not be ruled out in the absence of proof to the contrary. A “Mont Russelin” variant (high-salinity) of an Opalinus Clay pore water is modelled below based on data obtained from Mont Russelin.

Sample NT-7 (Koroleva and Mazurek 2009, Table 4-6, Table 4-7) was chosen. It shows the highest chloride content, has an acceptable charge balance (3.1 %), has consistent chloride concentrations from leaching and squeezing, does show a SO_4/Cl ratio slightly below that of sea water, a Br/Cl ratio very near sea water, and a Ca/Mg molal ratio of 1.68 that is somewhat too high for simultaneous calcite-dolomite equilibrium (should be near 1.33). Aqueous leaching (at University Bern) and squeezing (at CIEMAT) were not performed in a glove box environment, and some generation of sulphate from pyrite oxidation may be expected. The squeezed aliquot from NT-7 did have a pH of 4.47 and contained minor thiosulphate, both indicative of pyrite oxidation and related redox processes that may be active during drill core storage, squeezing and storage of the aliquot. The relative high Ca/Mg ratio will lead to adjustments (decrease in Ca and/or increase in Mg) during modelling when imposing saturation constraints with respect to calcite and dolomite. A subset of the analysis by the British Geological Survey is given in Table 6-3 based on Koroleva and Mazurek (2009).

The modelling approach chosen is somewhat different from the one presented in Section 6.3 because no cation populations were determined on the clay exchanger. The composition of pore water samples from squeezing are used instead, combined with saturation constraints given by the mineralogy that is identical to that at Mont Terri or Benken. Gypsum was used as an additional saturation limit due to the observation that final solutions were oversaturated with respect to gypsum. A partial pressure of CO_2 of $10^{-2.5}$ bar was chosen, to yield a final pH of near 7. A higher P_{CO_2} would lead to a lower pH. The redox system was treated the same as in Section 6.3, namely imposing siderite and pyrite saturation. The Phreeqc input file listed below, and the modelling result is given in Table 6-3. A printout of the full speciation and other solution parameters are provided in Appendix 2.

```
DATABASE NAPSI_300401DAV.DAT
TITLE  Ref pore water for Opalinus Clay and Brown Dogger
TITLE  High-salinity version based on Mont Russlin
SOLUTION 1 OPA_MontRusslin
# Koroleva&Mazurek 2009 Mont Terri TN 2006-24
# sample NT-7, squeezing CIEMAT + BGS Analyses
  pe      4.0 # initial value only
  redox  pe
  temp 25.0
  -units mol/kgw
  pH      7.0
  Cl      0.644 charge # 22.8 g/l
  S       0.0291      # initial SO4/Cl ratio of 0.045
  Na      0.5273
  K       0.00177
  Ca      0.05928
  Mg      0.03522
  Sr      0.00097
EQUILIBRIUM_PHASES 1
  CO2(g) -2.5      # range -1.8 to -2.8
  Calcite 0.0
  Dolomite(ord) 0.0
  Quartz 0.0
  Celestite 0.0
  Siderite 0.0
  Pyrite 0.0
  Gypsum 0.0 0.0
END
```

Compared to the input concentrations, the main adjustments required by the mineral saturation constraints result in a decrease of the Ca concentrations (calcite-dolomite equilibrium), a decrease in sulphate concentrations (limited by gypsum and celestite saturation), and a decrease in Sr concentration (celestite saturation). The final total alkalinity is just below 1 mmol/l, and the calculated pe is -2.563 at a pH of 7.009.

Tab. 6-3: Input and modelled composition of the Mont Russelin variant (high-salinity) of the reference pore water for the Opalinus Clay Formation.

Parameter	Units	Value Input	Value Mont Russelin	Comment
Temperature	°C	ambient	25	
pH		7.0	7.009	
pe			-2.563	siderite-pyrite equilibrium
Na (total)	mmol/kg _{H2O}	527.3	527.5	
K (total)	mmol/kg _{H2O}	1.77	1.77	
Ca (total)	mmol/kg _{H2O}	59.28	49.71	
Mg (total)	mmol/kg _{H2O}	35.22	37.55	
Sr (total)	mmol/kg _{H2O}	0.97	0.422	
Fe ^{II} (total)	mmol/kg _{H2O}		0.246	
Fe ^{III} (total)	mmol/kg _{H2O}		8.23·10 ⁻⁹	
Si (total)	mmol/kg _{H2O}		0.172	
Cl (total)	mmol/kg _{H2O}	644.0	662.0	charge balance
S ^{VI} (total)	mmol/kg _{H2O}	29.1	21.06	
S ^{II} (total)	mmol/kg _{H2O}		6.11·10 ⁻⁹	
C ^{IV} (total)	mmol/kg _{H2O}		1.057	
SO ₄ /Cl	mol/mol	0.045	0.032	
Alkalinity	Meq/kg _{H2O}		0.962	total alkalinity
HCO ₃ (species)	mmol/kg _{H2O}		0.631	
P(CO ₂)	bar	10 ^{-2.50}	10 ^{-2.50}	specified
Water activity			0.978	
Ionic strength	molal		0.762	
SI(gypsum)			0.00	
SI(strontianite)			-1.28	
Accessible porosity	% of water-loss porosity		50	

Calculations performed with Phreeqc (version 2.15.07) and Nagra-PSI data base Version 01/01. The solution is saturated with respect to calcite, dolomite (ordered), celestite, quartz, siderite and pyrite. Detailed speciation and solution parameters are given in Appendix 2.

6.5 Discussion and uncertainties

The reference pore water proposed above and listed in Table 6-2 is almost identical in its major components compared to that of Pearson (2002) and thus will result in very similar sorption and solubility properties for radionuclides. The revisions were performed to avoid the supersaturation with respect to celestite of the Pearson (2002) / Nagra (2002) reference pore water, and to decrease the dissolved potassium concentrations by adjusting the ion exchange equilibrium constant. This latter aspect could likely be further improved by a more careful data analysis at this specific potassium site occupancy which is relatively low compared to most constraining experimental literature data.

The main difference is the much reduced uncertainty in the partial pressure of CO₂ compared to the state of knowledge in 2002. Applying the same model with an upper limit of 10^{-1.8} bar and a lower limit of 10^{-2.8} bar, the following range in critical parameters is obtained (Table 6-4). As discussed above, a range in salinity has a comparatively minor influence on the relevant parameters (see results in Pearson 2002, for example). The variants of the pore water were created by simply changing the specified partial pressure of CO₂ to either 10^{-1.8} or 10^{-2.8} bar, as indicated in a comment in the Phreeqc input file listed in Section 6.2. Full listings of the speciation and other solution properties are given in Appendix 3.

This proposed reduced range of uncertainty may not yet be fully established (e.g. not yet confirmed at another location), but it reflects the current concert opinion of the geochemists involved at Mont Terri in experimental and modelling work, as indicated in latest published summaries (De Cannière et al. 2008, Wersin et al. 2009). The resultant range in pH is only 0.5 units, and the alkalinities differ by a factor of 3. This compares to a range of 1.0 pH unit and a factor of nearly 10 for alkalinity in Pearson (2002).

Tab. 6-4: Sensitivity of parameters in the reference pore water to a range in P_{CO_2}

Parameter	Units	$P_{CO_2}=10^{-1.8}$ bar	$P_{CO_2}=10^{-2.8}$ bar	Comment
Temperature	°C	25	25	
pH		7.001	7.505	
pε		-2.550	-3.126	Siderite-pyrite equilibrium
Na (total)	mmol/kg _{H2O}	165.0	163.8	
K (total)	mmol/kg _{H2O}	2.616	2.594	
Ca (total)	mmol/kg _{H2O}	12.68	12.37	
Mg (total)	mmol/kg _{H2O}	9.748	9.519	
Sr (total)	mmol/kg _{H2O}	0.2124	0.2091	
Fe ^{II} (total)	mmol/kg _{H2O}	0.0542	0.0509	
Fe ^{III} (total)	mmol/kg _{H2O}	$1.73 \cdot 10^{-9}$	$9.72 \cdot 10^{-9}$	
Si (total)	mmol/kg _{H2O}	0.178	0.179	
Cl (total)	mmol/kg _{H2O}	160.0	160.0	
S ^{VI} (total)	mmol/kg _{H2O}	24.70	24.74	
S ^{II} (total)	mmol/kg _{H2O}	$13.7 \cdot 10^{-9}$	$11.6 \cdot 10^{-9}$	
C ^{IV} (total)	mmol/kg _{H2O}	4.148	1.214	
SO ₄ /Cl	mol/mol	0.154	0.155	
Alkalinity	meq/kg _{H2O}	3.624	1.178	total alkalinity
HCO ₃ (species)	mmol/kg _{H2O}	3.222	1.028	
P(CO ₂)	bar	$10^{-1.80}$	$10^{-2.80}$	specified
Water activity		0.994	0.994	
Ionic strength	molal	0.231	0.229	
SI(gypsum)		-0.28	-0.29	
SI(strontianite)		-0.98	-0.98	
Accessible porosity	% of water-loss porosity	50	50	

Calculations performed with Phreeqc (version 2.15.07) and Nagra-PSI data base Version 01/01. The solution is saturated with respect to calcite, dolomite (ordered), celestite, quartz, siderite and pyrite. Detailed speciation and solution parameters are given in Appendix 3.

The “Mont Russelin” variant (Section 6-4) bears the same type of uncertainty with respect to the variables pH, P_{CO_2} and alkalinity as discussed above and illustrated in Table 6-4. The data base for Mont Russelin is comparatively small, lacking constraints on the ion-exchanger site occupancies, or any direct constraints on pH, alkalinity or P_{CO_2} . The choice was made to impose a partial pressure of CO₂ of $10^{-2.5}$ bar rather than $10^{-2.2}$ bar as in the "Mont Russelin" variant of the reference pore water. This choice was made to let the final pH not drop below 7. This choice leads also to a somewhat lower alkalinity compared to the reference pore water.

7 Reference porewater for "Brown Dogger"

7.1 Existing data on pore water composition

The data base for the "Brown Dogger" is limited to the work performed on the Benken borehole, and some unpublished chloride leaching data from Weiach (Nördliche Lägern, H.N. Waber, pers. comm.) that are difficult to scale to pore water chlorinity due to unreliable porosity data (see discussion in Section 6.1 with respect to Opalinus Clay).

The only truly quantitative constraints are from the Benken borehole, where chloride concentrations scaled to porosity show the same values as in the underlying Opalinus Clay for the lower part of the "Brown Dogger" in contact with Opalinus Clay (Nagra 2002). Opalinus Clay and "Brown Dogger" combined show a distinctly curved diffusion profile (Nagra 2002, Gimmi and Waber 2004, Mazurek et al. 2009). The profile is distinctly asymmetric with very low chlorinities at the lower bounding aquifer (Keuper, ca. 500 mg/L), and much higher chlorinities of ca. 4600 mg/L at the top, towards the Malm aquifer.

The mineralogy is very similar to that of Opalinus Clay including clay mineralogy and accessories (Nagra 2001, Nagra 1989) as summarized in Mazurek (in prep.). The same is true for the hydraulic properties (Nagra 2002).

7.2 Reference pore water for "Brown Dogger"

Based on the lack of directly constraining data on porewater chemistry and the evidence for a similar mineralogical and hydraulic environment, choosing a reference pore water identical to the one suggested for Opalinus Clay is reasonable, and defensible until additional data may prove this hypothesis in need for revision. Along the same line of argument, also the "Mont Russelin" variant may be adopted as a high-salinity limit for a reference pore water.

7.3 Discussion and uncertainties

There is no estimation of uncertainties possible – other than those discussed for Opalinus Clay – in the absence of constraining data. Choosing an Opalinus Clay-type pore water reflects the present state of knowledge.

8 Acknowledgements

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10 Appendix 1: Reference pore water (OPA and BD)

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.

```

-----Description of solution-----
                                pH = 7.203      Charge balance
                                pe = -2.781     Adjusted to redox equilibrium
      Activity of water          = 0.994
      Ionic strength             = 2.299e-01
      Mass of water (kg)        = 1.000e+00
      Total alkalinity (eq/kg)   = 2.308e-03
      Total CO2 (mol/kg)        = 2.506e-03
      Temperature (deg C)       = 25.000
      Electrical balance (eq)    = -1.349e-10
      Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
      Iterations                 = 18
      Total H                    = 1.110186e+02
      Total O                    = 5.561470e+01
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	2.141e-07	1.587e-07	-6.669	-6.799	-0.130
H+	8.455e-08	6.269e-08	-7.073	-7.203	-0.130
H2O	5.551e+01	9.938e-01	1.744	-0.003	0.000
C(-4)	2.907e-18				
CH4	2.907e-18	2.907e-18	-17.537	-17.537	0.000
C(4)	2.506e-03				
HCO3-	2.043e-03	1.515e-03	-2.690	-2.820	-0.130
CO2	2.148e-04	2.148e-04	-3.668	-3.668	0.000
NaHCO3	1.013e-04	1.013e-04	-3.994	-3.994	0.000
CaHCO3+	7.617e-05	5.648e-05	-4.118	-4.248	-0.130
MgHCO3+	5.180e-05	3.840e-05	-4.286	-4.416	-0.130
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000
CO3-2	3.749e-06	1.133e-06	-5.426	-5.946	-0.520
NaCO3-	3.384e-06	2.509e-06	-5.471	-5.600	-0.130
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000
FeHCO3+	2.322e-06	1.722e-06	-5.634	-5.764	-0.130
SrHCO3+	1.544e-06	1.145e-06	-5.811	-5.941	-0.130
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000
SrCO3	3.574e-08	3.574e-08	-7.447	-7.447	0.000
Ca	1.251e-02				
Ca+2	9.673e-03	2.923e-03	-2.014	-2.534	-0.520
CaSO4	2.755e-03	2.755e-03	-2.560	-2.560	0.000
CaHCO3+	7.617e-05	5.648e-05	-4.118	-4.248	-0.130
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000
CaSiO(OH)3+	2.736e-08	2.029e-08	-7.563	-7.693	-0.130
CaOH+	1.037e-08	7.691e-09	-7.984	-8.114	-0.130
CaSiO2(OH)2	3.803e-11	3.803e-11	-10.420	-10.420	0.000
Cl	1.600e-01				
Cl-	1.600e-01	1.186e-01	-0.796	-0.926	-0.130
FeCl+	2.511e-06	1.861e-06	-5.600	-5.730	-0.130
FeCl+2	2.129e-20	6.434e-21	-19.672	-20.192	-0.520
FeCl2+	4.598e-21	3.409e-21	-20.337	-20.467	-0.130
FeCl3	4.044e-23	4.044e-23	-22.393	-22.393	0.000
Fe(2)	5.238e-05				
Fe+2	3.762e-05	1.137e-05	-4.425	-4.944	-0.520
FeSO4	9.548e-06	9.548e-06	-5.020	-5.020	0.000
FeCl+	2.511e-06	1.861e-06	-5.600	-5.730	-0.130
FeHCO3+	2.322e-06	1.722e-06	-5.634	-5.764	-0.130
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000
FeOH+	7.686e-08	5.699e-08	-7.114	-7.244	-0.130
FeHSO4+	5.309e-12	3.936e-12	-11.275	-11.405	-0.130

Fe(3)	3.311e-12					
Fe(OH)3	1.971e-12	1.971e-12	-11.705	-11.705	0.000	
Fe(OH)2+	1.301e-12	9.649e-13	-11.886	-12.016	-0.130	
Fe(OH)4-	3.843e-14	2.849e-14	-13.415	-13.545	-0.130	
FeOH+2	6.083e-16	1.838e-16	-15.216	-15.736	-0.520	
FeSiO(OH)3+2	1.304e-17	3.941e-18	-16.885	-17.404	-0.520	
FeSO4+	1.254e-19	9.300e-20	-18.902	-19.031	-0.130	
Fe+3	2.652e-20	1.796e-21	-19.576	-20.746	-1.169	
FeCl+2	2.129e-20	6.434e-21	-19.672	-20.192	-0.520	
Fe(SO4)2-	1.296e-20	9.610e-21	-19.887	-20.017	-0.130	
FeCl2+	4.598e-21	3.409e-21	-20.337	-20.467	-0.130	
FeCl3	4.044e-23	4.044e-23	-22.393	-22.393	0.000	
FeHSO4+2	5.169e-26	1.562e-26	-25.287	-25.806	-0.520	
Fe2(OH)2+4	1.091e-28	9.094e-31	-27.962	-30.041	-2.079	
Fe3(OH)4+5	3.247e-37	1.833e-40	-36.489	-39.737	-3.248	
H(0)	2.252e-12					
H2	1.126e-12	1.126e-12	-11.948	-11.948	0.000	
K	2.604e-03					
K+	2.520e-03	1.868e-03	-2.599	-2.729	-0.130	
KSO4-	8.425e-05	6.246e-05	-4.074	-4.204	-0.130	
KOH	1.027e-10	1.027e-10	-9.988	-9.988	0.000	
Mg	9.625e-03					
Mg+2	7.171e-03	2.167e-03	-2.144	-2.664	-0.520	
MgSO4	2.399e-03	2.399e-03	-2.620	-2.620	0.000	
MgHCO3+	5.180e-05	3.840e-05	-4.286	-4.416	-0.130	
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000	
MgOH+	1.682e-07	1.247e-07	-6.774	-6.904	-0.130	
MgSiO(OH)3+	4.047e-08	3.001e-08	-7.393	-7.523	-0.130	
MgSiO2(OH)2	3.549e-10	3.549e-10	-9.450	-9.450	0.000	
Na	1.644e-01					
Na+	1.605e-01	1.190e-01	-0.795	-0.925	-0.130	
NaSO4-	3.798e-03	2.816e-03	-2.420	-2.550	-0.130	
NaHCO3	1.013e-04	1.013e-04	-3.994	-3.994	0.000	
NaCO3-	3.384e-06	2.509e-06	-5.471	-5.600	-0.130	
NaOH	1.246e-08	1.246e-08	-7.904	-7.904	0.000	
O(0)	0.000e+00					
O2	0.000e+00	0.000e+00	-68.306	-68.306	0.000	
S(-2)	1.240e-11					
HS-	8.524e-12	6.320e-12	-11.069	-11.199	-0.130	
H2S	3.872e-12	3.872e-12	-11.412	-11.412	0.000	
S-2	3.336e-23	1.008e-23	-22.477	-22.996	-0.520	
S(2)	2.631e-16					
S2O3-2	1.315e-16	3.975e-17	-15.881	-16.401	-0.520	
S(4)	1.288e-14					
SO3-2	9.044e-15	2.733e-15	-14.044	-14.563	-0.520	
HSO3-	3.837e-15	2.845e-15	-14.416	-14.546	-0.130	
S(6)	2.472e-02					
SO4-2	1.563e-02	4.723e-03	-1.806	-2.326	-0.520	
NaSO4-	3.798e-03	2.816e-03	-2.420	-2.550	-0.130	
CaSO4	2.755e-03	2.755e-03	-2.560	-2.560	0.000	
MgSO4	2.399e-03	2.399e-03	-2.620	-2.620	0.000	
KSO4-	8.425e-05	6.246e-05	-4.074	-4.204	-0.130	
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000	
FeSO4	9.548e-06	9.548e-06	-5.020	-5.020	0.000	
HSO4-	3.883e-08	2.879e-08	-7.411	-7.541	-0.130	
FeHSO4+	5.309e-12	3.936e-12	-11.275	-11.405	-0.130	
FeSO4+	1.254e-19	9.300e-20	-18.902	-19.031	-0.130	
Fe(SO4)2-	1.296e-20	9.610e-21	-19.887	-20.017	-0.130	
FeHSO4+2	5.169e-26	1.562e-26	-25.287	-25.806	-0.520	
Si	1.779e-04					
Si(OH)4	1.772e-04	1.772e-04	-3.751	-3.751	0.000	
SiO(OH)3-	5.906e-07	4.379e-07	-6.229	-6.359	-0.130	
MgSiO(OH)3+	4.047e-08	3.001e-08	-7.393	-7.523	-0.130	
CaSiO(OH)3+	2.736e-08	2.029e-08	-7.563	-7.693	-0.130	
MgSiO2(OH)2	3.549e-10	3.549e-10	-9.450	-9.450	0.000	
CaSiO2(OH)2	3.803e-11	3.803e-11	-10.420	-10.420	0.000	
SiO2(OH)2-2	1.081e-12	3.268e-13	-11.966	-12.486	-0.520	
FeSiO(OH)3+2	1.304e-17	3.941e-18	-16.885	-17.404	-0.520	
Sr	2.106e-04					
Sr+2	1.635e-04	4.942e-05	-3.786	-4.306	-0.520	
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000	
SrHCO3+	1.544e-06	1.145e-06	-5.811	-5.941	-0.130	
SrCO3	3.574e-08	3.574e-08	-7.447	-7.447	0.000	
SrOH+	5.419e-11	4.018e-11	-10.266	-10.396	-0.130	

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

Phase	SI	log IAP	log KT	
Anhydrite	-0.50	-4.86	-4.36	CaSO4
Aragonite	-0.14	1.85	1.99	CaCO3
Brucite	-5.10	11.74	16.84	Mg(OH)2
Calcite	0.00	1.85	1.85	CaCO3
Celestite	0.00	-6.63	-6.63	SrSO4
CH4 (g)	-14.68	-17.54	-2.86	CH4
CO2 (g)	-2.20	-10.02	-7.82	CO2
Dolomite (dis)	-0.55	3.57	4.12	CaMg (CO3)2
Dolomite (ord)	0.00	3.57	3.57	CaMg (CO3)2
Fe (cr)	-13.20	0.62	13.82	Fe
Fe (OH)3 (am)	-4.15	0.85	5.00	Fe (OH)3
Fe (OH)3 (mic)	-2.15	0.85	3.00	Fe (OH)3
FeCO3 (pr)	-0.44	-0.56	-0.12	FeCO3
Goethite	1.86	0.86	-1.00	FeOOH
Graphite	-5.88	-27.70	-21.82	C
Gypsum	-0.28	-4.87	-4.58	CaSO4:2H2O
H2 (g)	-8.84	-11.95	-3.11	H2
H2S (g)	-10.39	-18.40	-8.01	H2S
Hematite	0.60	1.72	1.12	Fe2O3
Magnesite	-0.32	1.72	2.04	MgCO3
Magnetite	1.16	11.18	10.02	Fe3O4
Melanterite	-5.08	-7.29	-2.21	FeSO4:7H2O
O2 (g)	-65.41	-68.31	-2.89	O2
Portlandite	-10.93	11.87	22.80	Ca(OH)2
Pyrite	0.00	-18.50	-18.50	FeS2
Quartz	0.00	-3.75	-3.75	SiO2
S (rhomb)	-7.42	-9.56	-2.14	S
Siderite	-0.00	-0.56	-0.56	FeCO3
SiO2 (am)	-1.03	-3.75	-2.71	SiO2
Strontianite	-0.98	0.08	1.06	SrCO3
Troilite	-3.63	-8.94	-5.31	FeS

11 Appendix 2: "Mont Russelin" variant of reference pore water (OPA and BD)

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.

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-----Description of solution-----
                                pH = 7.009          Charge balance
                                pe = -2.563          Adjusted to redox equilibrium
                                Activity of water = 0.978
                                Ionic strength = 7.622e-01
                                Mass of water (kg) = 9.997e-01
                                Total alkalinity (eq/kg) = 9.620e-04
                                Total CO2 (mol/kg) = 1.057e-03
                                Temperature (deg C) = 25.000
                                Electrical balance (eq) = -2.598e-15
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
                                Iterations = 11
                                Total H = 1.109886e+02
                                Total O = 5.558145e+01
-----Distribution of species-----
Species              Molality    Activity    Log Molality    Log Activity    Log Gamma
OH-                  1.320e-07    9.993e-08    -6.879          -7.000          -0.121
H+                   1.295e-07    9.800e-08    -6.888          -7.009          -0.121
H2O                  5.551e+01    9.781e-01    1.744          -0.010          0.000
C(-4)                9.555e-19
CH4                  9.555e-19    9.555e-19    -18.020        -18.020         0.000
C(4)                 1.057e-03
HCO3-                6.314e-04    4.779e-04    -3.200          -3.321          -0.121
CaHCO3+              1.166e-04    8.829e-05    -3.933          -4.054          -0.121
CO2                  1.077e-04    1.077e-04    -3.968          -3.968          0.000
NaHCO3               1.063e-04    1.063e-04    -3.974          -3.974          0.000
MgHCO3+              7.931e-05    6.004e-05    -4.101          -4.222          -0.121
CaCO3                5.549e-06    5.549e-06    -5.256          -5.256          0.000
FeHCO3+              3.556e-06    2.692e-06    -5.449          -5.570          -0.121
MgCO3                2.343e-06    2.343e-06    -5.630          -5.630          0.000
NaCO3-               2.224e-06    1.684e-06    -5.653          -5.774          -0.121
SrHCO3+              1.190e-06    9.008e-07    -5.924          -6.045          -0.121
CO3-2                6.966e-07    2.287e-07    -6.157          -6.641          -0.484
FeCO3                3.089e-07    3.089e-07    -6.510          -6.510          0.000
SrCO3                1.799e-08    1.799e-08    -7.745          -7.745          0.000
Ca                    4.971e-02
Ca+2                 4.411e-02    1.448e-02    -1.355          -1.839          -0.484
CaSO4                5.474e-03    5.474e-03    -2.262          -2.262          0.000
CaHCO3+              1.166e-04    8.829e-05    -3.933          -4.054          -0.121
CaCO3                5.549e-06    5.549e-06    -5.256          -5.256          0.000
CaSiO(OH)3+          8.229e-08    6.229e-08    -7.085          -7.206          -0.121
CaOH+                3.169e-08    2.399e-08    -7.499          -7.620          -0.121
CaSiO2(OH)2          7.468e-11    7.468e-11    -10.127         -10.127         0.000
Cl                    6.620e-01
Cl-                  6.619e-01    5.011e-01    -0.179          -0.300          -0.121
FeCl+                5.146e-05    3.895e-05    -4.289          -4.409          -0.121
FeCl+2               6.785e-19    2.227e-19    -18.168         -18.652         -0.484
FeCl2+               6.586e-19    4.985e-19    -18.181         -18.302         -0.121
FeCl3                2.498e-20    2.498e-20    -19.602         -19.602         0.000
Fe(2)                2.461e-04
Fe+2                 1.715e-04    5.632e-05    -3.766          -4.249          -0.484
FeCl+                5.146e-05    3.895e-05    -4.289          -4.409          -0.121
FeSO4                1.897e-05    1.897e-05    -4.722          -4.722          0.000
FeHCO3+              3.556e-06    2.692e-06    -5.449          -5.570          -0.121
FeCO3                3.089e-07    3.089e-07    -6.510          -6.510          0.000
FeOH+                2.348e-07    1.778e-07    -6.629          -6.750          -0.121
FeHSO4+              1.615e-11    1.223e-11    -10.792         -10.913         -0.121

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Fe (3)	8.225e-12					
Fe (OH) 2+	4.142e-12	3.135e-12	-11.383	-11.504	-0.121	
Fe (OH) 3	4.031e-12	4.031e-12	-11.395	-11.395	0.000	
Fe (OH) 4-	4.848e-14	3.670e-14	-13.314	-13.435	-0.121	
FeOH+2	2.890e-15	9.486e-16	-14.539	-15.023	-0.484	
FeSiO (OH) 3+2	6.099e-17	2.002e-17	-16.215	-16.698	-0.484	
FeCl+2	6.785e-19	2.227e-19	-18.168	-18.652	-0.484	
FeCl2+	6.586e-19	4.985e-19	-18.181	-18.302	-0.121	
FeSO4+	4.039e-19	3.058e-19	-18.394	-18.515	-0.121	
Fe+3	1.804e-19	1.472e-20	-18.744	-19.832	-1.088	
FeCl3	2.498e-20	2.498e-20	-19.602	-19.602	0.000	
Fe (SO4) 2-	1.674e-20	1.267e-20	-19.776	-19.897	-0.121	
FeHSO4+2	2.445e-25	8.028e-26	-24.612	-25.095	-0.484	
Fe2 (OH) 2+4	2.085e-27	2.422e-29	-26.681	-28.616	-1.935	
Fe3 (OH) 4+5	1.674e-35	1.587e-38	-34.776	-37.800	-3.023	
H (0)	2.011e-12					
H2	1.006e-12	1.006e-12	-11.998	-11.998	0.000	
K	1.771e-03					
K+	1.747e-03	1.322e-03	-2.758	-2.879	-0.121	
KSO4-	2.343e-05	1.774e-05	-4.630	-4.751	-0.121	
KOH	4.577e-11	4.577e-11	-10.339	-10.339	0.000	
Mg	3.755e-02					
Mg+2	3.270e-02	1.074e-02	-1.485	-1.969	-0.484	
MgSO4	4.768e-03	4.768e-03	-2.322	-2.322	0.000	
MgHCO3+	7.931e-05	6.004e-05	-4.101	-4.222	-0.121	
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000	
MgOH+	5.140e-07	3.891e-07	-6.289	-6.410	-0.121	
MgSiO (OH) 3+	1.217e-07	9.213e-08	-6.915	-7.036	-0.121	
MgSiO2 (OH) 2	6.970e-10	6.970e-10	-9.157	-9.157	0.000	
Na	5.275e-01					
Na+	5.224e-01	3.954e-01	-0.282	-0.403	-0.121	
NaSO4-	4.960e-03	3.754e-03	-2.305	-2.425	-0.121	
NaHCO3	1.063e-04	1.063e-04	-3.974	-3.974	0.000	
NaCO3-	2.224e-06	1.684e-06	-5.653	-5.774	-0.121	
NaOH	2.608e-08	2.608e-08	-7.584	-7.584	0.000	
O (0)	0.000e+00					
O2	0.000e+00	0.000e+00	-68.221	-68.221	0.000	
S (-2)	6.114e-12					
HS-	3.544e-12	2.683e-12	-11.450	-11.571	-0.121	
H2S	2.569e-12	2.569e-12	-11.590	-11.590	0.000	
S-2	8.339e-24	2.738e-24	-23.079	-23.563	-0.484	
S (2)	6.549e-17					
S2O3-2	3.274e-17	1.075e-17	-16.485	-16.969	-0.484	
S (4)	5.166e-15					
SO3-2	3.029e-15	9.944e-16	-14.519	-15.002	-0.484	
HSO3-	2.137e-15	1.618e-15	-14.670	-14.791	-0.121	
S (6)	2.106e-02					
SO4-2	5.770e-03	1.894e-03	-2.239	-2.723	-0.484	
CaSO4	5.474e-03	5.474e-03	-2.262	-2.262	0.000	
NaSO4-	4.960e-03	3.754e-03	-2.305	-2.425	-0.121	
MgSO4	4.768e-03	4.768e-03	-2.322	-2.322	0.000	
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000	
KSO4-	2.343e-05	1.774e-05	-4.630	-4.751	-0.121	
FeSO4	1.897e-05	1.897e-05	-4.722	-4.722	0.000	
HSO4-	2.385e-08	1.805e-08	-7.623	-7.744	-0.121	
FeHSO4+	1.615e-11	1.223e-11	-10.792	-10.913	-0.121	
FeSO4+	4.039e-19	3.058e-19	-18.394	-18.515	-0.121	
Fe (SO4) 2-	1.674e-20	1.267e-20	-19.776	-19.897	-0.121	
FeHSO4+2	2.445e-25	8.028e-26	-24.612	-25.095	-0.484	
Si	1.723e-04					
Si (OH) 4	1.717e-04	1.717e-04	-3.765	-3.765	0.000	
SiO (OH) 3-	3.585e-07	2.714e-07	-6.445	-6.566	-0.121	
MgSiO (OH) 3+	1.217e-07	9.213e-08	-6.915	-7.036	-0.121	
CaSiO (OH) 3+	8.229e-08	6.229e-08	-7.085	-7.206	-0.121	
MgSiO2 (OH) 2	6.970e-10	6.970e-10	-9.157	-9.157	0.000	
CaSiO2 (OH) 2	7.468e-11	7.468e-11	-10.127	-10.127	0.000	
SiO2 (OH) 2-2	3.945e-13	1.295e-13	-12.404	-12.888	-0.484	
FeSiO (OH) 3+2	6.099e-17	2.002e-17	-16.215	-16.698	-0.484	
Sr	4.220e-04					
Sr+2	3.753e-04	1.232e-04	-3.426	-3.909	-0.484	
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000	
SrHCO3+	1.190e-06	9.008e-07	-5.924	-6.045	-0.121	
SrCO3	1.799e-08	1.799e-08	-7.745	-7.745	0.000	
SrOH+	8.332e-11	6.307e-11	-10.079	-10.200	-0.121	

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

Phase	SI	log IAP	log KT	
Anhydrite	-0.20	-4.56	-4.36	CaSO4
Aragonite	-0.14	1.85	1.99	CaCO3
Brucite	-4.81	12.03	16.84	Mg(OH)2
Calcite	-0.00	1.85	1.85	CaCO3
Celestite	0.00	-6.63	-6.63	SrSO4
CH4 (g)	-15.16	-18.02	-2.86	CH4
CO2 (g)	-2.50	-10.32	-7.82	CO2
Dolomite (dis)	-0.55	3.57	4.12	CaMg (CO3)2
Dolomite (ord)	0.00	3.57	3.57	CaMg (CO3)2
Fe (cr)	-12.95	0.88	13.82	Fe
Fe (OH)3 (am)	-3.83	1.17	5.00	Fe (OH)3
Fe (OH)3 (mic)	-1.83	1.17	3.00	Fe (OH)3
FeCO3 (pr)	-0.44	-0.56	-0.12	FeCO3
Goethite	2.18	1.18	-1.00	FeOOH
Graphite	-6.27	-28.08	-21.82	C
Gypsum	0.00	-4.58	-4.58	CaSO4:2H2O
H2 (g)	-8.89	-12.00	-3.11	H2
H2S (g)	-10.57	-18.58	-8.01	H2S
Hematite	1.24	2.36	1.12	Fe2O3
Magnesite	-0.32	1.72	2.04	MgCO3
Magnetite	2.10	12.12	10.02	Fe3O4
Melanterite	-4.83	-7.04	-2.21	FeSO4:7H2O
O2 (g)	-65.33	-68.22	-2.89	O2
Portlandite	-10.64	12.16	22.80	Ca(OH)2
Pyrite	-0.00	-18.50	-18.50	FeS2
Quartz	0.00	-3.75	-3.75	SiO2
S (rhomb)	-7.54	-9.69	-2.14	S
Siderite	-0.00	-0.56	-0.56	FeCO3
SiO2 (am)	-1.03	-3.75	-2.71	SiO2
Strontianite	-1.28	-0.22	1.06	SrCO3
Troilite	-3.50	-8.81	-5.31	FeS

12 Appendix 3: High- P_{CO_2} and Low- P_{CO_2} variants of reference pore water (OPA and BD)

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.

High- P_{CO_2} variant ($10^{-1.8}$ bar)

```

-----Description of solution-----
                                pH = 7.001      Charge balance
                                pe = -2.550      Adjusted to redox equilibrium
                                Activity of water = 0.994
                                Ionic strength  = 2.311e-01
                                Mass of water (kg) = 1.000e+00
                                Total alkalinity (eq/kg) = 3.624e-03
                                Total CO2 (mol/kg) = 4.148e-03
                                Temperature (deg C) = 25.000
                                Electrical balance (eq) = 2.437e-11
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 0.00
                                Iterations = 11
                                Total H = 1.110186e+02
                                Total O = 5.561855e+01
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.347e-07	9.984e-08	-6.871	-7.001	-0.130
OH-	1.344e-07	9.964e-08	-6.872	-7.002	-0.130
H2O	5.551e+01	9.937e-01	1.744	-0.003	0.000
C(-4)	4.285e-18				
CH4	4.285e-18	4.285e-18	-17.368	-17.368	0.000
C(4)	4.148e-03				
HCO3-	3.222e-03	2.389e-03	-2.492	-2.622	-0.130
CO2	5.396e-04	5.396e-04	-3.268	-3.268	0.000
NaHCO3	1.604e-04	1.604e-04	-3.795	-3.795	0.000
CaHCO3+	1.214e-04	8.995e-05	-3.916	-4.046	-0.130
MgHCO3+	8.252e-05	6.117e-05	-4.083	-4.213	-0.130
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000
CO3-2	3.716e-06	1.122e-06	-5.430	-5.950	-0.520
FeHCO3+	3.700e-06	2.742e-06	-5.432	-5.562	-0.130
NaCO3-	3.364e-06	2.493e-06	-5.473	-5.603	-0.130
SrHCO3+	2.446e-06	1.813e-06	-5.612	-5.742	-0.130
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000
SrCO3	3.554e-08	3.554e-08	-7.449	-7.449	0.000
Ca	1.268e-02				
Ca+2	9.780e-03	2.952e-03	-2.010	-2.530	-0.520
CaSO4	2.771e-03	2.771e-03	-2.557	-2.557	0.000
CaHCO3+	1.214e-04	8.995e-05	-3.916	-4.046	-0.130
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000
CaSiO(OH) 3+	1.735e-08	1.286e-08	-7.761	-7.891	-0.130
CaOH+	6.579e-09	4.877e-09	-8.182	-8.312	-0.130
CaSiO2(OH) 2	1.514e-11	1.514e-11	-10.820	-10.820	0.000
Cl	1.600e-01				
Cl-	1.600e-01	1.186e-01	-0.796	-0.926	-0.130
FeCl+	2.536e-06	1.880e-06	-5.596	-5.726	-0.130
FeCl+2	3.664e-20	1.106e-20	-19.436	-19.956	-0.520
FeCl2+	7.905e-21	5.859e-21	-20.102	-20.232	-0.130
FeCl3	6.949e-23	6.949e-23	-22.158	-22.158	0.000
Fe(2)	5.423e-05				
Fe+2	3.803e-05	1.148e-05	-4.420	-4.940	-0.520
FeSO4	9.602e-06	9.602e-06	-5.018	-5.018	0.000

FeHCO3+	3.700e-06	2.742e-06	-5.432	-5.562	-0.130
FeCl+	2.536e-06	1.880e-06	-5.596	-5.726	-0.130
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000
FeOH+	4.875e-08	3.613e-08	-7.312	-7.442	-0.130
FeHSO4+	8.506e-12	6.305e-12	-11.070	-11.200	-0.130
Fe (3)	1.732e-12				
Fe (OH) 2+	8.823e-13	6.540e-13	-12.054	-12.184	-0.130
Fe (OH) 3	8.385e-13	8.385e-13	-12.077	-12.077	0.000
Fe (OH) 4-	1.027e-14	7.611e-15	-13.989	-14.119	-0.130
FeOH+2	6.573e-16	1.984e-16	-15.182	-15.702	-0.520
FeSiO (OH) 3+2	1.409e-17	4.255e-18	-16.851	-17.371	-0.520
FeSO4+	2.148e-19	1.592e-19	-18.668	-18.798	-0.130
Fe+3	4.571e-20	3.088e-21	-19.340	-20.510	-1.170
FeCl+2	3.664e-20	1.106e-20	-19.436	-19.956	-0.520
Fe (SO4) 2-	2.210e-20	1.638e-20	-19.656	-19.786	-0.130
FeCl2+	7.905e-21	5.859e-21	-20.102	-20.232	-0.130
FeCl3	6.949e-23	6.949e-23	-22.158	-22.158	0.000
FeHSO4+2	1.411e-25	4.260e-26	-24.850	-25.371	-0.520
Fe2 (OH) 2+4	1.276e-28	1.060e-30	-27.894	-29.975	-2.081
Fe3 (OH) 4+5	2.581e-37	1.448e-40	-36.588	-39.839	-3.251
H (0)	1.971e-12				
H2	9.857e-13	9.857e-13	-12.006	-12.006	0.000
K	2.616e-03				
K+	2.531e-03	1.876e-03	-2.597	-2.727	-0.130
KSO4-	8.428e-05	6.247e-05	-4.074	-4.204	-0.130
KOH	6.475e-11	6.475e-11	-10.189	-10.189	0.000
Mg	9.748e-03				
Mg+2	7.250e-03	2.189e-03	-2.140	-2.660	-0.520
MgSO4	2.413e-03	2.413e-03	-2.617	-2.617	0.000
MgHCO3+	8.252e-05	6.117e-05	-4.083	-4.213	-0.130
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000
MgOH+	1.067e-07	7.909e-08	-6.972	-7.102	-0.130
MgSiO (OH) 3+	2.567e-08	1.903e-08	-7.591	-7.721	-0.130
MgSiO2 (OH) 2	1.413e-10	1.413e-10	-9.850	-9.850	0.000
Na	1.650e-01				
Na+	1.611e-01	1.194e-01	-0.793	-0.923	-0.130
NaSO4-	3.797e-03	2.814e-03	-2.421	-2.551	-0.130
NaHCO3	1.604e-04	1.604e-04	-3.795	-3.795	0.000
NaCO3-	3.364e-06	2.493e-06	-5.473	-5.603	-0.130
NaOH	7.851e-09	7.851e-09	-8.105	-8.105	0.000
O (0)	0.000e+00				
O2	0.000e+00	0.000e+00	-68.190	-68.190	0.000
S (-2)	1.368e-11				
HS-	7.937e-12	5.883e-12	-11.100	-11.230	-0.130
H2S	5.741e-12	5.741e-12	-11.241	-11.241	0.000
S-2	1.952e-23	5.893e-24	-22.710	-23.230	-0.520
S (2)	3.888e-16				
S2O3-2	1.944e-16	5.869e-17	-15.711	-16.231	-0.520
S (4)	1.322e-14				
SO3-2	7.891e-15	2.382e-15	-14.103	-14.623	-0.520
HSO3-	5.327e-15	3.949e-15	-14.273	-14.404	-0.130
S (6)	2.470e-02				
SO4-2	1.558e-02	4.703e-03	-1.807	-2.328	-0.520
NaSO4-	3.797e-03	2.814e-03	-2.421	-2.551	-0.130
CaSO4	2.771e-03	2.771e-03	-2.557	-2.557	0.000
MgSO4	2.413e-03	2.413e-03	-2.617	-2.617	0.000
KSO4-	8.428e-05	6.247e-05	-4.074	-4.204	-0.130
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000
FeSO4	9.602e-06	9.602e-06	-5.018	-5.018	0.000
HSO4-	6.159e-08	4.566e-08	-7.210	-7.340	-0.130
FeHSO4+	8.506e-12	6.305e-12	-11.070	-11.200	-0.130
FeSO4+	2.148e-19	1.592e-19	-18.668	-18.798	-0.130
Fe (SO4) 2-	2.210e-20	1.638e-20	-19.656	-19.786	-0.130
FeHSO4+2	1.411e-25	4.260e-26	-24.850	-25.371	-0.520
Si	1.776e-04				
Si (OH) 4	1.772e-04	1.772e-04	-3.751	-3.751	0.000
SiO (OH) 3-	3.709e-07	2.749e-07	-6.431	-6.561	-0.130
MgSiO (OH) 3+	2.567e-08	1.903e-08	-7.591	-7.721	-0.130
CaSiO (OH) 3+	1.735e-08	1.286e-08	-7.761	-7.891	-0.130
MgSiO2 (OH) 2	1.413e-10	1.413e-10	-9.850	-9.850	0.000
CaSiO2 (OH) 2	1.514e-11	1.514e-11	-10.820	-10.820	0.000
SiO2 (OH) 2-2	4.266e-13	1.288e-13	-12.370	-12.890	-0.520
FeSiO (OH) 3+2	1.409e-17	4.255e-18	-16.851	-17.371	-0.520

Sr	2.124e-04					
Sr+2	1.644e-04	4.963e-05	-3.784	-4.304	-0.520	
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000	
SrHCO3+	2.446e-06	1.813e-06	-5.612	-5.742	-0.130	
SrCO3	3.554e-08	3.554e-08	-7.449	-7.449	0.000	
SrOH+	3.417e-11	2.533e-11	-10.466	-10.596	-0.130	

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

Phase	SI	log IAP	log KT	
Anhydrite	-0.50	-4.86	-4.36	CaSO4
Aragonite	-0.14	1.85	1.99	CaCO3
Brucite	-5.50	11.34	16.84	Mg(OH)2
Calcite	-0.00	1.85	1.85	CaCO3
Celestite	0.00	-6.63	-6.63	SrSO4
CH4(g)	-14.51	-17.37	-2.86	CH4
CO2(g)	-1.80	-9.62	-7.82	CO2
Dolomite(dis)	-0.55	3.57	4.12	CaMg(CO3)2
Dolomite(ord)	0.00	3.57	3.57	CaMg(CO3)2
Fe(cr)	-13.66	0.16	13.82	Fe
Fe(OH)3(am)	-4.52	0.48	5.00	Fe(OH)3
Fe(OH)3(mic)	-2.52	0.48	3.00	Fe(OH)3
FeCO3(pr)	-0.44	-0.56	-0.12	FeCO3
Goethite	1.49	0.49	-1.00	FeOOH
Graphite	-5.60	-27.42	-21.82	C
Gypsum	-0.28	-4.86	-4.58	CaSO4:2H2O
H2(g)	-8.90	-12.01	-3.11	H2
H2S(g)	-10.22	-18.23	-8.01	H2S
Hematite	-0.14	0.98	1.12	Fe2O3
Magnesite	-0.32	1.72	2.04	MgCO3
Magnetite	0.01	10.03	10.02	Fe3O4
Melanterite	-5.08	-7.29	-2.21	FeSO4:7H2O
O2(g)	-65.30	-68.19	-2.89	O2
Portlandite	-11.33	11.47	22.80	Ca(OH)2
Pyrite	-0.00	-18.50	-18.50	FeS2
Quartz	0.00	-3.75	-3.75	SiO2
S(rhomb)	-7.19	-9.33	-2.14	S
Siderite	0.00	-0.56	-0.56	FeCO3
SiO2(am)	-1.03	-3.75	-2.71	SiO2
Strontianite	-0.98	0.07	1.06	SrCO3
Troilite	-3.86	-9.17	-5.31	FeS

Low- P_{CO_2} variant ($10^{-2.8}$ bar)

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

pH	=	7.505	Charge balance
pe	=	-3.126	Adjusted to redox equilibrium
Activity of water	=	0.994	
Ionic strength	=	2.288e-01	
Mass of water (kg)	=	1.000e+00	
Total alkalinity (eq/kg)	=	1.178e-03	
Total CO2 (mol/kg)	=	1.214e-03	
Temperature (deg C)	=	25.000	
Electrical balance (eq)	=	6.875e-14	
Percent error, $100*(Cat- An)/(Cat+ An)$	=	0.00	
Iterations	=	12	
Total H	=	1.110186e+02	
Total O	=	5.561164e+01	

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	4.289e-07	3.180e-07	-6.368	-6.498	-0.130
H+	4.218e-08	3.128e-08	-7.375	-7.505	-0.130
H2O	5.551e+01	9.938e-01	1.744	-0.003	0.000
C(-4)	1.617e-18				
CH4	1.617e-18	1.617e-18	-17.791	-17.791	0.000

C (4)	1.214e-03					
HCO3-	1.028e-03	7.624e-04	-2.988	-3.118	-0.130	
CO2	5.396e-05	5.396e-05	-4.268	-4.268	0.000	
NaHCO3	5.085e-05	5.085e-05	-4.294	-4.294	0.000	
CaHCO3+	3.801e-05	2.818e-05	-4.420	-4.550	-0.130	
MgHCO3+	2.584e-05	1.916e-05	-4.588	-4.717	-0.130	
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000	
CO3-2	3.779e-06	1.143e-06	-5.423	-5.942	-0.519	
NaCO3-	3.402e-06	2.523e-06	-5.468	-5.598	-0.130	
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000	
FeHCO3+	1.159e-06	8.592e-07	-5.936	-6.066	-0.130	
SrHCO3+	7.743e-07	5.742e-07	-6.111	-6.241	-0.130	
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000	
SrCO3	3.592e-08	3.592e-08	-7.445	-7.445	0.000	
Ca	1.237e-02					
Ca+2	9.582e-03	2.898e-03	-2.019	-2.538	-0.519	
CaSO4	2.741e-03	2.741e-03	-2.562	-2.562	0.000	
CaHCO3+	3.801e-05	2.818e-05	-4.420	-4.550	-0.130	
CaCO3	5.549e-06	5.549e-06	-5.256	-5.256	0.000	
CaSiO (OH) 3+	5.435e-08	4.031e-08	-7.265	-7.395	-0.130	
CaOH+	2.060e-08	1.528e-08	-7.686	-7.816	-0.130	
CaSiO2 (OH) 2	1.514e-10	1.514e-10	-9.820	-9.820	0.000	
Cl	1.600e-01					
Cl-	1.600e-01	1.187e-01	-0.796	-0.926	-0.130	
FeCl+	2.489e-06	1.846e-06	-5.604	-5.734	-0.130	
FeCl+2	9.531e-21	2.883e-21	-20.021	-20.540	-0.519	
FeCl2+	2.060e-21	1.528e-21	-20.686	-20.816	-0.130	
FeCl3	1.813e-23	1.813e-23	-22.742	-22.742	0.000	
Fe (2)	5.087e-05					
Fe+2	3.726e-05	1.127e-05	-4.429	-4.948	-0.519	
FeSO4	9.501e-06	9.501e-06	-5.022	-5.022	0.000	
FeCl+	2.489e-06	1.846e-06	-5.604	-5.734	-0.130	
FeHCO3+	1.159e-06	8.592e-07	-5.936	-6.066	-0.130	
FeCO3	3.089e-07	3.089e-07	-6.510	-6.510	0.000	
FeOH+	1.527e-07	1.132e-07	-6.816	-6.946	-0.130	
FeHSO4+	2.636e-12	1.955e-12	-11.579	-11.709	-0.130	
Fe (3)	9.722e-12					
Fe (OH) 3	7.103e-12	7.103e-12	-11.149	-11.149	0.000	
Fe (OH) 2+	2.341e-12	1.736e-12	-11.631	-11.761	-0.130	
Fe (OH) 4-	2.775e-13	2.058e-13	-12.557	-12.687	-0.130	
FeOH+2	5.455e-16	1.650e-16	-15.263	-15.783	-0.519	
FeSiO (OH) 3+2	1.170e-17	3.538e-18	-16.932	-17.451	-0.519	
FeSO4+	5.639e-20	4.182e-20	-19.249	-19.379	-0.130	
Fe+3	1.186e-20	8.045e-22	-19.926	-21.094	-1.169	
FeCl+2	9.531e-21	2.883e-21	-20.021	-20.540	-0.519	
Fe (SO4) 2-	5.848e-21	4.337e-21	-20.233	-20.363	-0.130	
FeCl2+	2.060e-21	1.528e-21	-20.686	-20.816	-0.130	
FeCl3	1.813e-23	1.813e-23	-22.742	-22.742	0.000	
FeHSO4+2	1.159e-26	3.505e-27	-25.936	-26.455	-0.519	
Fe2 (OH) 2+4	8.757e-29	7.328e-31	-28.058	-30.135	-2.077	
Fe3 (OH) 4+5	4.681e-37	2.657e-40	-36.330	-39.576	-3.246	
H (0)	2.748e-12					
H2	1.374e-12	1.374e-12	-11.862	-11.862	0.000	
K	2.594e-03					
K+	2.509e-03	1.861e-03	-2.600	-2.730	-0.130	
KSO4-	8.422e-05	6.246e-05	-4.075	-4.204	-0.130	
KOH	2.050e-10	2.050e-10	-9.688	-9.688	0.000	
Mg	9.519e-03					
Mg+2	7.103e-03	2.148e-03	-2.149	-2.668	-0.519	
MgSO4	2.388e-03	2.388e-03	-2.622	-2.622	0.000	
MgHCO3+	2.584e-05	1.916e-05	-4.588	-4.717	-0.130	
MgCO3	2.343e-06	2.343e-06	-5.630	-5.630	0.000	
MgOH+	3.342e-07	2.478e-07	-6.476	-6.606	-0.130	
MgSiO (OH) 3+	8.040e-08	5.962e-08	-7.095	-7.225	-0.130	
MgSiO2 (OH) 2	1.413e-09	1.413e-09	-8.850	-8.850	0.000	
Na	1.638e-01					
Na+	1.599e-01	1.186e-01	-0.796	-0.926	-0.130	
NaSO4-	3.800e-03	2.818e-03	-2.420	-2.550	-0.130	
NaHCO3	5.085e-05	5.085e-05	-4.294	-4.294	0.000	
NaCO3-	3.402e-06	2.523e-06	-5.468	-5.598	-0.130	
NaOH	2.489e-08	2.489e-08	-7.604	-7.604	0.000	
O (0)	0.000e+00					
O2	0.000e+00	0.000e+00	-68.479	-68.479	0.000	
S (-2)	1.160e-11					

HS-	9.454e-12	7.011e-12	-11.024	-11.154	-0.130
H2S	2.143e-12	2.143e-12	-11.669	-11.669	0.000
S-2	7.410e-23	2.241e-23	-22.130	-22.650	-0.519
S (2)	1.460e-16				
S2O3-2	7.302e-17	2.209e-17	-16.137	-16.656	-0.519
S (4)	1.341e-14				
SO3-2	1.106e-14	3.346e-15	-13.956	-14.475	-0.519
HSO3-	2.344e-15	1.738e-15	-14.630	-14.760	-0.130
S (6)	2.474e-02				
SO4-2	1.567e-02	4.741e-03	-1.805	-2.324	-0.519
NaSO4-	3.800e-03	2.818e-03	-2.420	-2.550	-0.130
CaSO4	2.741e-03	2.741e-03	-2.562	-2.562	0.000
MgSO4	2.388e-03	2.388e-03	-2.622	-2.622	0.000
KSO4-	8.422e-05	6.246e-05	-4.075	-4.204	-0.130
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000
FeSO4	9.501e-06	9.501e-06	-5.022	-5.022	0.000
HSO4-	1.944e-08	1.442e-08	-7.711	-7.841	-0.130
FeHSO4+	2.636e-12	1.955e-12	-11.579	-11.709	-0.130
FeSO4+	5.639e-20	4.182e-20	-19.249	-19.379	-0.130
Fe (SO4) 2-	5.848e-21	4.337e-21	-20.233	-20.363	-0.130
FeHSO4+2	1.159e-26	3.505e-27	-25.936	-26.455	-0.519
Si	1.786e-04				
Si (OH) 4	1.773e-04	1.773e-04	-3.751	-3.751	0.000
SiO (OH) 3-	1.183e-06	8.776e-07	-5.927	-6.057	-0.130
MgSiO (OH) 3+	8.040e-08	5.962e-08	-7.095	-7.225	-0.130
CaSiO (OH) 3+	5.435e-08	4.031e-08	-7.265	-7.395	-0.130
MgSiO2 (OH) 2	1.413e-09	1.413e-09	-8.850	-8.850	0.000
CaSiO2 (OH) 2	1.514e-10	1.514e-10	-9.820	-9.820	0.000
SiO2 (OH) 2-2	4.338e-12	1.312e-12	-11.363	-11.882	-0.519
FeSiO (OH) 3+2	1.170e-17	3.538e-18	-16.932	-17.451	-0.519
Sr	2.091e-04				
Sr+2	1.628e-04	4.923e-05	-3.788	-4.308	-0.519
SrSO4	4.551e-05	4.551e-05	-4.342	-4.342	0.000
SrHCO3+	7.743e-07	5.742e-07	-6.111	-6.241	-0.130
SrCO3	3.592e-08	3.592e-08	-7.445	-7.445	0.000
SrOH+	1.082e-10	8.021e-11	-9.966	-10.096	-0.130

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

Phase	SI	log IAP	log KT	
Anhydrite	-0.50	-4.86	-4.36	CaSO4
Aragonite	-0.14	1.85	1.99	CaCO3
Brucite	-4.50	12.34	16.84	Mg (OH) 2
Calcite	0.00	1.85	1.85	CaCO3
Celestite	0.00	-6.63	-6.63	SrSO4
CH4 (g)	-14.93	-17.79	-2.86	CH4
CO2 (g)	-2.80	-10.62	-7.82	CO2
Dolomite (dis)	-0.55	3.57	4.12	CaMg (CO3) 2
Dolomite (ord)	-0.00	3.57	3.57	CaMg (CO3) 2
Fe (cr)	-12.52	1.30	13.82	Fe
Fe (OH) 3 (am)	-3.59	1.41	5.00	Fe (OH) 3
Fe (OH) 3 (mic)	-1.59	1.41	3.00	Fe (OH) 3
FeCO3 (pr)	-0.44	-0.56	-0.12	FeCO3
Goethite	2.41	1.41	-1.00	FeOOH
Graphite	-6.31	-28.13	-21.82	C
Gypsum	-0.29	-4.87	-4.58	CaSO4:2H2O
H2 (g)	-8.76	-11.86	-3.11	H2
H2S (g)	-10.65	-18.66	-8.01	H2S
Hematite	1.71	2.83	1.12	Fe2O3
Magnesite	-0.32	1.72	2.04	MgCO3
Magnetite	2.87	12.89	10.02	Fe3O4
Melanterite	-5.08	-7.29	-2.21	FeSO4:7H2O
O2 (g)	-65.58	-68.48	-2.89	O2
Portlandite	-10.33	12.47	22.80	Ca (OH) 2
Pyrite	-0.00	-18.50	-18.50	FeS2
Quartz	0.00	-3.75	-3.75	SiO2
S (rhomb)	-7.76	-9.90	-2.14	S
Siderite	-0.00	-0.56	-0.56	FeCO3
SiO2 (am)	-1.03	-3.75	-2.71	SiO2
Strontianite	-0.98	0.08	1.06	SrCO3
Troilite	-3.29	-8.60	-5.31	FeS

