

Transport and ion exchange between Na⁺ and Ca²⁺ in vermiculite: Modeling of experimental data obtained for static and stirred flow-through reactor methods

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Smectites are known to control the concentrations of many major cations in natural waters because of their high cationic exchange capacities and specific surface areas. Ion exchange properties of these minerals are deeply studied in static conditions, but these properties are not well understood when water flow conditions are applied. In literature, thermodynamic and kinetic constants obtained from batch experiments were often tested in advection/dispersion conditions, but in most of the cases, the obtained models failed to correctly reproduce the data without adjustment of the constants. However, these thermodynamic constants most often depend on chemical parameters, such as ionic strength, and rarely account for the non linearity of the element sorption. Moreover it is difficult to assess if constants obtained in batch experiments could be reliable or not to predict ion exchange with water flow. Indeed to our knowledge, experiments using an advection/dispersion flow were never performed in similar chemical conditions (solid/solution ratio, ionic strength) than those used in batch, at least concerning major cations.

In this study, we have investigated sorption/desorption of Ca²⁺ on a Na-vermiculite (Santa Olalla, 50 ϕ <math><150\mu\text{m}</math>) using both batch and stirred flow through reactor methods. All experiments were performed at 3 g/L, at I=10⁻² mol/L and for a range of equivalent fraction of sorbed Ca²⁺ from 0 to 100%.

At first, experiments performed in batch allowed us obtaining (1) Na/Ca selectivity coefficient (following 'Gaines Thomas' convention) which characterises chemical equilibrium and (2) sorption/desorption kinetics constants using a first order reaction. The selectivity coefficient thus obtained is independent of both ionic strength and exchanger composition, and could be used to predict ion exchange during an advective/dispersion flow experiments if instantaneous reaction is assumed. On the other hand, kinetic constants obtained in batch are independent of the initial concentration of Ca²⁺ in solution and could therefore be used to predict ion exchange when flow is applied to the system if we assume a controlled kinetic reaction. Then, we compared the breakthrough curves obtained for both aqueous Na⁺ and Ca²⁺ using stirred flow-through reactor with those predicted either by instantaneous ion exchange model or kinetic controlled reaction; both models being constrained by results obtained in batch experiments.

Molecular characterization of dissolved organic matter (DOM) in Northern peatlands: Identifying the chemical signatures of climate change

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Peatlands are unusual in greenhouse scenarios because on the one hand they sequester carbon from the atmosphere as peat, while on the other hand they re-emit it in large quantities as carbon dioxide and methane. Due to a general lack of understanding of the chemical processes that link solid phase peat and dissolved organic matter (DOM) within its porewaters, the response of these large carbon reservoirs to climate change remains uncertain. In this work we have applied absorption spectroscopy, Excitation/Emission Matrix (EEM) fluorescence spectroscopy and ultrahigh resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) to characterize the molecular composition of dissolved organic matter (DOM) in soil porewaters at varying depths from different sites (sedge-dominated fens and sphagnum-dominated bogs) within the Glacial Lake Agassiz Peatlands (GLAP) of northern Minnesota.

Results from previous studies that utilized stable and radiocarbon isotope data suggested that DOM formation and evolution was different in fens and bogs [1]. Here we describe absorption and fluorescence spectroscopy data that confirm qualitative and quantitative differences in porewater DOM that are consistent with the hypothesis that DOM in sedge-dominated peatlands preserves aromatic compounds at depth, in contrast to DOM in peatlands where *Sphagnum* or other vascular plants dominate. These data are supported by molecular level analyses of DOM by ultrahigh-resolution mass spectrometry that indicate more dramatic changes with depth in the composition of DOM in the sedge-dominated peats.

[1] Chanton *et al.* (2008) *Glob. Biogeochem. Cycles* **22**, GB4022.