# Absence of solid solution between Fe(II) and Mg(II) hydroxides and consequences on formation of fougerite and smectites

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**Abstract.** As there exists extended solid solutions between ferrous and magnesian silicates, experiments were conducted to check if ferrous and magnesian hydroxides can co-precipitate in a solid solution. Results show that no solid solution forms and instead Fe(II) and Mg(II) hydroxides precipitate separately with the same solubilities as pure components. However, in fougerite, F(III), Fe(II) and Mg(II) coexist in a brucitic type hydroxide, with an extended solid solution. This implies that fougerite formation results from Fe(III) precipitation, Fe(III) being surrounded by divalent Fe(II) and Mg(II) to comply with the exclusion rule: Fe(III) ions cannot be direct neighbours. Consequently, Fe(III) - Fe(II) - Mg(II) smectites cannot form by oxidation of a ferrous - magnesian brucitic layer, but by silication of fougerite. The impossibility of formation of a solid solution between Fe(II) hydroxide and Mg(II) hydroxide, while their electric charge and ionic radii are identical can be explained by the differences of electronegativities of the elements. Fe(II) and Mg(II) can dimerize separately in aqueous solution, but an heterodimer cannot form.

## 1 Introduction

Extended solid solutions between ferrous end member and magnesian end member are known in many silicates such as olivines (forsterite - fayalite), pyroxenes (enstatite - ferrosilite), biotites (annite - phlogopite). Fe(II) and Mg(II) bear the same electric charge and ionic radii are very close to each other, respectively 0.72 and 0.78 Å. In clay minerals, Fe(II) and Mg(II) coexist in smectites. In fougerite, Fe(II) and Mg(II) coexist with Fe(III) in a brucitic layer [1, 2]. As the brucitic layer is formed by a compact stacking of octahedra, it is currently admitted that smectites form by silication of a preexisting brucitic layer. Green rusts form by partial oxidation of ferrous hydroxide, with creation of an excess of positive charge, separation of the layers with formation of an hydrated interlayer in which anions enter to compensate for the excess positive charge of the layer. Calorimetric measurements [3,4] show that enthalpies of formation of hydrotalcite-like minerals and of other layered double hydroxides (LDHs) such as nickel - aluminum hydroxide become more negative as soon as the electric charge of the layer is non

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zero and interlayers hydrate. Enthalpy of hydration of the layer is the dominant term, and contribution of anion exchange is negligible [5]. However, when silicate anion enters the layer, which results in water molecules being expelled, enthalpy becomes even more negative. This was ascribed to the silication of the octahedral layer [5], with condensation and formation of Si-O-Fe bonds. As a consequence, it can be hypothesized that smectites form by silication of a mixed hydroxide. In trioctahedral sites of smectites, such as in the montmorillonite - nontronite series Fe(III), Fe(II), Mg(II) coexist. The aim of this paper is to address the following question: is it possible to co-precipitate in anoxic conditions a mixed Fe(II) - Mg(II) hydroxide, before oxidation and silication, or does oxidation of Fe(II) precede precipitation? To this end, experiments were conducted in controlled anoxic conditions.

## 2 Material and methods

Ferrous and magnesium hydroxides were precipitated separately and co-precipitated by adding NaOH to solutions of ferrous chloride $FeCl_2.4H_2O$ and magnesium sulfate $MgSO_4.7H_2O$ under nitrogen atmosphere in a glove box. All solutions were prepared with degassed deionized water. In order to scan largely the pH interval and obtain evenly distributed pH values, the solutions were first simulated by using PHREEQC geochemical software [6], pH being computed for a solution simultaneously in equilibrium with ferrous hydroxide and magnesium hydroxide. Initial concentrations in the final volume are given in Table 1 (col 2-4). All experiments were made at room temperature, *ca*. 25 °C.

After precipitation, pH and redox potential were measured, 5 mL of solutions were filtered in the glove box at 0.2 μm pore diameter, poured into anoxic flasks 8 mL, acidified by adding 50 μL conc. HCl; total Fe and Mg were analyzed by atomic absorption spectrometry. XRD was used to characterize the precipitate, but due to technical reasons, not immediately on the fresh precipitate, but after several weeks. Redox potential Eh was measured with a platinum electrode and a reference Ag / AgCl electrode. The measured potential E(V) was converted to the scale of the normal hydrogen electrode, then to pe = -log{e}, where {e} stands for the activity of the electron as follows:

$$Eh = E + E° \tag{1}$$

$$pe = FEh/(ln\ 10)\ RT° \tag{2}$$

where F = 96485.3289 C/mol, R = 8.3144598 J/(mol.K), T° = 298.15 K and E°(Ag/AgCl) = 0.2249 V [7]. At equilibrium, one has:

$$Fe(OH)_2 + 2H^+ = Fe^{2+} + 2H_2O \tag{3}$$
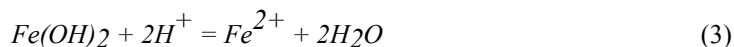
and Ionic activity product of ferrous hydroxide (Feh) (IAPFeh), defined as :

$$IAPFeh = \{Fe^{2+}\}\{H^+\}^{-2}\{H_2O\}^2 \tag{4}$$

where brackets {} designate activities, is constant and equal to the solubility product Ksp of the mineral. By taking the logarithms, the saturation index SI is defined as:

$$SIFeh = log\{Fe^{2+}\} + 2pH + 2\ log\{H_2O\} - log\ Ksp(Feh) \tag{5}$$

and the same equations hold for magnesium hydroxide (Mgh), by substituting Mg for Fe. In STP conditions, log Ksp(Feh) = 13.133 [8] and log Ksp(Mgh) = 17.1 [6]. Activities were computed with PHREEQC [6] with Specific Interaction Theory and the modified database sit_mod_2017.dat [8].

# 3 Results

Complete analytical results, and saturation indices SI for ferrous hydroxide (Feh) and magnesium hydroxide (Mgh) are given in Table 1. The regression equation between simulated and measured pH is:

$$pH\ sim. = 1.0049\ pH\ meas. - 0.0725, R^2 = 0.9972, N = 12 \qquad (6)$$

so that the difference is not significant; in a (pe, pH) diagram, all points are situated in the basic / reducing domain of water stability; though the pe value of experiment 10, with pe = - 4, is too high, it did not separate from other points and was kept. Variations of total dissolved Fe and Mg with pH (Fig. 1) show that points fit to the solubility curves of pure ferrous hydroxide and magnesium hydroxide. In a large domain of pH variation (Fig. 2 and 3), IAPs remain constant and close to the theoretical solubility products of pure hydroxides.

**Table 1.** Composition of initial mixed solutions, of solutions at equilibrium and saturation indices.

| No. | MgSO$_4$ | FeCl$_2$ | NaOH | pH sim. | pH mes. | pe | log Mg | log Fe | SI Feh | SI Mgh |
|---|---|---|---|---|---|---|---|---|---|---|
| | /mM | /mM | /mM | | | | total | total | | |
| 1 | 3 | 16.9 | 40 | 10.55 | 10.60 | -6.87 | -3.86 | -6.54 | -0.10 | -0.15 |
| 2 | 7 | 2.4 | 18 | 10.29 | 10.25 | -6.36 | -3.29 | -6.02 | 0.05 | -0.29 |
| 3 | 3 | 116 | 238 | 10.50 | 10.47 | -6.67 | -3.49 | -6.40 | -0.17 | -0.28 |
| 4 | 8 | 0.5 | 3.5 | 9.79 | 9.84 | -5.89 | -2.17 | -5.69 | -0.11 | 0.03 |
| 5 | 120 | 3.2 | 47 | 9.60 | 9.54 | -5.04 | -1.00 | -4.92 | -0.09 | 0.12 |
| 6 | 0.5 | 0.5 | 90 | 9.20 | 9.36 | -5.49 | -1.00 | -4.36 | 0.18 | -0.22 |
| 7 | 3 | 12 | 50 | 12.15 | 12.22 | -8.69 | -6.52 | -7.50 | 0.03 | -0.01 |
| 8 | 3 | 17.7 | 50 | 11.91 | 11.85 | -8.39 | -5.93 | -7.29 | 0.11 | 0.03 |
| 9 | 19 | 197 | 438 | 11.57 | 11.67 | -8.19 | -5.68 | -7.13 | 0.14 | -0.29 |
| 10 | 10 | 301 | 1 M | 13.54 | 13.45 | -4.02 | -8.00 | -7.32 | -0.21 | -0.20 |
| 11 | 1 | 3 | 191 | 13.20 | 13.14 | -8.41 | -7.64 | -7.41 | -0.06 | -0.10 |
| 12 | 3 | 10 | 1 M | 13.72 | 13.85 | -8.45 | -8.34 | -7.14 | -0.35 | -0.14 |

Initial solutions: col. 2 to 4; solutions at equilibrium: col. 6 to 9; SI Feh and SI Mgh (cf. eq. 5).
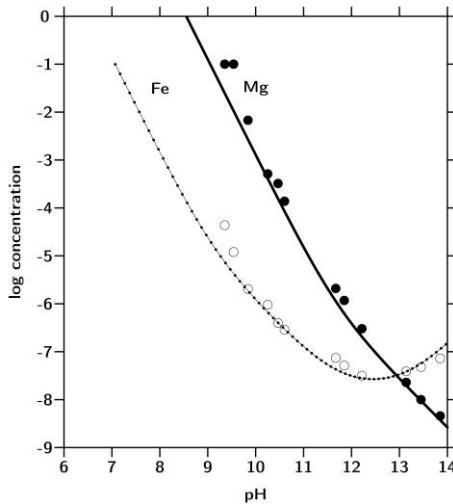


**Fig. 1.** Variation of total Fe (open circles) and total Mg (closed circles) vs. pH; curves are theoretical concentrations in equilibrium with ferrous hydroxide (dots) and magnesium hydroxide (line).

XRD on the *aged* precipitate showed the presence of brucite, and of goethite, instead of ferrous hydroxide, that was obtained in other experiments on the *fresh* precipitate [7]. If an ideal solid solution $[Fe(II)_x, Mg(II)_{(1-x)}](OH)_2$ was formed, one would obtain a solubility curve asymptotic to the solubility straight lines in the (log IAP Feh, log IAP Mgh) diagram.
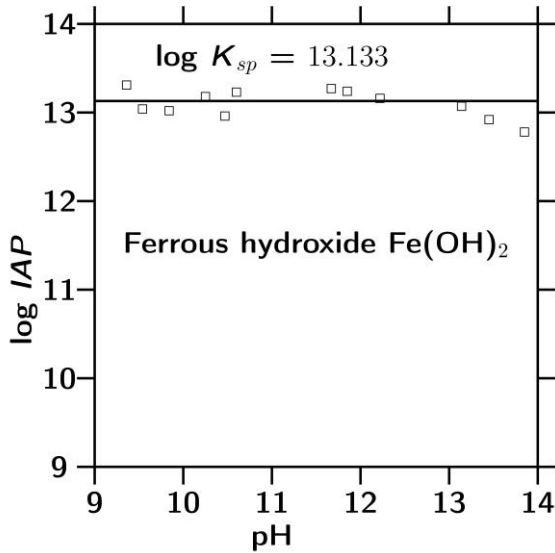


**Fig. 2.** Variation of Ionic activity product of ferrous hydroxide versus pH; value of solubility product taken from thermodynamic database sit_mod_2017.dat [6].
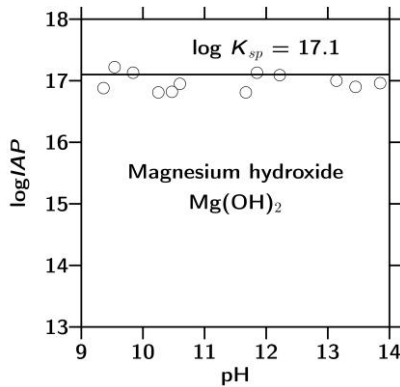


**Fig. 3.** Variation of Ionic activity product of magnesium hydroxide versus pH; value of solubility product taken from thermodynamic database sit_mod_2017.dat [6].

## 4 Discussion and conclusions

No solid solution is obtained when ferrous hydroxide and magnesium hydroxide precipitate by adding NaOH to a mixed solution of ferrous chloride and magnesium sulfate. Ferrous and magnesium hydroxides precipitate separately. The fact that goethite formed during ageing of the precipitate, as DRX was not immediately measured, can be ascribed to oxidation of ferrous hydroxide by water; indeed ferrous hydroxide can reduce water with hydrogen formation (P. Refait, pers. comm.). In other experiments, DRX was performed on the fresh precipitate and ferrous hydroxide showed its characteristic lines [9]. All points are in equilibrium with both pure hydroxides, and no solid solution forms (Fig. 3). As Fe(II) and Mg(II) bear the same electric

charge and very close ionic radii, and as they form extended solid solutions in silicates, the explanation lies in the difference of electronegativity. If we consider the formation of a dimer in solution as the first step of precipitation, there is a competition between homodimers Fe-Fe (aq.) or Mg-Mg (aq.) on one hand and a hypothetical heterodimer Fe-Mg (aq.) $[FeMg(OH)_2(OH_2)_8]^{2+}$. The partial charge model [10] gives a partial charge +0.5 for Fe atom and +0.8 for Mg atom. This large difference makes that a hypothetical bridge μ2-OH would be disequilibrated, so that Fe and Mg form preferably homodimers.
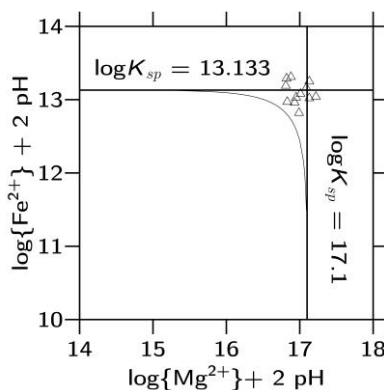


**Fig. 4.** Variation of IAP of ferrous hydroxide versus IAP of magnesium hydroxide.

As a consequence, oxidation of Fe(II) is the requisite. Fe(III) precipitates first in the brucitic layer of fougerite, surrounded by Fe(II) and Mg(II), which prevents two Fe(III) from being direct neighbors [10]. Ferri-ferromagnesian smectites thus form by silication of preexisting fougerite, and inherit Vucelic's rule of octahedral occupancy [2].

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