Thermodynamics of long-term metastable magnesium (chloro) hydroxo carbonates at 25°C

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The thermodynamics of magnesium (chloro) hydroxo carbonate phases is important to assess the geochemical conditions in carbonate-containing magnesium chloride-rich solutions for nuclear waste disposal scenarios in rock salt. Though Magnesite ($MgCO_3$) is known to be the thermodynamically stable solid in the Mg-Cl-HCO_3-CO_3-H-OH-H_2O system at room temperature, long-term metastable carbonates are observed to control the solution chemistry (Hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) and Chlorartinite ($Mg_2CO_3OHCl \cdot 3H_2O$)). In the present study we focus on determining the phase transition between Hydromagnesite and Chlorartinite in order to estimate the equilibrium constant for Chlorartinite, which has not been reported so far.

Batch experiments with $MgCl_2$ solutions (0.25 to 4.5 M $MgCl_2$) and 0.05 M Na_2CO_3 are conducted over >3 years in Ar glove boxes. The pH_c ($-\log(m_{H+})$) is monitored with time and the respective precipitates are analysed with different methods (Raman, XRD, SEM-EDS, XPS). The equilibrium constant for Chlorartinite is calculated based on the equilibrium at the Hydromagnesite and Chlorartinite phase transition $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O(s) + 3Mg^{2+} + 4Cl^- + 10H_2O(l) \Leftrightarrow 4Mg_2(OH)CO_3Cl \cdot 3H_2O(s) + 2H^+$. Calculations are done using the known $MgCl_2$-concentration, the measured pH_c and published solubility constants of Hydromagnesite. Under the given conditions, stability of Hydromagnesite is observed in solutions of less than 2.5 M $MgCl_2$, while Chlorartinite is found to exist in solutions with $MgCl_2$ concentrations higher than 3.2 M $MgCl_2$. In the intermediate solution of 2.8 M $MgCl_2$, both solid phases are detected with the analytical methods. Assuming a phase transition between 2.5 M and 3.2 M $MgCl_2$, the equilibrium constant for Chlorartinite is calculated as $\log K_{CA} = 13.15 \pm 0.36$ for reaction $Mg_2(OH)CO_3Cl \cdot 3H_2O(s) + 2 H^+ \Leftrightarrow 2 Mg^{2+} + HCO_3^- + Cl^- + 4 H_2O(l)$, using the Pitzer approach for activity corrections. This equilibrium constant together with literature data allows for a comprehensive thermodynamic description of the system Mg-Cl-HCO_3-CO_3-H-OH-H_2O at room temperature.

Fluids in the upper continental crust

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The brittle upper continental crust consists predominantly of granite and gneiss. Fractures form an interconnected network of water conducting structures with an appreciable permeability also providing substantial fluid saturated fracture porosity.

The chemical composition of fluids in the fracture porosity of granite and gneiss changes with depth. Near the surface Ca-Na-HCO_3 waters dominate. With increasing depth water contains increasing amounts of alkalis and sulphate and grade into chloride-rich waters at greater depth. Total dissolved solids (TDS) of 10^5 mg L^{-1} are common at 5 km depth in most basement rocks. All reported deep fluids from the upper crust contain predominantly NaCl and $CaCl_2$. The brines vary from NaCl-rich in granites to $CaCl_2$-rich in mafic reservoir rocks such as amphibolites and gabbros.

In regions of the crust with strong topography, fluid flow is important and recharge water may have flushed the basement efficiently thereby removing old brine components from the granites.

Water samples from the new Gotthard Rail Base Tunnel of the Alps, from Norwegian road tunnels, from Korean granites and other localities represent this type of basement fluid. Analyzed fluids from up to 2.5 km depth differ from basement fluids from areas with less extreme topography in the following ways. Such waters have relatively low TDS of some 100 mg L^{-1} and are typically of the Na_2CO_3-Na_2SO_4 type. pH tends to be high and varies from 9 to more than 10. Low Ca and ultra-low Mg of such waters result from efficient deposition of secondary Ca-Mg-minerals as coatings on fracture walls. Reduction of CO_2 to amorphous carbon or further to CH_4 provides the oxidation capacity for sulphate production from primary rock sulphides. Ferrous iron silicate minerals (e.g. biotite) are oxidized to ferric oxides and hydroxides (e.g. hematite). Evidence for this mechanism is the presence carbon in sheared, water conducting granite and measurable quantities of methane in fracture water. Extreme local variations of redox conditions are reflected by the presence of pyrrhotite and other sulphides in a fracture system and anhydrite in nearby fractures of the same granite.