PROGRESS REPORT NO 1

WORK AREA 3 - GEOCHEMISTRY

CONTRACT N° : **ENK6-1999-00014**

PROJECT N° :

ACRONYM : **SACS2**

TITLE : **Saline Aquifer CO_2 Storage**

PROJECT CO-ORDINATOR : **Statoil**

WORK AREA 3 CO-ORDINATOR : **BRGM**

WORK AREA 3 PARTNERS : **BGS, BRGM, GEUS, IFP**

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REPORTING PERIOD : **FROM 1 April TO 31 December 2000**

PROJECT START DATE : **1 April 2000** **DURATION : 24 months**

Date of issue of this report : 22 December 2000

Project funded by the European Community under the ‘Energie’ Programme (1998-2002)

4. Scientific and Technical Performance

4.1 Summary of the Specific Project Objectives for the relevant period

The objective of the geochemical work within the SACS2 project is to characterise the initial geochemical conditions within the Utsira formation (Task 3.1) and assess the changes that would be caused by CO_2 injection. Present work is based on laboratory experiments for timescales up to 24 months (Task 3.2). Numerical modelling is then used to interpret the experimental data by considering thermodynamic, kinetic and transport processes (Task 3.3).

Specific objectives during 2000 were:

- refine the assesment of the initial geochemical conditions within the reservoir carried out within SACS, by considering new available data;
- continue a series of long term batch experiments under in-situ conditions (37°C, 10 MPa)
- initiate long term batch experiments at a temperature above in-situ conditions (70°C, 10 MPa)
- carry out CO_2 solubility measurements under and above in-situ conditions
- initiate long term, long pathlength flow experiments (70°C, 10 MPa)
- develop an in-situ pH measuring technique
- carry out the dynamic CO_2 flooding experiments at reservoir conditions (37°C, 10 MPa)
- continue flooding at temperature above in-situ conditions
- model and interpret the 1, 2, and 3-months batch experiments

4.2 Technical Progress and Main Results

Task 3.1. Initial fluid/rock equilibrium state of the Utsira formation *BRGM*

The only available formation fluid analysis was from the Oseberg field, some 200 km north of Sleipner. During the reporting period a sample of Utsira porewater from the Brage field became available. This field lies adjacent to the Oseberg field. Analyses were carried out and were used to refine the assessment of the initial geochemical state of the Utsira formation, as reported in the final geochemical report of the SACS Thermie project.

The Oseberg and Brage fluid compositions are very similar. This increases confidence in the assumption of widespread, relatively constant Utsira porewater composition throughout the formation. We can reasonably assume that the chemical composition of the Utsira porewater at Sleipner is well constrained for pH, CO_2 fugacity, major species (Na, K, Ca, Mg, Cl, HCO_3, SO_4) and trace elements such as Li, Br and Sr. However, baseline fluid chemistry at Sleipner is still far from being well-constrained, especially regarding the concentrations of dissolved silica and aluminium. The Brage analysis provides a dissolved Si concentration, but lack of knowledge on in-situ temperature in the Brage field prevents from assessing the concentration of dissolved silica at Sleipner. The Al concentration needs to be determined using analytical techniques with lower detection limits.

Task 3.2. Geochemical laboratory experiments *BGS, GEUS*

Long term batch experiments under in-situ conditions (37°C and 10 MPa) BGS

Results on fluid chemistry changes after 1, 2 and 3 month durations were reported in the SACS Thermie final report. During the reporting period, experiments having durations of 4 and 14 months were terminated. Analysis of reaction products extracted from these experiments is underway. Corrosion problems became apparent in the 14 month experiment. Other sets of experiments up to 24 month duration are still underway.

Long term batch experiments at a temperature above in-situ conditions (70°C and 10 MPa) BGS
These experiments have only recently been initiated.

CO_2 solubility measurements (37-70°C and 8-12 MPa) BGS
A suite of experiments have been undertaken but solubility values determined were lower than expected. It is thought that some aspect of the experimental equipment might be causing degassing of the extracted fluids, and further experiments to check this are planned.

CO_2 long term, long pathlength flow experiment (2.4 m long, 10 month duration, 70°C and 10 MPa) BGS
Started in late June 2000. Samples of output fluid are taken approximately weekly.

Assessment of in-situ pH measuring technique BGS
A high pressure optical cell was designed and manufactured at BGS. Various pH buffers and a colourimetric indicator were used, and the spectral response of the liquid monitored. However further development of this technique would consume too many resources to be worthwhile continuing as part of SACS2. But BGS will go on developing this technique outside the SACS2 programme.

CO_2 flooding experiments at reservoir conditions (70 mm long, 38 mm diameter, 37°C and 10 MPa) GEUS
Three experiments were carried out during the reported period:

1- *A23.5 – Blind run*: Utsira sand sample A23.5 flooded by Synthetic Utsira fluid, 2 weeks duration, high flow rate (1.9 ml/h). 11 brine aliquots were extracted and later analyzed by BGS.
2- *A23.5 – CO2 run*: same conditions as above but using CO2-saturated Synthetic Utsira fluid.
3- *A23.6 – CO2 run*: CO_2 -saturated Synthetic Utsira fluid was flooded on sample A23.6, 1 month duration, medium flow rate (0.57 ml/h). 10 brine aliquots were extracted and later analyzed by BGS.

The mineralogical analysis of the samples after experiment are presently under consideration and compared with an unreacted reference sample.

In an attempt to be able to measure very slight changes in the petrophysical parameters permeability and porosity, GEUS has produced a new core holder that can handle core samples up to 500 mm in length, and with the sample diameter reduced to 25 mm, the differential pressure is enhanced 40 times compared to earlier experiments. A special rubber sleeve suited for long core experiments and resistant to CO_2 is presently being manufactured.

Task 3.3. Interpret the geochemical experiments *BRGM, IFP*

Main activities during the relevant period were focused on the modelling of the batch experiments carried out at BGS at reservoir conditions, for which experimental results are available for 1, 2 and 3 month durations. However only fluid analyses are available. Mineralogical analyses are still underway and cannot be yet compared to modelling results.

Selection of a rock composition of the Utsira sand for geochemical modelling BRGM
A typical mineralogical composition for the Utsira sand has been agreed between BRGM and IFP in order to start the modelling of the experiments. It will be refined by comparing modelling and experimental results and by taking into account the results of task 1.1 which should provide a mean mineralogical composition representative of the Utsira formation.

Chemical speciation of the Synthetic Utsira Porewater used in the experiments BRGM
Given the SUP chemical composition provided by BGS, EQ3/6 calculations were carried out at 20°C (ambient temperature) and 37°C (experimental conditions) to determine aqueous speciation, pH, CO_2 fugacity, total dissolved carbon and saturation indices with respect to minerals. Comparison was made with the actual Utsira porewater at Sleipner as assessed in Task 3.1.

Modelling the batch experiments for 1, 2, and 3 month durations using the UTSIRA simulator BRGM

The 3 pairs of experiments (pressurised with ‘CO_2’, ‘experimental blank’ pressurised with N_2) were modelled using the UTSIRA simulator developed during the SACS project as described in the final geochemical report of the SACS Thermie project.

Modelling the batch experiments for 1, 2, and 3 month durations using the DIAPHORE model IFP

The 3 pairs of experiments were modelled using the DIAPHORE model described in the final geochemical report of the SACS Thermie project. Some other investigations were carried out by changing the selection of minerals involved or the fluid/rock ratio.

4.3 Comparison of planned and actual work

Compared to the workplan for geochemistry dated April 11, 2000, activities are running as expected except:

- CO_2 solubility experiments: ran OK, but results unexpected, need checking
- in-situ pH determination: preliminary investigations show technique has potential, but some significant further development will be required (not possible as part of SACS, but may be continued outside the project).

4.4 Planned activities for the next six months

- Refinements of the initial geochemical conditions at Sleipner
- Continuation of batch and flow experiments
- Repeat CO_2 solubility experiments
- Re-analysis of experimental solutions for low levels of Al and additional elements
- Measurements of gas and liquid permeability, specific surface areas, CEC and exchangeable cations
- Modelling of (i) the batch experiments up to 14 months, (ii) the 3 flooding experiments described in 4.2, (iii) the CO_2 solubility experiments
- Discussions on the interpretation of the modelled experiments

6. Dissemination and Use of the results

Conferences attended and planned:

- 13-16 August 2000, GHGT-5 Conference in Cairns
- 8 – 12 April 2001, EUG 11 Conference in Strasbourg.

Papers presented/published:

Pearce J.M., Czernichowski-Lauriol I., Rochelle C.A., Springer N., Brosse E., Sanjuan B., Bateman K. and Lanini S. (2000) - How will reservoir and caprock react with injected CO_2 at Sleipner? Preliminary evidence from experimental investigations. Paper presented at the Fifth International Conference on Greenhouse Gas Control Technologies, Cairns, Australia, August 2000.

Czernichowski-Lauriol I., Rochelle C.A., Brosse E., Springer N., Pearce J.M., Bateman K.A., Sanjuan B., Kervevan C. (2001) - Disposal of CO_2 in deep aquifers: geochemical investigations of water-rock-CO_2 interactions at Sleipner (North Sea) as part of the SACS project. Abstract submitted for presentation at the EUG XI conference, Session D1 “Greenhouse Gas Disposal”, Strasbourg, April 8th – 12th 2001.

7. Management and co-ordination aspects

IEA Leeuwenhorst Workshop, 4-5 April 2000: Presentation of the SACS and SACS2 activities in geochemistry

SACS technical meetings:

- Stavanger, 12-13 April 2000: Technical meeting discussing the workplans for SACS2.
- Orleans, 26-27 September 2000: Technical meeting discussing the progress.

SACS technical meetings on geochemistry:

- Orleans, 30 November 2000: Technical meeting with BRGM and IFP discussing modelling.
- Paris, 19 January 2001: Technical meeting with the whole geochemical team (BRGM, IFP, BGS, GEUS) to discuss the work achieved so far and next activities.

International umbrella cooperation: Examination of the proposals submitted by LLNL and Battelle (USA)

- LLNL: Reactive transport modelling of CO_2 storage within the Utsira formation at Sleipner.
- Battelle: Hydrogeologic and Geochemical Modeling for Sleipner Aquifer Sequestration Project.

ANNEX

Task 3.1. Initial fluid/rock equilibrium state of the Utsira formation (BRGM)

The aim of this task is to describe the initial fluid/rock interaction state within the Utsira formation of the Sleipner field before CO_2 injection. Relative to the data available in the first progress report, only additional results to improve the knowledge of the chemical composition of the Utsira porewater have been obtained.

Work during previous reporting periods has highlighted the shortage of reliable fluid chemical data for the Utsira porewater at Sleipner. Porewater samples from frozen Utsira core from Sleipner were severely contaminated by drilling fluid and cannot be used to assess fluid chemistry at Sleipner. The only available analysis of the Utsira formation fluid was from the Oseberg field, some 200 km north of Sleipner.

During the reporting period a sample of Utsira porewater from the Brage field became available. This field is also some 200 km north of Sleipner, and lies adjacent to the Oseberg field. Analyses were carried out by BGS and GEUS laboratories. Details of the composition of the various fluids are given in Table 1. It appears that additional new data are available for the concentrations of dissolved silica, total organic and inorganic carbon, bromine, lithium, manganese, nitrate and phosphorus. However, there is still no data for dissolved aluminium. Unfortunately, we were not able to obtain information about depth, temperature and pressure of the Utsira formation at Brage.

The analytical results obtained by GEUS have a relatively bad ion balance value (about 8%) whereas those for the BGS results are close to zero. Moreover, numerous important dissolved species for geochemical modelling such as bicarbonate, silica, total organic carbon were not analysed by GEUS. Consequently, the chemical analyses performed by BGS were selected to describe the initial chemical composition of the Utsira porewater.

These analyses indicate that Oseberg and Brage fluid compositions are very similar for major species (Na, K, Ca, Mg, Cl, HCO_3, SO_4) and some trace elements such as Sr. They seem to validate the assumption that the chemical composition of the Utsira porewater is relatively homogeneous in all these fields. As for the Oseberg field, the Brage fluid is a NaCl brine with a TDS around 31-32 g/l, slightly lower than that of sea water (around 35 g/l). The Cl/Br ratio of this fluid (270 and 259 respectively), lower than that of sea water (296), suggests two probable origins:

- a sea water slightly diluted by fresh water and enriched in bromine by organic matter,
- a marine origin brine evaporated up to halite formation (depletion in chloride) and diluted after by fresh water.

Relative to a diluted sea water, the Brage fluid is enriched in calcium, bicarbonate, silica, strontium, baryum, lithium and iron. It is depleted in potassium, magnesium and sulphate. All these species are affected by fluid-rock interactions.

The TOC and TIC determinations allow to show that alkalinity is essentially represented by bicarbonate ions and that organic ions such as acetate can be considered as negligible in the Utsira fluid. In this case, the reconstruction of pH and CO_2 fugacity from alkalinity measurements (assimilated to bicarbonate concentrations) and assuming the Utsira porewater equilibrated with respect to calcite at 37°C is validated. At this temperature, a pH value of 6.53-6.57 and a CO_2 fugacity of 0.12-0.17 were found (see Table 3.4 in the final geochemical report of the SACS Thermie project).

The dissolved silica analysis indicates a concentration (50 mg/l) higher than those obtained assuming the equilibrium at 37°C between porewater and quartz (or chalcedony) from the EQ3/6 database data0.com.R2

(Wolery, 1995), even if the salt effect is considered (see Tables 3.4 and 3.5 in the previous report). The analytical value remains higher than that obtained at 37°C (15 mg/l) using the quartz solubility equation as a function of temperature given by Rimstidt (1997). According to this equation, the analytical value corresponds to a temperature of 90°C. Nevertheless, this concentration is close to that estimated (43 mg/l) from the chalcedony geothermometer proposed by Fournier and Rowe (1966): log $[SiO_2] = 0.125-1015/T$. $[SiO_2]$ is the concentration of dissolved silica (in mol/l) and T the temperature (in °K). As the temperature of the Utsira fluid in the Brage field is unknown, it is difficult to assign a value for the Utsira porewater in the Sleipner field. In the absence of appropriate data and according to Kharaka et al. (1985), we recommend to use the concentrations of dissolved silica obtained assuming the equilibrium between porewater and chalcedony at 37°C.

The concentrations of dissolved barium and iron are relatively different for the Oseberg and Brage fluids. Local constraints ($BaSO_4$ and ferric hydroxide precipitation?) could influence on the concentrations of these elements. Consequently, these lelements cannot be estimated for the Utsira porewater in the Sleipner field. For other trace elements such as Br, Li, very soluble, it can be assumed that their concentrations in the Utsira porewater are similar in the different fields.

The detection limit for Al analysis (0.1 mg/l) is relatively high. As the concentration of aqueous Al must be known to calculate the saturation indices of all the alumino-silicate minerals, it would be necessary to improve the determination of this element to obtain an accurate value, even if this value is very low. The application of the classical Na-K geothermometer (Nicholson, 1993) already shows that the Utsira fluid is not in equilibrium with Na and K-feldspars at 37°C.

In conclusion, if we assume that the Utsira fluid is relatively homogeneous in the three fields, the chemical composition of the Utsira porewater in the Sleipner field is well constrained for pH, CO_2 fugacity, major species and trace elements such as Li, Br and Sr. The concentrations of dissolved silica and aluminium are badly known. The temperature knowledge of the Utsira fluid in the Brage field would allow to select a concentration of dissolved silica for the fluid of this formation in the Sleipner field. In this case, it would be interesting to perform other Al analyses in the Brage fluid with a lower detection limit. In the absence of additional analytical data, we recommend to assume that dissolved silica and aluminium are controlled at 37°C in the Utsira pore-water of the Sleipner field by chalcedony and kaolinite, respectively.

References

FOURNIER R.O. and ROWE J.J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and wet steam wells. Amer. J. Sci., 264, 685-697.

KHARAKA Y.K., HULL R.W. and CAROTHERS W., 1985. Water-rock interaction in sedimentary basins. In relationship of organic matter and mineral diagenesis (Eds D.L. Gauthier, Y. K. Kharaka and R.C. Surdam). Soc. Econ. Paleont. Mineral., 17, 79-174.

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RIMSTIDT J.D., 1997. Quartz solubility at low temperatures. Geochim. Cosmochim. Acta, 61, n°13, 2553-2558.

WOLERY T.J., 1995. EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, user's guide and related documentation (version 7.0). UCRL-MA-110662-PT-I, Lawrence Livermore National Laboratory, Livermore

Task 3.2. Geochemical laboratory experiments (BGS, GEUS)

The overall objective of this task is to determine the potential for chemical reactions between the host formations (e.g. reservoir rock - Utsira sand) and injected CO_2 using laboratory experiments. It aims to provide information relevant to an improved understanding of:-

- the types of reactions that occur when CO_2 reacts with siliciclastic rocks and associated porewaters,
- how much CO_2 can be trapped by geochemical reactions (as dissolved CO_2, bicarbonate or carbonate minerals),

- the chemical behaviour of caprock and its susceptibility to damage by the injected CO_2,
- broad indications of how chemical changes might impact upon porosity and permeability of the reservoir, which constrain fluid flow within the reservoir,

It also aims to provide test cases of well-quantified data with which to test geochemical modelling packages.

Long term batch experiments under in-situ conditions (involving Utsira sand, synthetic Oseberg porewater and CO_2 at 37°C and 10 MPa) *BGS*

A series of these experiments were initiated in early August 1999. Results on fluid chemistry changes after 1, 2 and 3 month durations were reported in the SACS Thermie final report for geochemistry (see also Table 2 of the present progress report). The aim of these experiments, carried out at reservoir conditions (37 °C, 10 MPa), is to investigate the reactions caused by adding CO_2 to Utsira sand and synthetic Oseberg porewater. The experiments are being done in pairs, with each pair set up identically to one another. The only difference is of the timescale of reaction, which varies from 1 month to 24 months. Each pair of experiments consists of one pressurised with CO_2 and an ‘experimental blank’ pressurised with nitrogen. The experiment pressurised with nitrogen is useful for finding out just how close the Oseberg porewater is to equilibrium with the Utsira sand. In other words, the data from these experiments will help to compensate for the lack of information on baseline geochemistry at Sleipner. The experiment pressurised with CO_2 will allow observation of changes over and above those occurring in the experiments pressurised with nitrogen.

During the reporting period, experiments having durations of 4 and 14 months were terminated. Analysis of reaction products extracted from these experiments is underway. However, one immediate finding from the 14 month experiment was that the high-quality, high pressure stainless steel valves used to seal the experiments were suffering from severe corrosion. The duration of the experiments appears to have been long enough for corrosion problems to become apparent (these were not observed in shorter-term experiments). A future experimental strategy might be to investigate the potential of titanium valves where long-term exposure to wet CO_2 is necessary.

Maintenance of other long-term batch experiments up to 24 months duration is continuing.

Long term batch experiments at a temperature above in-situ conditions (involving Utsira sand, synthetic Oseberg porewater and CO_2 at 70°C and 10 MPa) *BGS*

These experiments have only recently been initiated. They will be very similar to those described above, except for their higher temperature (70 °C). The elevated temperature was chosen so as to increase the possibility of achieving an observable reaction over a laboratory timescale whilst not encouraging the formation of unrepresentative secondary phases. It is hoped that their generally short durations (compared to some of the experiments described above) will limit corrosion of experimental equipment.

CO_2 solubility measurements (involving CO_2 and de-ionised water or synthetic Oseberg porewater, at 37-70°C and 8-12 MPa) *BGS*

A suite of experiments have been undertaken under conditions between 8-12 MPa and 37-70 °C. These were to serve as a check on published literature and to help interpret the batch experiments above. However, the results of fluids analysis were not clear. In general, solubility values determined were lower than expected. It is thought that some aspect of the experimental equipment might be causing degassing of the extracted fluids, and further experiments to check this are planned.

CO_2 long term, long pathlength flow experiment (involving Utsira sand, synthetic Oseberg porewater and CO_2 at 70°C and 10 MPa) *BGS*

A single long pathlength experiment was started in late June 2000. This consists of 4 lengths of PEEK tubing (each 60 cm long), making a total length of 2.4 m. Each column has an internal diameter of 0.7 cm, and was packed with Utsira sand to a porosity of approximately 40%. This experiment is being run at 70 °C and 10 MPa, and is being flushed with synthetic Utsira porewater saturated with CO2 under the same conditions.

The experiment appears to be running successfully, and samples of output fluid are taken approximately weekly. The experiment will run until mid 2001, after which it will be depressurised and dismantled prior to mineralogical analysis.

It is hoped that this type of experiment will provide the geochemical modelling groups with 'test cases' with which to 'benchmark' the various modelling packages being employed in SACS.

It was hoped originally that a second, more generic experiment could also be conducted. Unfortunately, this was not possible within the resources available, and this may be continued outside the SACS project.

Assessment of in-situ pH measuring technique *BGS*

Solution pH is a critical parameter in most aqueous geochemical systems, and standard techniques exist for its determination. However, pH electrodes do not exist that are capable of withstanding pressures above 1 MPa. As a consequence, in-situ pH has to be calculated using predictive geochemical modelling packages. This is a well-tried technique for many systems. However, the CO_2-rich experiments of this study present an added complexity in that large amounts of degassing occur during sampling, and pH changes might be relatively large

Published information related to uranium processing suggested that a colourimetric technique could be applied to the experiments of this study. It was hoped that this could provide a direct method of checking computer predictions of in-situ pH.

A high pressure optical cell was designed and manufactured at BGS. Various pH buffers and a colourimetric indicator were used, and the spectral response of the liquid monitored. Several points became apparent:

- results could be obtained, but the procedure was complex and slow (partly related to the spectrometer available)
- a linear correlation between pH and spectral response was obtained, but the useable 'window' of the available colourimetric indicator was very limited
- even with an updated spectrometer and better indicator, there would still be arguments as to *exactly* what the results meant (them being measured relative to 'standard solutions' rather than a high pressure hydrogen electrode

It was decided that further development of this technique would consume too many resources to be worthwhile continuing as part of SACS2. However, given that new equipment will become available at BGS soon, further development of the technique will probably take place outside the SACS2 programme.

CO_2 flooding experiments at reservoir conditions (involving Utsira sand, synthetic Oseberg porewater and CO_2 at 37°C and 10 MPa) *GEUS*

Sample data for these experiments are as follows: nominal diameter 38 mm, nominal length 70 mm, porosity at overburden ~39%. Two preserved plug samples taken from the frozen core have been run under the short to mid term dynamic flooding programme performed at GEUS. Three experiments were carried out at reservoir temperature (37 °C) during the reported period:

1. *A23.5 – Blind run*: Synthetic Utsira porewater / Utsira sand (sample A23.5), 2 weeks duration, high flow rate (1.9 ml/h equal to a front velocity of 11 cm/d, or 10 pore volumes a week). 11 brine aliquots were extracted and later analyzed by BGS for a number of elements.
2. *A23.5 – CO_2 run*: CO_2-saturated Synthetic Utsira fluid was used at the same conditions as for the blind run.
3. *A23.6 – CO_2 run*: CO_2-saturated Synthetic Utsira fluid was flooded on sample A23.6, 1 month duration, medium flow rate (0.57 ml/h equal to a front velocity of 3.2 cm/d, or 3 pore volumes a week). 10 brine aliquots were extracted and later analyzed by BGS for a number of elements

The brine flow rate was set at two different values to look for changes in reaction rate between CO_2 -saturated brine and the minerals of the Utsira sand. Fig. 1 shows injection versus time curves for the 3 experiments.

Table 3 is an overview of the planned flooding and sampling scheme. The 2 month flooding experiment (injection of 1 pore volume of CO_2 –saturated formation brine per week) as well as experiments at elevated temperature was postponed until next year as explained below.

Table 4 is a listing of the analytical results obtained for fluid chemistry. As appears Ca is the most reactive element – presumably this represents dissolution of calcite shell fragments in the Utsira sand samples. Unfortunately the liquid fractions were only analyzed for cations, but for the last experiment (sample A23.6) the liquid fraction was split in 2 aliquots and a second set of analytical data, expected to be released in mid December this year, will give both cations, anions, pH and alkalinity as well as total organic and inorganic carbon.

The mineralogical analysis of the samples after experiment are presently under consideration and compared with an unreacted reference sample. The two reacted samples were deep frozen after experiment and then cut into 2-3 pieces determined for mineralogical analysis. The surface area was measured by nitrogen absorption and compared with an unreacted reference sample, table 5. The results are presently under consideration as commented below. Material intended for XRD (X-ray Diffraction) identification was crushed to pass a 250 µm sieve and spectrograms have been recorded for all sample pieces. Interpretation is ongoing.

From unreacted and reacted samples material have been investigated for surface dissolution/precipitation processes by Atomic Force Microscopy (AFM). A large number of scans were carried out for each sample specimen. Final images were prepared for two different particles from each sample, one type being a sheet type, probably mica, and another being blocky, probably quartz. However, it was not possible to observe any surface changes due to reaction with CO_2-saturated formation brine in any of the images produced, fig. 2.

In 2001, a few additional unreacted samples will be measured for specific surface area to clarify if there is a wide scatter within the Utsira sand core, or if the low values measured for the reacted samples really are significant. From the modelling group there has been a request for CEC data (Cation Exchange Capacity). Measurements is in preparation at GEUS and will be available early in 2001. Material from flooding experiments carried out at elevated temperature during 2001 will be analyzed as outlined above, but it is speculated if the small amounts of feldspar known to be present in the Utsira sand could be separated and investigated by AFM. Any dissolution phenomena present is more likely to occur in feldspar than in quartz grains.

It should be observed that the unconsolidated core material recovered from the A23 well has never been subject to routine core analysis. During the experiments the petrophysical parameters permeability and porosity should be recorded for the sample under test. When chemical reaction is subtle, changes in porosity is not observed, and the very low differential pressure (< 0.1 bar), recorded during the initial high flowrate (blind test) runs, makes the measured liquid permeabilities very uncertain. With the low flowrates used during the flooding experiments a simultaneous measurement of permeability is simply impossible. In an attempt to solve this problem GEUS has produced a new core holder that can handle core samples up to 500 mm in length, and with the sample diameter reduced to 25 mm, the differential pressure is enhanced 40 times compared to earlier experiments. A special rubber sleeve suited for long core experiments and resistant to CO_2 is presently being manufactured. Early in 2001 GEUS will determine the gas and liquid permeability at reservoir conditions using the new “long core” holder for at least 2 representative sandpacks taken from the 0.9 meter frozen core available for experiments. Future flooding experiments will be carried out in the same core holder at elevated temperature (70 °C).

Task 3.3. Interpret the geochemical experiments (BRGM, IFP)

Main activities during the relevant period were focused on the modelling of the batch experiments carried out at BGS at reservoir conditions, for which experimental results are available for 1, 2 and 3 month durations. However only fluid analyses are available. Mineralogical analyses are still underway and cannot be yet compared to modelling results.

Selection of a rock composition of the Utsira sand for geochemical modelling *BRGM*

A selection of a mineralogical composition representative of the Utsira sand was proposed in Table 3.11 of the final SACS Thermie report for geochemistry. This was based on the results of the mineralogical studies carried out by SINTEF, GEUS and BGS in Task 1.1. Further simplification has been decided by BRGM and IFP:

- Fe-bearing minerals (chlorite and smectite) are not presently considered as their amounts are low, their exact compositions are badly known, and the thermodynamic and kinetic data relative to these minerals are very inaccurate;
- As a consequence, redox reactions are not considered.

These minerals or reactions may be later introduced in the geochemical modelling only if the experimental data suggest that they have a significant influence on the variations of mineralogical composition and fluid chemistry.

Table 6 presents the mineralogical composition of the Utsira sand used in the modelling. Although not identified among the observed carbonate phase, a small amount of dolomite was added as calculations carried out in SACS1 suggested that this mineral may control Mg concentration.

Chemical speciation of the Synthetic Utsira Porewater (SUP) used in the experiments *BRGM*

Given the SUP chemical composition provided by BGS (Table 2), EQ3/6 calculations were carried out at 20°C (ambient temperature) and 37°C (experimental conditions) to determine aqueous speciation, pH, CO_2 fugacity, total dissolved carbon and saturation indices with respect to minerals.

The SUP water at 20°C is slightly oversaturated with respect to calcite, dolomite and strontianite. Thus there is the possibility that, as the stock SUP stands in the laboratory, minor precipitation of carbonates occur. At 37°C, the SUP water is even more oversaturated with respect to carbonates. Hence in the blank experiments, we should expect a slight precipitation of carbonates.

Remember that the SUP water was made as close as possible to the Utsira formation fluid (as analysed at Oseberg). Major anions and cations are very similar for both waters, but some significant differences concern pH, alkalinity and total dissolved carbon ($0.64\ 10^{-2}$ mole C / kg h_2o for SUP, $1.26\ 10^{-2}$ mole C / kg h_2o for Oseberg formation fluid). However this difference is not detrimental to the project as what is important to point out is the difference of impact of a fluid versus the same fluid saturated with CO_2.

Modelling the batch experiments for 1, 2, and 3 month durations using the UTSIRA simulator *BRGM*

The 3 pairs of experiments (pressurised with 'CO_2', 'experimental blank' pressurised with N_2) were modelled using the UTSIRA simulator developed during the SACS project as described in the final geochemical report of the SACS Thermie project. Initial conditions are (i) rock composition as given in Table 6, (ii) SUP water composition as given in Table 2, (iii) rock-to-fluid ratio of the batch experiments (1 to 10 by weight).

We present here a very first comparison between batch experimental results and both IFP and BRGM modelling results. At this stage of the project, our purpose was not to propose a definitive model but, as a preliminary step, to evaluate the orders of magnitudes of the discrepancies between experiments and modelling in order to adjust some poorly known parameters of our models (such as the reactive surfaces for example).

The choice was made to get all the kinetic parameters from the literature so that we carried out “blind” calculations, without attempting to fit with the experimental results. As an illustration, dissolved calcium and magnesium are represented on fig. 3. As the batch experiment is planned to last 2 years, we simulated the evolution of the system on this period of time.

For calcium, the behaviour is clearly different between blank and CO_2 experiments as the concentration notably increases. In BRGM simulations, the general trend is similar though the slope is much lower; at the opposite, the slope of the IFP curve is much higher than the experimental one. This discrepancy is probably due to a problem of kinetic constants. In BRGM simulations, calcite, anorthite, and dolomite dissolve simultaneously, thus giving a satisfying explanation for this increase in dissolved calcium.

For magnesium, the experimental results, limited to a 96 day period, do not enable neither to distinguish any trend nor to have any idea on the possible effect of CO_2 injection for this element. Consequently, it is difficult to conclude on the acceptability of the modelling results even though the obtained orders of magnitude are closer to the measurements than what was obtained for calcium.

The remaining work will thus consist in four main steps:

1) acquire the last experimental points in order to be able to highlight more precisely the majors trends of evolution of the major dissolved species;
2) verify and compare more carefully the parameters and the databases used for BRGM and IFP calculations in order to attempt to explain some discrepancies in our results;
3) as we have relatively poor confidence on their intrinsic values, experiment some other kinetic parameters tuning aiming to fit better with the experimental results.
4) consider a slightly different mineralogical assemblage and investigate the possible effect of ion exchange reactions.

Then, once this batch step give acceptable results, we will start the coupled modelling.

Modelling the batch experiments for 1, 2, and 3 month durations using the DIAPHORE model *IFP*

The experiments pressurised with CO_2 at 100 bars for 1, 2, and 3 month durations were modelled using the DIAPHORE model (standard version with no gas phase) described in the final geochemical report of the SACS Thermie project. Initial conditions are (i) rock composition as given in Table 6, (ii) SUP water composition as given in Table 2, (iii) rock-to-fluid ratio of the batch experiments (1 to 10 by weight).

Figure 4 represents the evolution of the water composition computed by the geochemical model and figures 4 and 5 the evolution of the mineralogical composition (‘porosity’ represents the rock-to-fluid ratio). Comparison is made with the available analytical results (month 1, month 2 and month 3). The observed increase of Ca concentration was captured by the model. It is mainly due to the slight dissolution of calcite (fig. 5). However, as the disordered dolomite was not stable and was completely dissolved (fig. 6), it contributed to the enrichment of the modelled solution in calcium. This effect might explain the discrepancy between the Ca values simulated and measured.

Some other investigations were carried out by changing the selection of minerals involved or the fluid/rock ratio. They are not reported here.

Planned activities for the next period are the following:

1. Simulations exploring the effects, on the (gas)-water-rock interactions, of the following parameters : (a) mineralogical composition ; (b) partial pressure of carbon dioxide ; (c) water-flow velocity (in relation with the core-flood experiment).
2. Improvement of the Diaphore-gas version.
3. Continuation of the geochemical modelling undertaken for simulating the core-flood experiment (see the final SACS Thermie report for geochemistry).

	UTSIRA FORMATION FLUID SAMPLED AT SURFACE				**POREWATERS FROM SLEIPNER CORE**					
	BRAGE			**OSEBERG**						
	Analysed by GEUS	**Analysed by BGS**		**T. Zero rpt**	**Analysed by GEUS**				**Analysed by BGS**	
Depth (m)					1084,13	1084,28	1084,65	1084,94	1085,1	1085,9
GWR (Sm3/Sm3)		?		0.14						
Gas composition		?								
CH4 (mol%)				96.64						
CO2 (mol%)				3.14						
pH		7,59	7,71	7,1					7,97	7,99
Salinity (g/l)				33-43						
Conc. (mg/l)										
Li		1,66	1,88						1,25	1,09
Na	11100	9725	10142	10392	8200	7500	7700	8800	9138	8307
K	363	305	328	208	36400	36200	50400	38000	24081	29578
Mg	863	651	676	630	390	390	370	480	400	345
Ca	675	410	413	426	270	250	260	310	237	215
Sr		9,44	9,86	10					4,76	4,33
Ba		6,05	6,28	0,5					1,66	1,33
Mn		<0.02	<0.02						0,041	0,092
Fe		0,3	0,26	2					<0.01	<0.01
Al		<0.1	<0.1						<0.02	<0.02
Si		23,9	23,5						5,46	5,51
SiO2 (calc)		51,1	50,3						11,7	11,8
P		<0.1	<0.1						0,11	0,14
S (total)		<2.5	<2.5							
HCO3		865	818	707					262	311
TOC		<20	<20						5188	6796
TIC		198	163						31,6	37,2
Cl	19440	18903	18938	18482	43100	41200	46600	41700	47612	49317
Br		70	73		443	423	521	406	415	442
NO3		<8	8,8						7,65	5,73
SO4	69	<60	<60	n.d.	182	153	177	146	113	144

Table 1: Available data on Utsira formation fluid chemical composition

INFORMATION FROM BGS BATCH EXPERIMENTS AT 37 °C

		OSEBERG	SUP	1 MONTH REACTION		2 MONTHS REACTION		3 MONTHS REACTION	
		Oseberg compositio from Task 0 report	Synthetic Utsira Porewater starting solution (Average)	Run 859 CO_2 expt 10 MPa CO_2	Run 860 Blank 10 MPa N_2	Run 838 CO_2 expt 10 MPa CO_2	Run 839 Blank 10 MPa N_2	Run 840 CO_2 expt 10 MPa CO_2	Run 841 Blank 10 MPa N_2
Exact duration				30 days	30 days	59 days	59 days	96 days	96 days
pH (20 °C)		7.1	7,77	6,62	7,82	6.68	8.03	6,43	7,82
Na	mg/l	10392	10306	9326	9400	10438	9979	10226	10528
K	mg/l	208	225	228	226	277	251	240	239
Mg	mg/l	630	633	580	578	659	622	625	629
Ca	mg/l	426	432	1577	332	1817	372	1840	376
Sr	mg/l	10	10,0	13,6	7,84	17,1	9,16	16,7	9,29
Ba	mg/l	0,5	0,31	2,12	4,22	2,78	3,80	2,44	3,70
Total Fe	mg/l	2	1,21	0,71	1,41	6,48	0,40	5,72	9,07
Al	mg/l	-	<2.00	<2.00	<2.00	7,44	3,04	<2.00	1,94
Total S	mg/l	-	1,05	23,3	11,2	33,2	15,3	34,1	16,9
Si	mg/l	-	BD	2,36	0,87	2,88	2,76	3,23	0,87
SiO2	mg/l	-	BD	5,06	1,86	6,16	5,90	6,91	1,86
Cl	mg/l	18482	18659	18166	17952	18849	18549	18556	18621
Br	mg/l	-	<2.00	<2.00	<6.00	<6,00	<6,00	<6.00	<6.00
SO_4	mg/l	ND	<2.00	<2.00	<60.00	66,8	<60,0	68,2	<60.00
HCO_3 **	mg/l	707	386	3102	300	1558	368	4423	349
Ionic balance	%	-	-	-2,27	-3,25	4,20	-1,77	-0,20	0,43
TIC (CO_3^{2-})*	mol/l	-	-	0.58 ?	-	1,03	-	0.47 ?	-

** Analyses done several days after sampling so be aware of possible decreases over time due to loss of CO_2 to the atmosphere. Alkalinity measurements by potentiometric titration.

* CO_2-rich solutions captured in 4M NaOH whilst at 10 Mpa pressure. Potentiometric titrations represent total inorganic carbon (i.e. CO_2, H_2CO_3, HCO_3^-, CO_3^{2-} etc).

? Analyses being checked/re-analysed as concentrations appear low.

Table 2: Experimental results for the BGS shorter-term batch experiments

Nom. plug data:	L, [cm]	D, [cm]	BV, [cc]	Ø, [%]	PV, [cc]				**Reservoir conditions**			**T=37 °C**
	7.5	3.8	85.1	38	32.3				**Flooding schedule: 1, 3, 10 PV per week**			
Flow rate: 1 PV/week ~ 32 ml/week ~ 4.57 ml/d ~ 0.190 ml/h					**Front velocity: 1 cm/d ~0.045 cm/h**				**Sample no.:**		**Kl = mD**	
Fluid sampling point:	Day 0	Day 1	Day 5	Day 8	Day 12	Day 17	Day 23	Day 30	Day 38	Day 47	Day 57	Total [ml]
Fluid sample 1 ID												
Fluid sample 2 ID												
Σ fluid injected	0	4.6+10	33+10	57+10	85+10	118+10	155+10	197+10	244+10	295+10	350+10	360
Σ fluid injected, recorded												
Flow rate: 3 PV/week ~ 96 ml/week ~ 13.7 ml/d ~ 0.57 ml/h					**Front velocity: 3.2 cm/d ~0.134 cm/h**				**Sample no.: A23.6**		**Kl = 990 mD**	
Fluid sampling point:	Day 0	Day 1	Day 2	Day 3	Day 4	Day 6	Day 9	Day 13	Day 18	Day 24	Day 31	Total [ml]
Fluid sample 1 ID												
Fluid sample 2 ID												
Σ fluid injected	0	13.7+10	37+10	61+10	85+10	122+10	173+10	238+10	317+10	409+10	515+10	525
Σ fluid injected, recorded												
Flow rate: 10 PV/week ~ 320 ml/week ~ 45.7 ml/d ~ 1.90 ml/h					**Front velocity: 11 cm/d ~0.45 cm/h**				**Sample no.: A23.5**			
Fluid sampling point:	Day 0	Day 0+12h	Day 1	Day 1+12h	Day 2+6h	Day 3	Day 4	Day 5	Day 7	Day 10	Day 14	Total [ml]
Fluid sample 1 ID												
Fluid sample 2 ID												
Σ fluid injected	0	23+10	56+10	89+10	133+10	177+10	233+10	289+10	390+10	537+10	730+10	740
Σ fluid injected, recorded												

Abbr.: L – sample length D – sample diameter BV – bulk volume PV – pore volume Ø – porosity

Table 3: Experiment plan for the short to medium term dynamic flooding experiments. Flow rates within one order of magnitude is tested, and the flow front velocity, applicable on a field scale as well, is given. Fluid samples of 10 ml volume are withdrawn from the experiment downstream line at the specified periods. The sum of the injected CO_2 – saturated formation brine is given at a nominal scale; the actual volume is listed in table 4. Refer also to fig.1 for further details.

LIMS Code	Sample Code	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Total P mg/l	Si mg/l	Ba mg/l	Sr mg/l	Mn mg/l	Total Fe mg/l	Al mg/l	Li mg/l	Run type	Time hours	Recorded brine production	Corrected brine production
06642-00001	Distilled water	0.098	<0.010	<0.350	<0.500	0.016	<0.075	<0.002	<0.002	0.003	<0.010	<0.100	<0.025			ml	ml
06642-00002	Synthetic brine	172	568	9450	233	<0.100	0.389	0.311	5.11	0.046	0.371	<1.00	<0.250				
06642-00003	5/14.02A	256	612	10957	293	<0.100	2.95	0.642	7.60	2.61	0.389	<1.00	<0.250	blind run	0.0	0.0	0.0
06642-00004	5/14.02B	237	627	10925	302	<0.100	1.53	0.563	7.33	0.536	0.394	<1.00	<0.250	-	11.0	21.0	20.9
06642-00005	5/15.02A	230	598	10600	258	<0.100	3.19	0.676	7.07	0.630	0.375	<1.00	<0.250	-	25.5	142.6	48.5
06642-00006	5/15.02B	243	609	10574	260	<0.100	3.20	0.696	7.57	0.468	0.387	<1.00	<0.250	-	35.5	178.2	67.5
06642-00007	5/16.02	167	559	10106	235	<0.100	3.13	0.557	5.84	0.394	0.365	<1.00	<0.250	-	50.5	221.7	96.0
06642-00008	5/17.02	165	567	10652	236	<0.100	2.93	0.563	5.72	0.391	0.371	<1.00	<0.250	-	70.5	270.6	134.0
06642-00009	5/18.02	186	583	9828	242	<0.100	2.57	0.566	5.67	0.458	0.390	<1.00	<0.250	-	96.0	327.2	182.4
06642-00010	5/19.02	241	647	10572	269	<0.100	2.74	0.709	7.37	0.444	0.403	<1.00	<0.250	-	120.5	386.6	229.0
06642-00011	5/21.02	180	559	9634	236	<0.100	2.21	0.568	5.36	0.634	0.365	<1.00	<0.250	-	167.0	488.2	317.3
06642-00012	5/24.02	227	600	10387	254	<0.100	2.19	0.695	7.04	0.847	0.378	<1.00	<0.250	-	238.5	634.6	453.2
06642-00013	5/28.02	202	607	10712	258	<0.100	1.85	0.672	6.05	1.27	0.369	<1.00	<0.250	-	335.5	828.2	637.5
06642-00014	5/06.03A	185	560	10553	231	<0.100	2.95	0.725	6.35	1.28	0.360	<1.00	<0.250	blind run	0.0	0.0	0.0
06642-00015	5/06.03B	273	575	9734	251	<0.100	7.87	0.322	3.59	3.16	0.363	<1.00	<0.250	CO2 run	10.0	20.0	19.0
06642-00016	5/07.03A	174	640	10990	289	<0.100	1.77	0.174	1.18	0.850	0.408	<1.00	<0.250	-	23.0	67.2	43.7
06642-00017	5/07.03B	176	630	10301	270	<0.100	1.04	0.152	1.15	0.433	0.402	<1.00	<0.250	-	35.0	102.3	66.5
06642-00018	5/08.03	492	675	10415	286	<0.100	3.91	0.253	4.43	1.25	0.409	<1.00	<0.250	-	47.5	140.0	90.3
06642-00019	5/09.03	444	629	10794	264	<0.100	3.09	0.221	4.13	0.993	0.394	<1.00	<0.250	-	69.5	200.0	132.1
06642-00020	5/10.03	401	630	10761	265	<0.100	2.37	0.147	3.53	1.05	0.396	<1.00	<0.250	-	94.5	265.1	179.6
06642-00021	5/13.03	493	593	10746	244	<0.100	2.90	0.203	5.25	1.21	0.391	<1.00	<0.250	-	166.5	416.4	316.4
06642-00022	5/16.03	536	578	10853	242	<0.100	3.12	0.155	5.59	1.09	0.365	<1.00	<0.250	-	237.0	569.4	450.3
06642-00023	5/20.03	823	629	10557	259	<0.100	2.72	0.115	7.41	1.47	0.423	<1.00	<0.250	-	334.5	771.2	635.6
06642-00024	6/19.04	282	581	9723	261	<0.100	4.12	0.544	6.05	1.88	0.376	<1.00	<0.250	blind run	0.0	0.0	0.0
06642-00025	6/21.04	56.6	624	11032	302	<0.100	4.44	0.106	0.689	2.60	0.392	<1.00	<0.250	CO2 run	48.5	27.3	27.6
06642-00026	6/22.04	214	570	10291	267	<0.100	2.56	0.239	2.04	5.96	0.378	<1.00	<0.250	-	76.5	58.1	43.6
06642-00027	6/23.04	174	578	10311	259	<0.100	0.766	0.189	1.62	1.18	0.374	<1.00	<0.250	-	94.0	94.0	53.6
06642-00028	6/25.04	317	568	10650	246	<0.100	3.36	0.201	3.68	2.40	0.366	<1.00	<0.250	-	140.0	138.1	79.8
06642-00029	6/28.04	176	535	9795	230	<0.100	0.601	0.170	1.55	0.253	0.365	<1.00	<0.250	-	211.0	197.1	120.3
06642-00030	6/02.05	234	569	10896	237	<0.100	1.09	0.201	1.91	1.11	0.351	<1.00	<0.250	-	307.5	269.6	175.3
06642-00031	6/07.05	206	561	10190	235	<0.100	1.42	0.158	1.63	0.419	0.357	<1.00	<0.250	-	428.5	355.0	244.2
06642-00032	6/22.05	350	590	10740	246	<0.100	3.55	0.137	3.40	0.714	0.384	<1.00	<0.250	-	571.5	457.8	325.8
06642-00033	6/13.05	380	502	10884	211	<0.100	3.28	0.154	4.14	2.40	0.357	<1.00	<0.250	-	789.0	605.2	449.7

Table 4: Chemical data measured at BGS analytical facility on small liquid fractions withdrawn from short to medium term dynamic flooding experiments performed at GEUS during 2000. The table presents data from one blind run and 2 runs where Utsira sand was reacted with fresh CO_2-saturated formation brine injected into the upstream end of the core sample at reservoir temperature (37 °C). Runtime, brine injected as well as brine volume corrected for withdrawal of liquid samples are given in the table.

Plug sample no:	**Specific surface area**
	m^2/g
Reference sample	0.5
A 23.5 upstream end	0.1
A 23.5 downstream end	0.1
A 23.6 upstream end	0.2
A 23.6 central part	0.2
A 23.6 downstream end	0.1

Table 5: Measured specific surface areas. Accusorp determinations on reacted Utsira sand show significantly lower surface areas than the unreacted reference sample.

Phase	**Volume % (average)**
Quartz	75.0
K-feldspar	10.3
Albite	2.6
Anorthite	0.5
Calcite	6.0
Muscovite	3.4
Kaolinite	0.2
Illite	1.5
Dolomite-dis	0.5
Total	*100*

Table 6: Selected mineralogical composition of the Utsira Sand for geochemical modelling

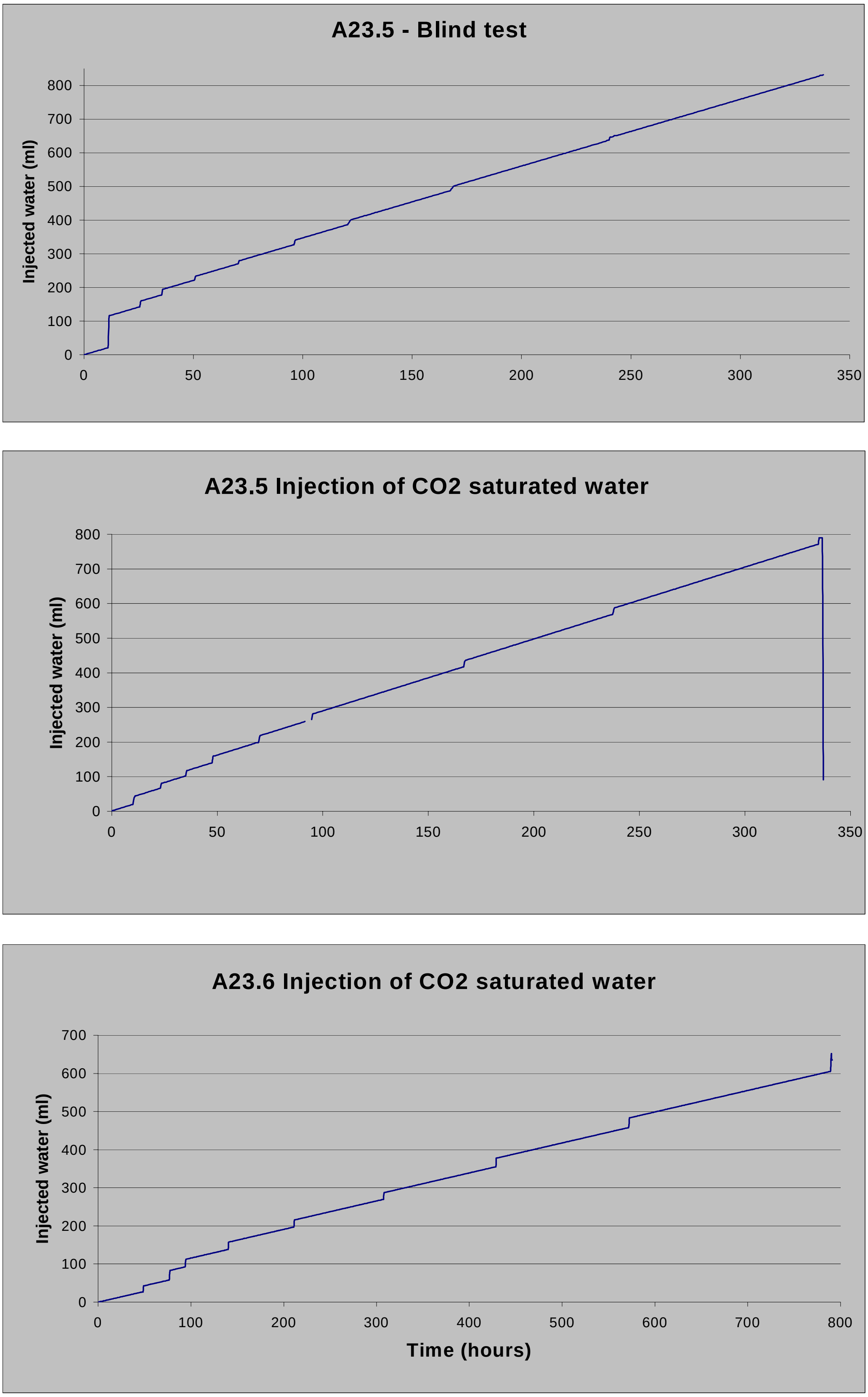
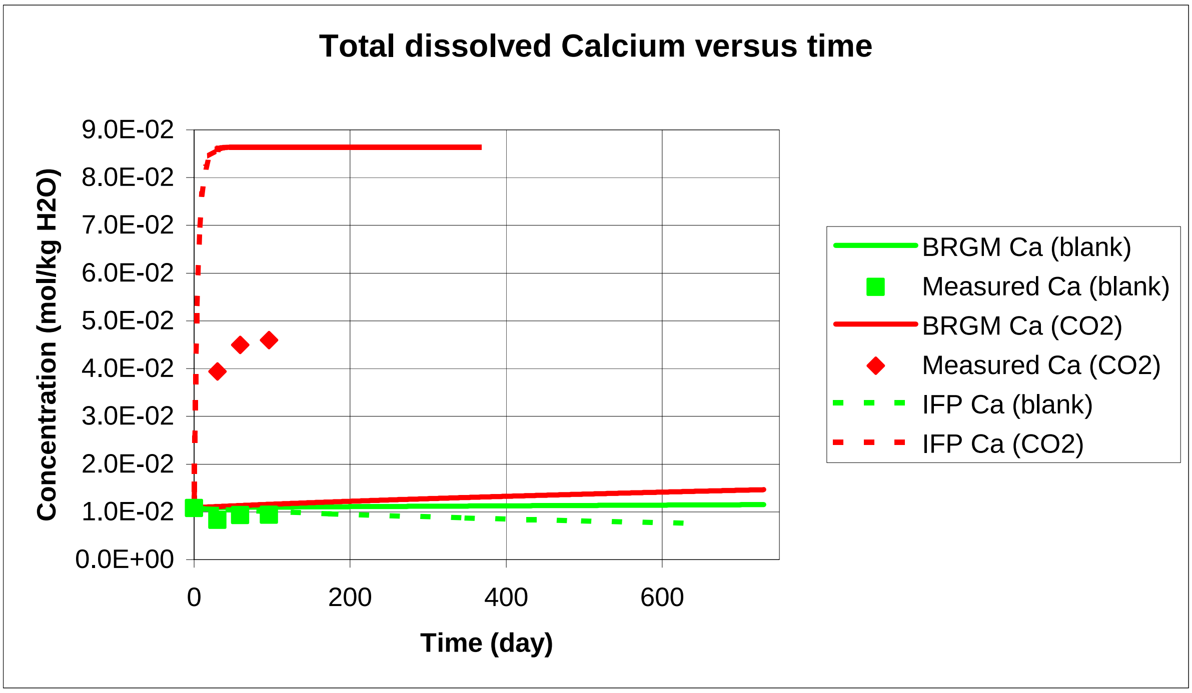


Figure 1: Injection vs. time curves for the three experiments. A step on the curve represents withdrawal of a fluid sample of approx. 10 ml from the downstream side of the sample – a volume which is immediately replaced, at the upstream side, by the computer controlled pumping system to keep up the system pressure.

Figure 2: Rasterscope 3D AFM-images of selected grains from unreacted and CO_2-reacted Utsira sand samples from the GEUS flooding experiments.

see figure in separate file



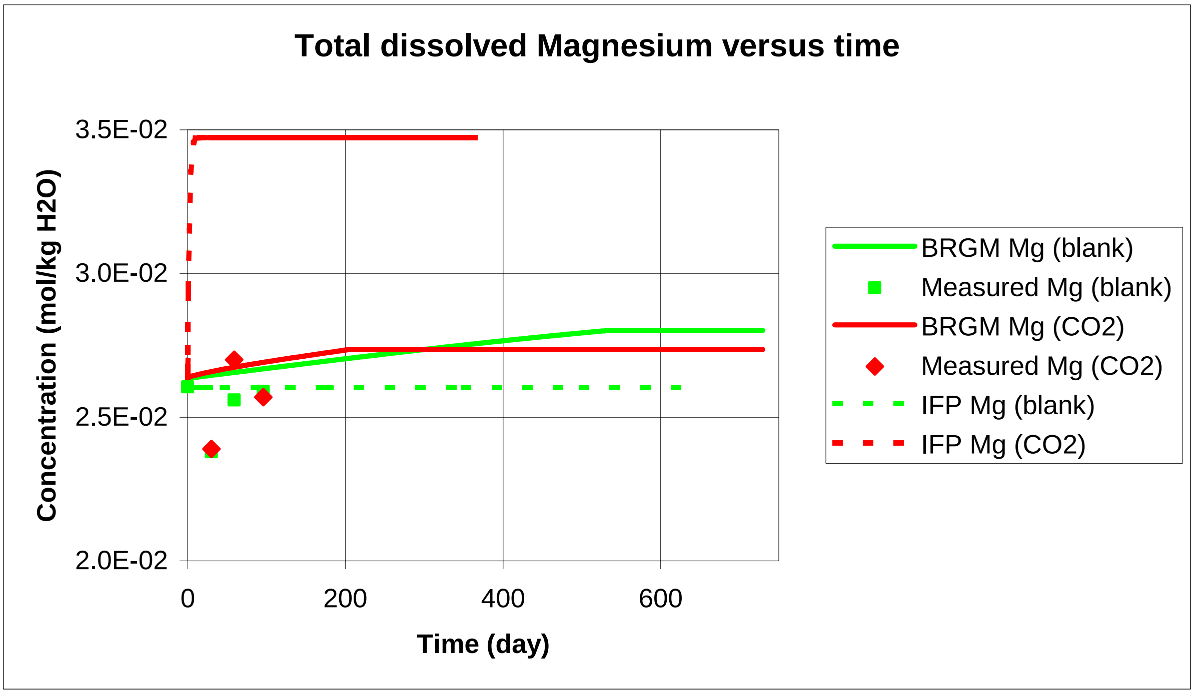


Figure 3: Modelling results of the batch experiments pressurised with N_2 (blank) and CO_2 using the UTSIRA simulator and the DIAPHORE model. Comparison of the modelled and observed water composition with time..

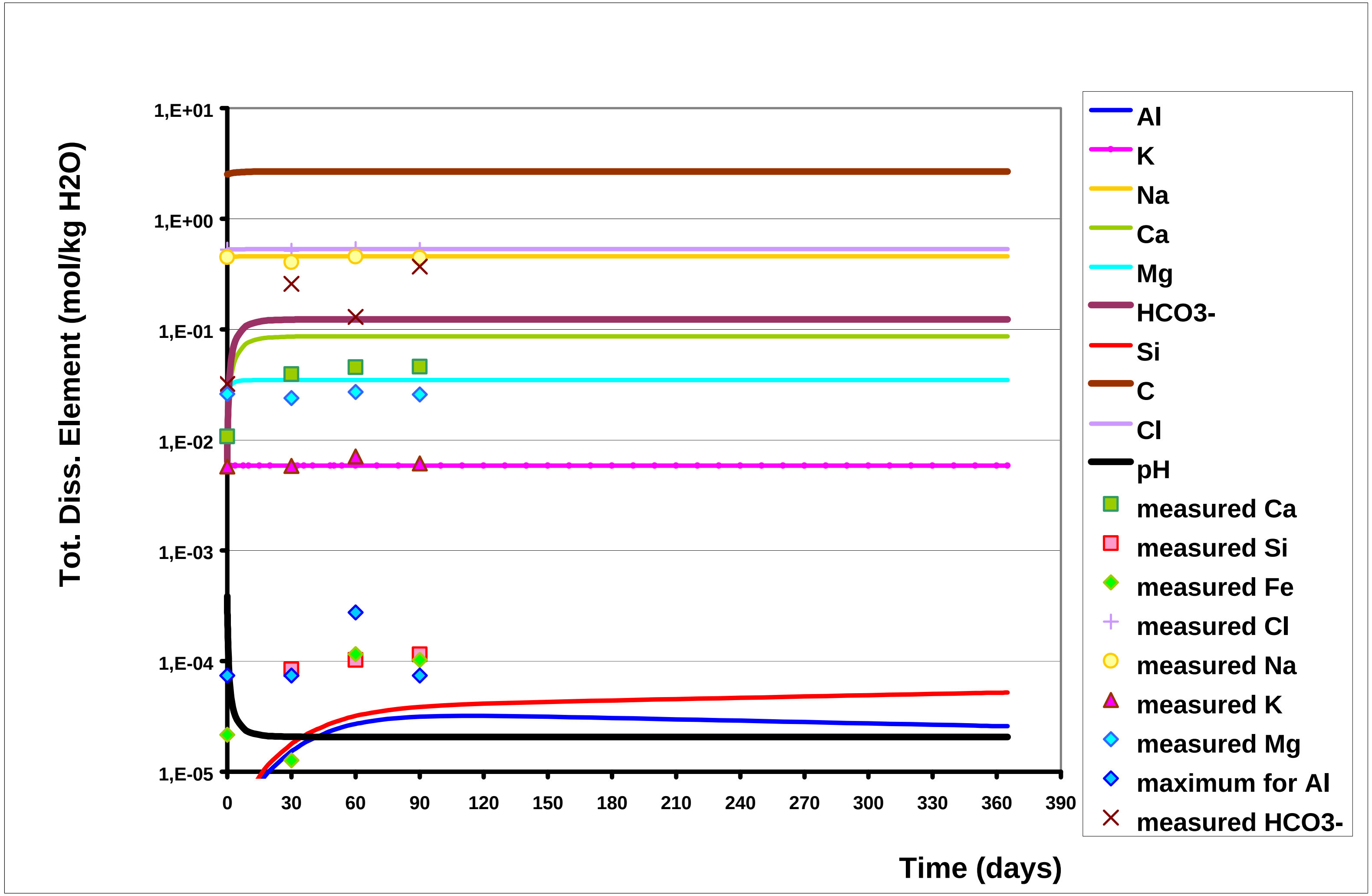


Figure 4: Modelling results of the batch experiments pressurised with CO_2 using DIAPHORE. Comparison of the modelled and observed water composition with time.

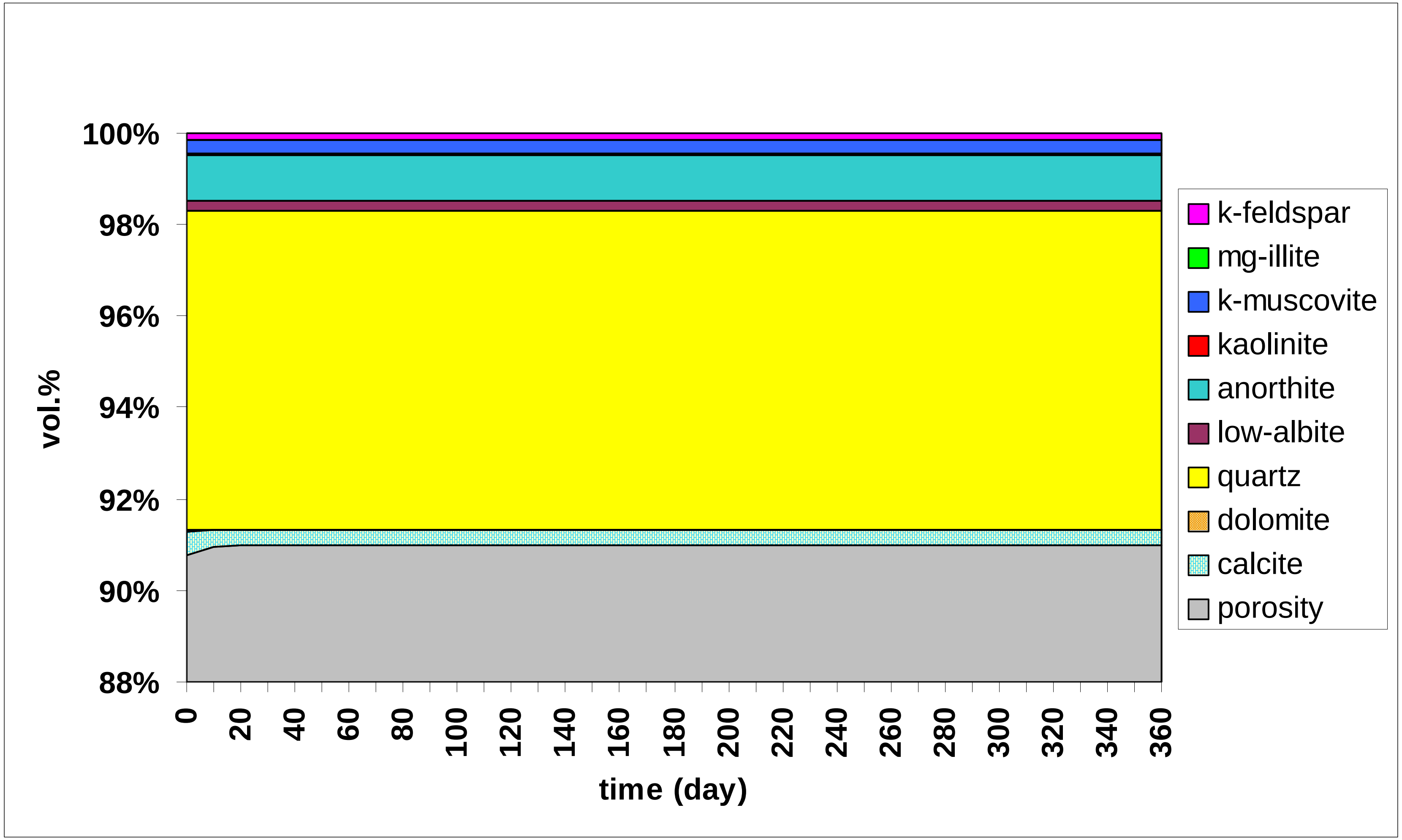


Figure 5: Modelling results of the batch experiments pressurised with CO_2 using DIAPHORE. Changes in rock mineralogy with time.

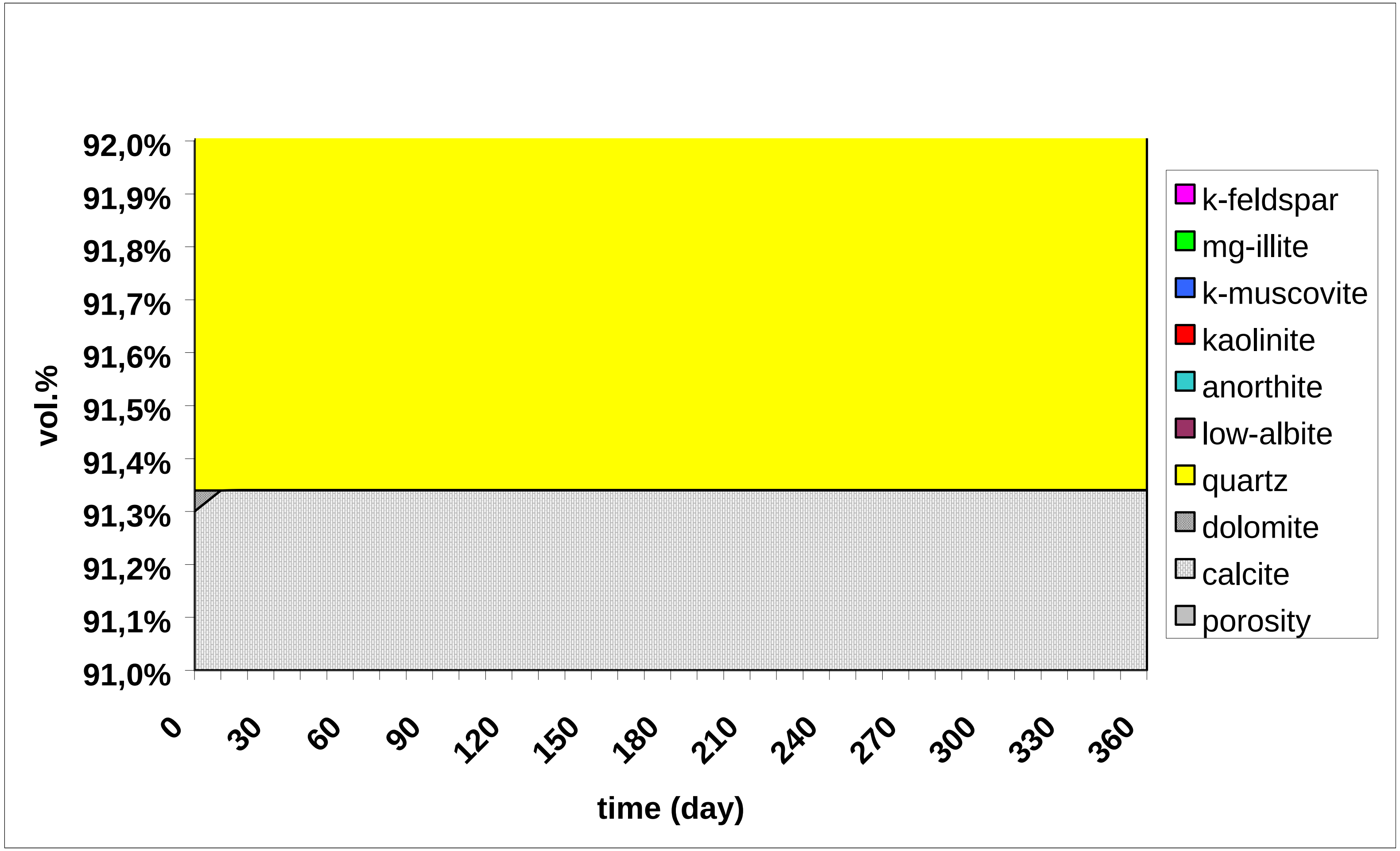


Figure 6: Modelling results of the batch experiments pressurised with CO_2 using DIAPHORE. Changes in rock mineralogy with time(zoom).