Stability of iron minerals in Icelandic peat areas and transport of heavy metals and nutrients across oxidation and salinity gradients – a modelling approach

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Abstract

The storage of carbon, metals and nutrients in peatlands at high latitude is sensitive to climate- and land usage changes. This work shows that the thermodynamically most stable iron phases in Icelandic peat areas, like hematite or magnetite do not form, but rather the metastable ferrihydrite, which forms in abundance. Model calculations suggest that this ferrihydrite is able to adsorb high concentrations of natural derived heavy metals (Pb, As, Cr, Cu) and nutrients (P). If this ferrihydrite comes in contact with the oceans, these elements will be released through ferrihydrite-seawater interaction. This process may have significant effects to the chemistry of the near shore environments if ferrihydrite transport to the oceans increase due to future increased flooding and sea level rise.

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1. Introduction

Peat lands cover huge areas in the sub-polar region and store vast amounts of organic carbon [1]. Their soil waters are reduced and rich in dissolved carbon, metals and nutrients [2,3]. Peat lands buffer natural floods as well as metal- and nutrient-fluxes to the oceans [2]. These fluxes are probably affected by climate change and man-made drainage channels. The overall objective of this project is to define the in situ mineralogy and soil water composition in Icelandic peat under conditions of high dust fluxes and their evolution along oxidation, pH and salinity gradients. The

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dust is mostly composed of basaltic glass and is the main source of the dissolved metals, and tends to increase the pH and alkalinity of the soil solutions when it dissolves [4, 5]. Icelandic soils are reported to contain up to 8 wt. % ferrihydrite (Fe₁₀O₁₄(OH)₂), typically estimated with ammonium oxalate extraction methods [6], whereas other thermodynamically more stable secondary iron phases are absent [7]. However, most of the Icelandic rivers are of drinking water quality; the concentrations of toxic metals are in most cases below the drinking water quality guidelines published by the World Health Organization [8].

Some rivers and soil waters have high dissolved and particulate iron content, as evidenced by chemical analysis and commonly observed as red precipitates. The importance of these widely observed iron phases and their role in heavy metals and nutrients transport from within the soil until reaching the ocean, across oxygen, pH and salinity gradients, is not yet fully understood. Through geochemical modelling, we attempt to get insight into this process.

Here we present: 1) the predominant fields of the metastable iron phases along pH, Eh, alkalinity and dissolved Fe gradients and 2) a model of the adsorption and desorption of metals and nutrients on ferrihydrite surfaces along an Eh and salinity gradient. The modelling was constrained by reported chemistry of soil waters under reduced conditions within Icelandic peat [9]. The adsorption desorption modelling mimic the mechanical transport of ferrihydrite surfaces saturated with adsorbed metals and nutrients to the ocean and its eventual interaction with ocean waters.

To understand these adsorption-desorption processes and transport along various gradients, the identification and characterization of the mineral phases in the soil as well as the precipitates in the drainage channels is required. This will be the focus of future studies.

2. Methods

2.1. Geochemical modelling

The stability of various iron mineral phases and dissolved species were predicted using PHREEQC Interactive 3.3.8.11728 [10] together with its minteq.v4 database [11] after adding data for green rust carbonate taken from Drissi et al. [12]. The calculations include the chemical analysis of different soil water samples from West-Iceland containing major and trace elements, alkalinity, pH as well as the reference temperature during the pH measurements [9].

In addition to PHREEQC and the databases described above, the graphical output program PhreePlot [13] was used to illustrate the stability relations between the iron phases to predict the dominant solid phase or aqueous species as a function of pH and Eh at 25 °C. Results are achieved by a simple looping feature, which can either calculate each single point in the diagram by a ‘grid’ approach or track internal boundaries via a ‘hunt and track’ approach. While the ‘hunt and track’ approach is faster, it also makes the assumption that all fields can be delineated by tracking the boundaries starting from a domain boundary. In contrast, the ‘grid’ approach calculates the dominating phase for each defined point. [13]

The diagrams in Fig. 1 and 2 are calculated for a pH range from 4 to 10 covering the most common pH range in natural waters [14]. All calculations are limited by the stability of water under oxidized conditions (pO₂ > 0.21 atm) and methane (pCH₄ > 1 atm) under reduced conditions (the lower part of the diagrams). The predominance diagrams were not extended to the lower stability line of water (pH₂ > 1 atm), which lies below the methane stability field, because this would require and open system where the methane could degas from solution to keep the partial pressure below 1 atm.

For the study of transport across Eh, pH and salinity gradients, the soil solution is specified (Table 1) and then equilibrated with O₂ at atmospheric pressure to simulate the oxidation of the soil solution when in contact with the atmosphere. In addition, ferrihydrite is allowed to precipitate and then used as a surface for adsorption and desorption. The concentration of weak and strong adsorption sites are maintained as the default values of PHREEQC: 0.2 mol weak sites per mol ferrihydrite with a surface area of 5.33×10⁴ m²/mol and 0.5×10⁻² mol of strong sites per mol ferrihydrite. It is then assumed that the adsorption-desorption process on ferrihydrite surfaces attained equilibrium at 25 °C and atmospheric O₂ pressure.

The oxidized solution and the precipitated ferrihydrite, as a surface adsorbent, are mixed with seawater during a second reaction step using the composition published by Stefánsdóttir et al. [15] for North Atlantic seawater. The mixing ratio of the oxidized soil solution and the seawater is varied from 3:1 to 1:100.000 in the models to simulate
the effect of increasing fluid mixing. All element concentrations are then corrected for the dilution during mixing and the final values are normalized to 100% for each element compared to the original soil solution as shown in Fig. 3.

2.2. Soil water sampling and analysis

The soil solution used for calculations in this study (Table 1) was collected in the peat area in Hvammssendi on the eastern shore of Hvalfjöður in western Iceland [9]. The sample 98-JA086 was collected on the 8th of September 1998 [9]. This sample was collected from a hole made using a stainless steel auger with 2.5 cm diameter at 45° to a depth of 50 cm. A soil solution sampler used was made of PTFE (Teflon) and quartz (Prenart, Denmark) was installed as reported in detail by Sigfusson et al. [3]. The soil solution was analyzed for pH, alkalinity (by titration with 0.1 M HCl), major anions and cations (by ion chromatography and inductively coupled plasma atomic emission spectrometry), trace elements (by High Resolution Inductively Coupled Plasma Mass Spectrometry) and nutrients (by autoanalyzer) as described by Sigfusson et al. [5] and Gislason et al. [9]. The composition of this soil solution is given in Table 1. This sample represents a typical soil water composition from natural peat areas in western Iceland.

Table 1: pH, alkalinity and concentrations of nutrients, major and trace elements of soil solution 98-JA086, used for the geochemical model

<table>
<thead>
<tr>
<th>Major constituents</th>
<th>Concentration per liter</th>
<th>Nutrients</th>
<th>Concentration nmol/l</th>
<th>Trace elements</th>
<th>Concentration nmol/l</th>
<th>Trace elements</th>
<th>Concentration nmol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.39</td>
<td>NH₄</td>
<td>0.746</td>
<td>Al</td>
<td>634</td>
<td>Hg</td>
<td>0.02</td>
</tr>
<tr>
<td>alkalinity</td>
<td>1.170 meq</td>
<td>NO₂</td>
<td>0.086</td>
<td>As</td>
<td>3.08</td>
<td>Mn</td>
<td>7010</td>
</tr>
<tr>
<td>Ca</td>
<td>350 μmol</td>
<td>NO₃</td>
<td>0.145</td>
<td>Ba</td>
<td>20.5</td>
<td>Mo</td>
<td>1.21</td>
</tr>
<tr>
<td>Cl</td>
<td>810 μmol</td>
<td>PO₄</td>
<td>0.127</td>
<td>Cd</td>
<td>0.09</td>
<td>Ni</td>
<td>44.0</td>
</tr>
<tr>
<td>F</td>
<td>2.82 μmol</td>
<td></td>
<td></td>
<td>Co</td>
<td>60.6</td>
<td>Pb</td>
<td>0.12</td>
</tr>
<tr>
<td>Mg</td>
<td>320 μmol</td>
<td></td>
<td></td>
<td>Cr</td>
<td>2.25</td>
<td>Sr</td>
<td>188</td>
</tr>
<tr>
<td>Na</td>
<td>900 μmol</td>
<td></td>
<td></td>
<td>Cu</td>
<td>4.78</td>
<td>Ti</td>
<td>3.46</td>
</tr>
<tr>
<td>SiO₂</td>
<td>480 μmol</td>
<td></td>
<td></td>
<td>Fe</td>
<td>138000</td>
<td>Zn</td>
<td>42.1</td>
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<tr>
<td>SO₄</td>
<td>240 μmol</td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

3. Results

Based on the soil water composition shown in Table 1, predominance diagrams for the most stable iron phases were calculated (Fig. 1). The iron concentrations in Fig. 1 were set at 50 and 500 μmol/l Fe to cover variations in the measured soil water samples reported in Gislason et al. [9]. The most thermodynamically stable iron minerals are hematite (α-Fe₂O₃) and magnetite (Fe₃O₄). At low pH and at high reducing conditions the aqueous Fe²⁺ specie dominates the predominance diagram. By decreasing the iron concentration to 50 μmol/l pyrite (FeS₂) becomes present (Fig. 1, right) in a narrow field covering most of the pH range at very reduced conditions right above the stability line for methane (pCH₄ > 1 atm). These results are in agreement with the findings of Rickard and Luther [16] for seawater conditions.

Despite these results, soil waters and associated minerals do not reach an equilibrium state under natural conditions [17]. The reaction rates are the limiting factors for the formation of iron oxides like hematite and magnetite from solution. Precipitation of ferrihydrite from Fe²⁺/Fe³⁺ bearing solutions is favored over the formation of goethite (FeO(OH)) or hematite [18]. A wide range of literature shows that ferrihydrite is the most common iron phase in natural soils, soil water and surface water [7, 16, 18].
Ferrihydrite transforms slowly into goethite and is therefore the most common but metastable iron phase [19, 20]. Hence, the pH Eh diagram showing hematite and magnetite as the dominant iron phases cannot be used as a guide for natural processes, especially at low temperature in the sub-polar region.

By prohibiting the kinetically hindered mineral phases - hematite, magnetite, goethite and maghemite (γ-Fe₂O₃) - to form in the model, we constructed a new predominance diagram showing the metastable but natural occurring iron phases. The robustness of the model was tested by varying the total dissolved iron and alkalinity concentrations within reasonable range based on chemical analysis of soil water in western Iceland [9]. As shown in Fig. 2, all pH Eh diagrams are dominated by the presence of ferrihydrite over the whole pH range at oxidizing and moderate reducing conditions. In addition, iron carbonates can form at pH >7.5 at very reduced conditions. They are represented by siderite (FeCO₃) and green rust carbonate (GR), a mixed Fe²⁺ Fe³⁺ metal hydroxide phase with intercalated carbonate anions (Fe₆(OH)₁₂CO₃). It is reported that green rust phases were found in soils and sediments under suboxic and anoxic conditions [21, 22, 23]. While the variation of alkalinity shows little effect on the dominant phases, a decrease in the iron concentration leads to the formation of pyrite under most reducing conditions. Our predominance diagrams are in good agreement with published data [16, 19].

The superimposed data for peat bogs (shaded area in the upper left diagram, Fig. 2) from Baas Becking et al. [14] show, that the pH-Eh conditions in peats can vary substantially and cover nearly the whole predominance diagram. Therefore, the formation of all shown phases could be possible under natural conditions. Natural peat bogs can also exhibit very low reducing conditions reaching down below CH₄ degassing pressure (pCH₄ > 1 atm). Presently, there is very limited data about the occurrence of siderite in Icelandic soils [24]. As described by the author, siderite was found only in very small amounts and with probably negligible importance [24]. To our knowledge, to date there is no published data about any green rust phases in Icelandic soils. The pyrite predominance field disappears when decreasing the dissolved sulfur concentration by a factor of 5 or more in the modeled solution. At alkaline pH, siderite takes predominance over pyrite, whereas at lower pH aqueous Fe²⁺ dominates, similar to what can be observed at higher iron concentrations (Fig. 2, left side). The predominance fields of green rust and ferrihydrite are not affected by these changes. The models show that the pyrite stability is mostly effected by the Fe:S ratio, whereas alkalinity has less effect on the predominance field of pyrite in the pH-Eh diagrams. A change of the Fe and S concentrations while keeping the total dissolved Fe : S ratio constant does not affect the extent of the pyrite field.
Atmospheric O$_2$ (pO$_2$ = 0.21 atm), the mixing of this fluid with seawater was simulated in 41 steps covering oxidized soils. After the equilibration of the reduced soil solution (Table 1) with seawater, the following concentration changes were observed: Ni by 4.1%, Cd by 5.0%, Zn by 15.7%, Cu by 92.8%, Cr by 95.9%, Pb by 99.8%, and As by 99.8%. Elements whose concentration changes less than 1% during the simulations are not shown in the diagram. After the equilibration of the reduced soil solution with seawater, 95.9% of P was released, 99.7% of Pb, and 99.8% of As. The concentration changes less than 1% during the simulations for Ni, Cd, and Zn are 4.1%, 5.0%, and 15.7%, respectively.

Figure 2: Predominance diagrams for metastable iron phases under varying iron and carbonate concentrations, shaded field in the upper left diagram represents common pH Eh conditions in peat bogs (data from Baas Becking et al. [14]).

Based on the observation that ferrihydrite covers most of the predominance diagram, as shown in Fig. 2, and is abundant in Icelandic peat areas [7], we modeled the oxidation of the soil solution in Table 2 to ferrihydrite and its effect on other dissolved species. Furthermore, the stepwise mixing of the newly formed ferrihydrite and its oxidized soil water with seawater simulates the transport of the ferrihydrite by water to the ocean and a subsequent mixing in coastal waters across a salinity gradient. Our model shows that oxidation of a Fe$^{2+}$ rich soil water leads to the formation of ferrihydrite, which then acts as a surface for adsorption processes. The initial oxidation of the fluid leads to a decrease of the fluid concentration of (Fig. 3, circles): Ni by 4.1%, Cd by 5.0%, Zn by 15.7%, Cu by 92.8%, Cr by 95.9%, Pb by 99.8%, and As by 99.8%. Elements whose concentration changes less than 1% during the simulations are not shown in the diagram. After the equilibration of the reduced soil solution (Table 1) with atmospheric O$_2$ (pO$_2$ = 0.21 atm), the mixing of this fluid with seawater was simulated in 41 steps covering oxidized soil water to seawater ratios from 3:1 to 1:100,000 – see Fig. 3.
By mixing the oxidized peat water with seawater, the different adsorbed constituents are released from the ferrihydrite. Cadmium is fully released during the first mixing step, followed by Ni, Zn, Cr and P at a ratio of 1:100, whereas Cr and P was initially nearly completely adsorbed. Copper is fully desorbed at a ratio of 1:5'000, the release during the first steps is relatively low. Arsenic and lead release requires the greatest quantity of seawater, 25 % of each element is released at a ratio of 1:100 and 75 % at 1:1000. At a mixing ratio of 1:100,000 As and Pb are fully desorbed, whereas ferrihydrite is still supersaturated with respect to the aqueous solution. Based on calculations from Jones et al. [25] this mixing ratio could occur within the first 10 to 15 km from the river inlet into the ocean.

4. Discussion and conclusions

Based on geochemical modelling, we gained insight into the predominance of iron phases within Icelandic peat soils and their effect on heavy metal and nutrient retention upon oxidation and a subsequent release in costal water. Note that our models assume equilibrium between the solid phases and aqueous solutions, which may not be attained under natural conditions [16, 17]. Also, the interaction of other phases, especially natural organic matter, are not considered in our models. Models for adsorption of metals to humic and fulvic substances suggest strong Cu adsorption onto these compounds. Therefore, the Cu concentration in aqueous solution might be lower than in our model calculations. Additionally, the model is only capable of simulating the adsorption to pure ferrihydrite. Incorporation of heavy metals by coprecipitation cannot be simulated or any modification of the adsorption behavior of ferrihydrite by its interaction with other natural occurring phases or bacteria.

Our results indicating the high retention of phosphate, arsenate and lead by ferrihydrite are in good agreement with published data [26, 27, 28]. Poorly crystalline ferrihydrite, which has a high surface area, shows high retention capacity, but also so too do soils with high ferrihydrite content [29]. Therefore, the release of the adsorbed phases directly from the soil should be investigated.

The work of Hawley et al. [30] proposed that the export of iron(oxy)hydroxides with surface adsorbed constituents and their transport to the ocean is negligible in non-glacial Icelandic rivers. This conclusion is in contrast to the calculations presented in this report. Nevertheless, even if the transport and release of heavy metals to the ocean is limited at present, this process might become more important due to future flooding events or sea level rise.
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