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## GaMin'11 – an international inter-laboratory comparison for geochemical CO<sub>2</sub> - saline fluid - mineral interaction experiments

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### Abstract

Due to the strong interest in geochemical CO<sub>2</sub>-fluid-rock interaction in the context of geological storage of CO<sub>2</sub> a growing number of research groups have used a variety of different experimental ways to identify important geochemical dissolution or precipitation reactions and – if possible – quantify the rates and extent of mineral or rock alteration. In this inter-laboratory comparison the gas-fluid-mineral reactions of three samples of rock-forming minerals have been investigated by 11 experimental labs. The reported results point to robust identification of the major processes in the experiments by most groups. The dissolution rates derived from the changes in composition of the aqueous phase are consistent overall, but the variation could be reduced by

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using similar corrections for changing parameters in the reaction cells over time. The comparison of experimental setups and procedures as well as of data corrections identified potential improvements for future gas-fluid-rock studies.

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## 1. Introduction

During the past decade numerous groups worldwide have used facilities to investigate gas-fluid-rock reactions at elevated pressure-temperature (P-T) conditions utilizing different experimental techniques. These approaches are relevant to geological CO<sub>2</sub> sequestration, but can also be used to address processes in hydrothermal or geothermal systems, enhanced oil/gas recovery operations, in-situ hydrocarbon production from oil shales, disposal of radioactive wastes, and other exploitation of the subsurface. As a consequence of the strong interest in geochemical reactions during CO<sub>2</sub> injection and geological storage, many research groups started to use experimental setups initially designed for other applications at different P-T-salinity conditions or began to set up new experimental facilities to investigate CO<sub>2</sub>-fluid-rock reactions.

As the insights – e.g. identified mineral dissolution/precipitation reactions, quantified rates and changes of petrophysical properties of rocks – derived from the gas-fluid-rock experiments are used in risk assessment for geological CO<sub>2</sub> storage at individual sites, uncertainties, pitfalls and possible improvements of the experimental strategies should be known. Therefore an international inter-laboratory comparison study was initiated in 2011 and carried out in 2012-2013 to undertake geochemical experiments investigating CO<sub>2</sub>-saline fluid-mineral reactions at elevated temperatures and pressures.

The major goals were: to strengthen the collaboration among experimental laboratories around the world, to explore different experimental avenues and identify possible problems with currently used equipment (for geochemical experiments with gases or gas mixtures, e.g. CO<sub>2</sub>+O<sub>2</sub>, or for coupled dissolution-precipitation processes in gas-fluid-rock experiments). Another goal was to provide an estimate of potential variance in kinetic data derived from gas-fluid-mineral interaction experiments.

## 2. Materials and methods

Different experimental approaches were used in the laboratories involved in the study, but the starting minerals and fluids used were the same. All the labs received: three purified natural mineral separates in a narrow grain size fraction, detailed mineralogical and chemical analyses of these materials, and NaCl for the preparation of saline brine. All labs successfully completed the experiments under given conditions of fluid-rock-ratio (1:20) with 150 g/l saline NaCl brine, constant temperature (80°C) and pressure (200 bars, lab F at 100 bars) conditions at CO<sub>2</sub>-saturated aqueous fluid throughout the experiments (durations varied between 3 and 21 days). Three mineral separates were selected for the purpose of the inter-laboratory study: an iron carbonate (i.e. siderite:ankerite mixture), a feldspar (i.e. labradorite) and a clay (i.e. illite).

The iron carbonate sample was a mixture of siderite and ankerite with trace amounts of quartz. Quantitative analyses by XRD with Rietveld refinement, LECO, DTA-MS and IR determined 80% siderite, 17% ankerite, and 3% quartz. The chemical analyses of individual grains by SEM-EDX and IM revealed the stoichiometric composition of the siderite as Fe<sub>0.8</sub>Mn<sub>0.1</sub>Mg<sub>0.07</sub>Ca<sub>0.03</sub>CO<sub>3</sub>, of the ankerite as Ca(Fe<sub>0.7</sub>Mg<sub>0.2</sub>Mn<sub>0.1</sub>)(CO<sub>3</sub>)<sub>2</sub>. The grain size of the distributed samples was between 100-200 μm, the samples have been washed with ethanol to remove fines, were dried and sealed under an argon atmosphere before shipment.

The feldspar sample was characterized as an alkaline plagioclase (labradorite) by XRD with Rietveld refinement, IR and DTA-MS analyses with no detectable additional mineral phases present. The chemical analysis of the labradorite by XRF and SEM-EDX revealed a stoichiometric composition of  $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$ . The particle size was between 100 to 200  $\mu\text{m}$ . The analyses of the clay mineral sample by XRD with Rietveld refinement, IR, LECO and DTA-MS revealed the presence of 80% illite (an illite-smectite showing R3 order with 10-15% smectitic layers), of 13% of a potassium feldspar and of 7% quartz. Chemical spot analyses on illite by SEM-EDX point to a stoichiometry of  $(\text{K}_{0.6})(\text{Mg}_{0.2}\text{Al}_{1.8})(\text{Al}_{0.5}\text{Si}_{3.5})\text{O}_{10}(\text{OH})_2$ . The grain size of the illite sample ranged from 0.1 to 63  $\mu\text{m}$ .

The laboratory-members of the project used a variety of experimental equipment (see Table 1): Materials exposed to the corrosive saline fluids were Teflon beakers, uncoated stainless-steel, Hastelloy, passivated titanium or gold in the flexible Dickson-type gold-titanium cells – all with different advantages/disadvantages with respect to sample handling, leaks or corrosion resistance. Another major difference between the equipment used was the pressure control during sampling: the flexible Dickson-type gold-titanium cells, a similar flexible all-titanium cell and a custom-made titanium cell with adjustable volume, allowed sampling at constant pressure, whilst other systems in fixed-volume batch reactors only allowed sampling concomitant with a potential significant pressure drop – which was then adjusted by addition of additional  $\text{CO}_2$ . In one case, the experimental setup required that the reactor was depressurized and opened for each sampling.

Table 1. Overview of experimental setups used by different laboratories.

Experimental setup	used by labs	internal volume	initial brine volume
Rocking Dickson-type flexible gold-titanium cells	C, G, K	ca. 200 ml	ca. 200 ml
Non-Rocking Dickson-type flexible gold-titanium cells	H	ca. 120 ml	ca. 110 ml
Non-Rocking flexible all-titanium cells	I	ca. 150 ml	ca. 110 ml
Rocking moving-piston all-titanium cells	B	ca. 200 ml	ca. 200 ml
Non-stirred Teflon-lined SS316 batch reactors	F	ca. 250 ml	ca. 140 ml
Non-stirred Teflon-beakers in SS316 batch reactors	E, J	ca. 250 ml	ca. 200 ml, ca. 100 ml
Stirred Hastelloy batch reactors	D	ca. 600 ml	ca. 200 ml
Non-stirred SS316 batch reactors	A	28 ml	ca. 26 ml

As the internal reactor or reaction cell volumes varied, the requirements for the inter-laboratory comparison in addition to using the same P-T conditions and the same initial brine composition were a brine:mineral mass ratio of 20:1 and that the brine should be  $\text{CO}_2$ -saturated all the time. In parts due to the different reactor or reaction cell volumes – and the use of  $\text{CO}_2$  by some groups as the pressurizing medium, the  $\text{CO}_2$ :brine ratios varied between labs. This could be problematic if significant amounts of water dissolve in the supercritical  $\text{CO}_2$  with high – and sometimes due to sampling and repressurization increasing –  $\text{CO}_2$ :brine ratios. In addition, despite initial consistent brine:mineral ratios, the reduction in brine volume during sampling affected the brine:mineral ratio over time in the experiments, especially if a high percentage of the brine was removed by sampling.

Another important variation was the degree of mixing of the fluids during the experiments in the reaction cells – the systems used were either static non-mixed batch reactors, or stirred reactors respectively rocking autoclaves with significant convective fluid mixing. Even the position of the mineral grains within the reaction cells varied: Most groups had the mineral grains sitting at the bottom of the reaction cell (or moving/in suspension for the clay sample in the mixed systems) in the reaction cell whilst two groups (lab F, lab H) enclosed the minerals in bags of polypropylene with 70  $\mu\text{m}$  mesh size hanging in the non-mixed brine from the head of the reaction cell. The addition of  $\text{CO}_2$  was defined as starting time for all experiments, but some groups (lab B, lab K) used an initial brine-mineral equilibration time of several days before adding the  $\text{CO}_2$ .

These variations in experimental approaches could potentially result in significant differences of type, succession and rate of geochemical reactions during the experiments and hence information on predominating processes and solution derived kinetic data.

### 3. Results and discussion

All participating laboratories reported the time-resolved evolution of solution chemistry for the three experiments. From the solution chemistry each laboratory had to come up with an estimate of the dissolution rate of the mineral(s). The inter-laboratory comparison study also investigated whether dissolution-precipitation processes occur at similar rates when different experimental equipment is employed.

In the experiments studying the dissolution of the iron carbonates, all (but one) participants reported an initial increase in dissolved iron concentrations (see Fig. 1) and then a decrease to lower levels, pointing towards the precipitation of a secondary mineral phase in the experiments. The reported peak concentrations of dissolved iron before the decline were similar from all groups, but the timing of peak concentrations was significantly different. The continuously mixed systems generally showed an earlier and shorter lived peak in iron concentrations than the reaction cells not being continuously mixed.

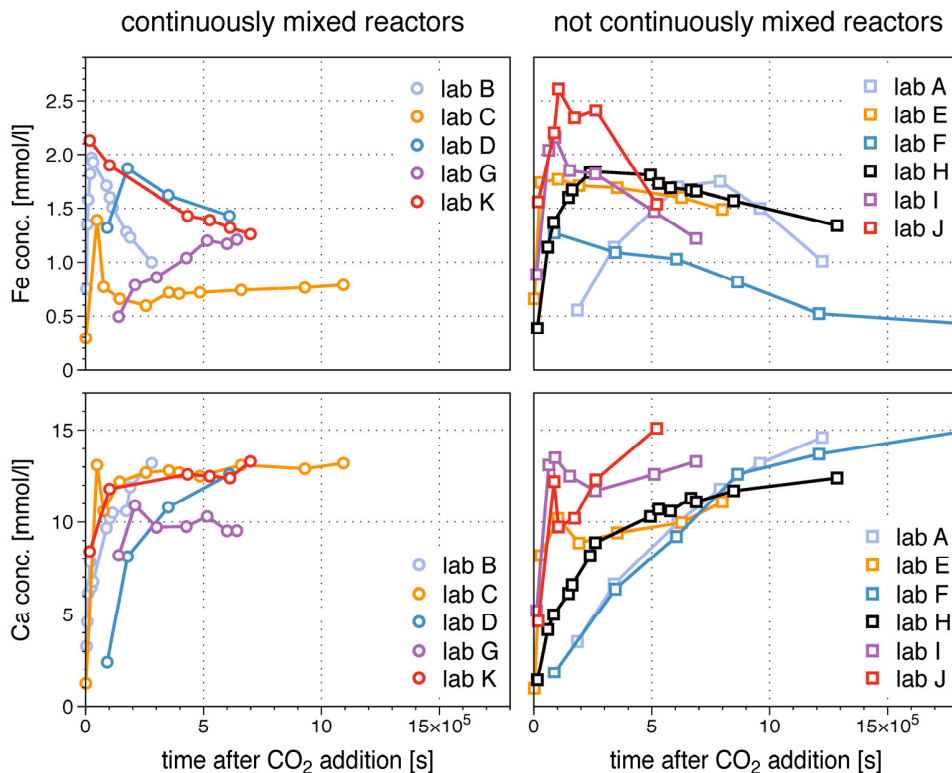


Figure 1: Concentrations of major ions in aqueous solution during the gas-fluid-mineral interaction experiment with the iron carbonates as reported by participating labs. On the left side results are displayed from labs with thorough mixing, on the right side without continuous mixing.

No lab had severe problems with preventing the oxygenation of dissolved reduced iron during the experiment and sampling. The manganese concentrations show a similar trend in concentrations (not shown) pointing to the secondary precipitation of a Fe and Mn containing mineral phase. One lab had severe corrosion problems with a stainless steel valve. The dissolved concentrations of calcium increase towards possible near-equilibrium values of

12-14 mmol/l in most experiments, in some experiments the concentrations increase beyond that concentration. The stoichiometry of the solutions show that the ankerite is dissolved preferentially compared to the siderite.

In the gas-fluid-mineral experiments with the feldspar sample, the results of all labs point to a limited and continuing dissolution of the feldspar, far lower concentrations of dissolved ions are detected than in the iron carbonate experiment. Both labs (lab B & lab K) with an initial brine:mineral equilibration time before the CO<sub>2</sub> addition noted elevated calcium concentrations at times of the CO<sub>2</sub> addition – but after that the concentrations decreased in the experiments of lab K and increased for lab B.

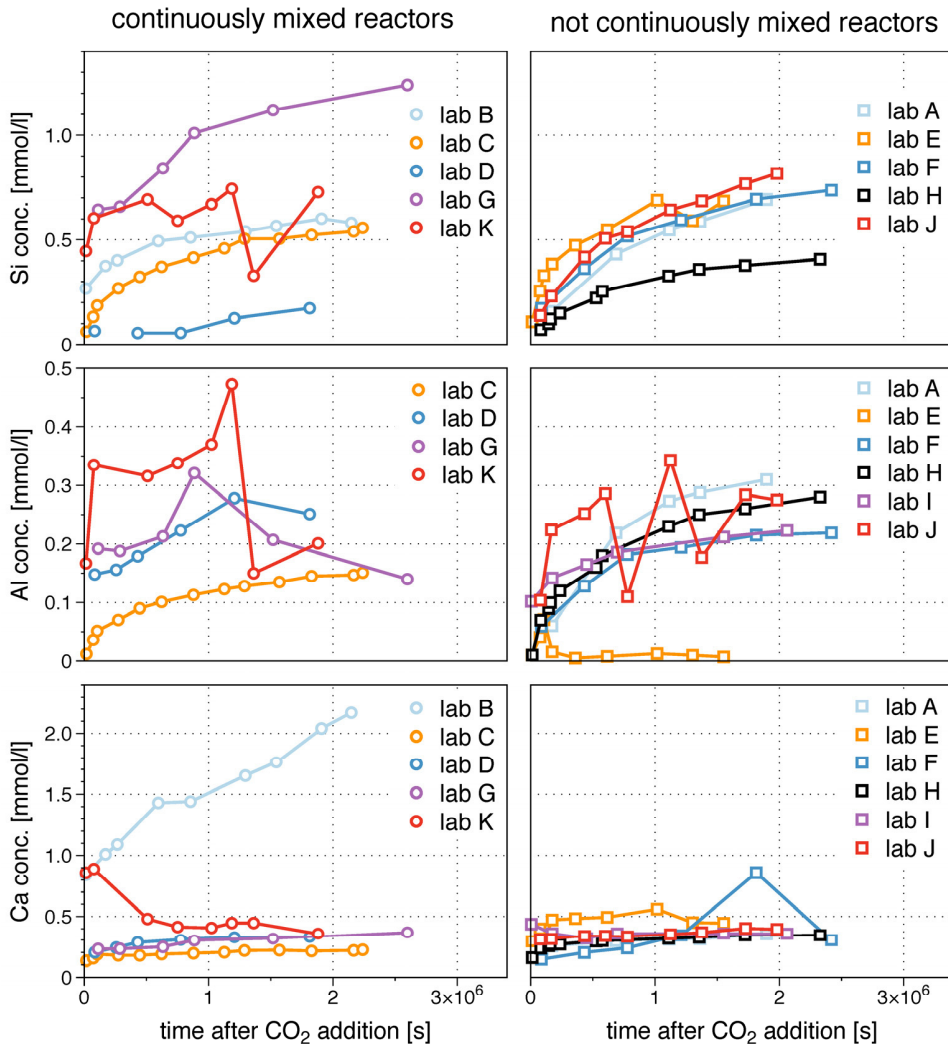


Figure 2: Concentrations of major ions in aqueous solution during the gas-fluid-mineral interaction experiment with the labradorite (feldspar) as reported by participating labs. On the left side results are displayed from labs with thorough mixing, on the right side without continuous mixing.

As evident in the fluctuating concentrations reported for Al and Si by some groups, problems during sampling or analysis of these ions were significant. Interestingly, the concentrations reported by the labs using not continuously mixed reaction cells are generally more consistent – with the exception of the Al concentration of lab E. It is not

possible to detect processes in addition to the dissolution of the feldspar despite that lab G reported decreasing Al concentrations after  $10^6$  s.

Despite the very different experimental setups used, the reported estimates on the dissolution rates of the main mineral phases vary by only an order of magnitude, e.g. for the iron carbonate gas-fluid-mineral interaction experiment from  $3 \times 10^{-9}$  to  $8 \times 10^{-8}$  mol m<sup>-2</sup> s<sup>-1</sup> with one outlier of  $6 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup>, for the feldspar gas-fluid-mineral interaction experiments from  $6 \times 10^{-11}$  to  $6 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> with one outlier of  $6 \times 10^{-12}$  mol m<sup>-2</sup> s<sup>-1</sup>. The range in reported estimates can be explained mainly in terms of the chosen time window in the experiment for calculation of the dissolution rate and by differences between well-mixed and static experimental setups (transport versus diffusion control). Other controls, such as sampling techniques, were of secondary importance

#### 4. Conclusions

The inter-laboratory comparison enabled a close collaboration of several labs exchanging ideas and knowledge on experimental setups for gas-fluid-rock interaction studies. The main findings by comparing reported concentration data and derived dissolution rates hint to several possible areas of improvements for future gas-fluid-rock interaction experiments:

- Corrosion resistance of wetted materials of the reaction cells – and the sampling lines
- Consistent – or at least explicitly described – procedures during start of experiments (removal of air, time of brine:mineral interaction before CO<sub>2</sub> addition, timing of heating before/after CO<sub>2</sub> addition)
- Sampling of only low percentages of brine to minimize changes in the brine:mineral ratio due to brine removal
- Low CO<sub>2</sub>:brine ratios in the reaction cell to minimize H<sub>2</sub>O loss from brine
- Implementation of adequate corrections to concentrations used for deriving dissolution rates for changes in brine volume and brine:mineral ratio due to repeated sampling.
- Improving sampling procedures (and analyses methods) of Al and Si at low concentrations and especially for fine-grained mineral suspensions
- Controlling the oxygen fugacity in experiments with minerals containing reduced elements (e.g. Fe<sup>II</sup>)
- Documentation of the complete set of ions analyzed in solution in publications

A detailed comparison of derived dissolution rates – and dissolution rates calculated for identical time windows – with published values from other studies of the minerals investigated will be published elsewhere. A follow-up inter-laboratory comparison will focus on using mixed-flow reactors (in comparison to the batch reactor systems tested here) for gas-fluid-mineral interaction experiments and will include additional experiments with a CO<sub>2</sub>+SO<sub>2</sub> mixture.

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