Hydration of forsterite at 1 atm PCO_2 and 80 to 120°C – Comparisons of numerical simulations and laboratory experiments to understand the factors that govern the overall mineral transformation rate

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We have characterized the coupled mineral reactions following hydration of forsterite at 80 to 120°C and a CO_2 pressure of 1 atm in a closed well-mixed system. To do so we compare numerical simulations with laboratory experiments. The numerical simulations use far-from-equilibrium dissolution rate parameters obtained from the literature and a reaction rate equation that govern both dissolution and precipitation through an affinity term. This is a common way of modeling coupled mineral dissolution and precipitation in numerical codes like TOUGHREACT and EQ3/6, and we suspect that errors in factors like the affinity term and the reactive precipitation area lead to deviations between natural reactions and corresponding numerical simulations. To gain some more insight into this we use the simple fast reacting forsterite hydration system and tune parameters like the reactive surface area in order to fit the simulated data to the experimental datapoints.

Some preliminary numerical simulations have been done to predict the outcome of the laboratory experiments. The simulations show that hydration of a pure forsterite at 1 atm CO_2 leads to formation of magnesite and talc and at some conditions quartz gets supersaturated. The reactions are suggested to be rapid at 120°C with a large fraction of the forsterite hydrated after one week and with an almost complete conversion after 21 days. By using rate data from the literature and change the reactive surface area by ± 1 order of magnitude we see that the formation rate of magnesite is independent of the talc and magnesite precipitation rates and only dependent on the slower dissolution rate of forsterite. Moreover, eventhough the mineral fractions can not be used to trace the sensitivity of the reactive surface areas, the aqueous Mg/Si ratio is suggested to be a strong carrier of information regarding the precipitation rate parameters. A slow talc precipitation rate relative to magnesite leads for instance to a low Mg/Si ratio.

Transformation of iron(oxyhydr)oxides in the presence of dissolved sulphide

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The transformation of iron (oxyhydr)oxides by Fe(II) has been the subject of a number of studies and is reasonably well understood with respect to the end products goethite and magnetite. The mechanism of the electron transfer and the process of transformation especially the modification of crystal lattice remain to be clarified. Poulton *et al.* (2004, Geochim. et Cosmo) found out, that ferrous iron which is formed by the reaction of iron oxides with dissolved sulphide strongly interacted with the mineral surface.

In our experiments we intended to study the fate of the bounded Fe(II) and the potential recrystallisation of new solid phases. In particular, the reaction over time and the competition between iron sulphide formation and ferric oxide mineral transformation was studied. Therefore anoxic and abiotic batch experiments with an excess of synthetic lepidocrocite and dissolved sulphide were performed at circumneutral pH. The water phase was sampled over time and analyzed with respect to the concentrations of S°, $S(-II)_{aq}$, $Fe(II)_{aq}$, $Fe(II)_{HCl}$.and Fe_{TOT}. The solid phase was investigated by XRD, TEM and Mössbauer spectroscopy.

Dissolved sulphide was consumed in the first minutes of the reaction leading to high Fe(II) release and the solution turned black. 25% of the total dissolved sulphide reacted to S° and 75% to FeS. 24 % of the lepidocrocite-Fe was extractable Fe(II) with HCl and only 0.8% was found as $Fe(II)_{aq}$. TEM measurements demonstrated that Fe(II) interacted with the surface of lepidocrocite which lead to the formation of magnetite. The presence of sulphur species (S° or S(-II)) furthermore caused the precepitation of mackinawite (FeS) at the magnetite surface.

After 2 weeks reaction mackinawite had transformed into the more stable FeS_2 species marcasite and the black colour disappeared.

Our results indicate, that the reaction between dissolved sulphide and iron oxides is a fast surface-controlled process with magnetite as an important intermediate.