

# Competitive sorption of protons and metal cations onto kaolinite: experiments and modeling

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## Abstract

Competitive sorption of protons, Cu, and Pb onto kaolinite (KGa-2) was investigated over wide concentration ranges and quantitatively described using three different models based on surface complexation and cation exchange reactions. In all models, two types of binding sites were assumed for kaolinite: edge sites ( $\text{SOH}^{0.5-}$ ) with pH-dependent charge and face sites ( $\text{X}^-$ ) with permanent negative charge. In a first step, proton sorption was measured by potentiometric acid–base titrations of kaolinite dispersed in 0.01, 0.03, and 0.1 M  $\text{NaNO}_3$  electrolyte solutions. The acid–base titration data were fitted to obtain site densities and protonation constants for the edge and face sites, respectively. In a second step, the sorption of Cu and Pb onto kaolinite was investigated at fixed pH values by metal titration using ion-selective electrodes for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , respectively, and by independent batch sorption experiments. Our metal sorption data cover a range of pH 4–8 for Cu and pH 4–6 for Pb, three different ionic strengths (0.01, 0.03, and 0.1 M  $\text{NaNO}_3$ ), and up to eight orders of magnitude in free metal ion activity. An additional experiment was conducted to explore the sorption competition between Cu and Pb. In all three models, sorption of protons and metal cations to the edge sites of kaolinite was described with a 1-pK basic Stern (BS) approach. The three models differed only in the description of cation sorption to the face sites. In the first model (BS/GT), we used a Gaines–Thomas (GT) cation exchange equation for the face sites. This model yielded a satisfactory description of Cu sorption, but failed to describe Pb sorption isotherms at pH 4, 5, and 6. In the second model (BS/BS), we replaced the Gaines–Thomas equation by a basic Stern surface complexation formulation, thereby introducing electrostatic terms for sorption to face sites and allowing for free binding sites  $\text{X}^-$ . This did not improve the fits of Cu or Pb sorption to kaolinite, however. In the third model (BS/BS<sub>ext</sub>), we extended the BS/BS-model by introducing additional monodentate sorption complexes at face sites ( $\text{X-Cu}^+$  and  $\text{X-PbNO}_3$ ). This model described both Cu and Pb sorption very well over the entire range in metal concentrations and pH. It also correctly predicted the competitive effect of Pb on sorption of Cu. Model calculations with all three models suggested that Cu and Pb were sorbed mainly to face sites at low pH, while sorption to edge sites dominated at high pH values.

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## 1. Introduction

The mobility and bioavailability of trace metals in the environment is controlled to a large extent by sorption reactions at mineral surfaces [1]. Clay minerals are among the most important sorbents for metal cations in soils and sediments, which is due to their high abundance, large specific surface area, negative surface charge, and reactive surface

hydroxyl groups [2]. Most clay minerals possess both a permanent negative charge on the face surfaces of the platy crystals, resulting from isomorphous substitution in the crystal lattice, and pH-dependent charge on edge surfaces, resulting from reactive surface hydroxyl groups [2,3]. Major cations in soils (e.g., Ca, Mg, Na) are adsorbed primarily by cation exchange, a readily reversible sorption mechanism caused by electrostatic attraction of cations to negatively charged surfaces [2,4,5]. Many trace metals, however, also form specific inner-sphere complexes with reactive surface hydroxyl groups at the edges of clay minerals, leading to different

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sorption behavior [6]. At high pH values, trace-metal sorption can clearly exceed the cation exchange capacity of clay minerals, indicating specific sorption or surface precipitation. In general, specific sorption of trace-metal cations onto clays strongly increases with increasing pH, while metal sorption by cation exchange is considered to be less pH-dependent.

Predicting the environmental behavior of trace metals requires models capable of describing sorption equilibria over wide ranges in dissolved and total metal concentrations, pH, and concentrations of competing ions [7,8]. Sorption of metal cations onto oxide minerals has been studied extensively during the past decades by batch experiments, titration experiments, and spectroscopic techniques [9–11]. For well-characterized iron oxides, such as goethite ( $\alpha$ -FeOOH) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), surface complexation models were successfully used for describing experimental sorption data [8,9,12,13]. In some studies, the modeled datasets included proton sorption, pH-dependent metal sorption, and proton-to-metal exchange ratios [8–10,12]. Complementary information about mechanisms of sorption onto oxide surfaces at the molecular level has been gained with spectroscopic and microscopic techniques [11,14–17]. For clay minerals, only a few studies are available in which trace-metal sorption was investigated and modeled over large concentration ranges [18,19]. Most studies on trace-metal sorption onto clays have employed batch experiments, measuring either so-called sorption edges (pH-dependent sorption at fixed total metal concentration) or sorption isotherms (concentration-dependent sorption at fixed pH), frequently covering only small ranges in dissolved metal concentrations [5,20–22]. Baeyens and Bradbury [18,19] have investigated proton, Ni, and Zn sorption onto montmorillonite clay over wide concentration ranges. They used a combined cation exchange/surface complexation model to describe their data. Other studies modeled smaller datasets of proton and metal sorption onto kaolinite with a combined cation exchange/surface complexation model [20], with a three-layer model [23], and with constant-capacitance surface complexation models [5,22]. Proton-to-metal exchange ratios and sorption competition between different trace metals have rarely been reported for clay minerals.

Here, we investigate the sorption of Cu(II) and Pb(II) onto kaolinite clay. Kaolinite was chosen for two reasons: (1) it is one of the most abundant clay minerals in many acidic, weathered soils of humid climatic regions [24], and (2) the sorption of cations onto kaolinite is influenced both by a permanent negative charge on the face surfaces and by a pH-dependent charge on edge surfaces. The crystal structure of kaolinite consists of silica tetrahedral sheets connected over apical oxygen atoms with aluminum dioctahedral sheets. These 1:1 layers are held together by hydrogen bonds [2,3,24]. Previous investigations of ion sorption to kaolinite indicated two distinct sorption mechanisms on kaolinite, which were described by cation exchange and

specific sorption reactions, respectively [5,20,21]. However, studies investigating and modeling trace metal sorption onto kaolinite over large concentration ranges are still lacking. Therefore the objectives of this study were (i) to investigate the sorption of protons, Cu, and Pb onto kaolinite over large ranges in dissolved metal concentration, pH, and ionic strength, and (ii) to model the entire dataset including the competition between Cu and Pb, using surface complexation and/or cation exchange reactions.

## 2. Materials and methods

### 2.1. Kaolinite

A standard kaolinite from the Source Clays Repository of the Clay Minerals Society was used for this study (KGa-2, Warren County, Georgia). Ten-gram samples of the KGa-2 kaolinite were suspended in 250 ml of doubly deionized water. To facilitate the dispersion of the clay particles, the pH value of the suspension was adjusted to 9.5 by addition of NaOH. The clay suspension was treated with an ultrasonic tip and the fraction of particles with hydrodynamic diameters  $<1\ \mu\text{m}$  was separated by repeated centrifugation and dispersion steps. The kaolinite fraction  $<1\ \mu\text{m}$  was collected and washed five times with 1 M NaCl to saturate the clay with Na<sup>+</sup>. Excess salt was then removed by repeated washing with deionized water. The Na-saturated, salt-free kaolinite suspension was quickly frozen at  $-40\ ^\circ\text{C}$  in an ethanol bath and freeze-dried.

The kaolinite was characterized by X-ray diffraction (XRD) analysis and visual inspection by transmission electron microscopy (TEM). No mineralogical impurities could be detected. Previous analyses of this source clay indicated that it may contain trace impurities of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Although not detectable by XRD, trace inclusions of 2:1 layers in the kaolinite also cannot entirely be excluded. The kaolinite particles exhibit a typical hexagonal, platy shape with partially rounded edges [25,26]. The specific surface area of the  $<1\text{-}\mu\text{m}$  size fraction was analyzed by multipoint N<sub>2</sub>-BET analysis. The freeze-dried kaolinite was degassed under a constant N<sub>2</sub> stream for 20 h at 110 °C and analyzed on a Micrometrics Gemini 2360 surface area analyzer (Micrometrics, Zaventem, Belgium). The measured specific surface area was  $23.8\ \text{m}^2\ \text{g}^{-1}$ , which is in excellent agreement with previous reports for the KGa-2 kaolinite [26].

### 2.2. Acid–base titrations

The pH- and ionic-strength-dependent protonation behavior of kaolinite was determined by acid–base titrations. All titration experiments were conducted in a thermostated room at  $25 \pm 1\ ^\circ\text{C}$  using a computer-controlled titration system [27,28]. Four burettes (Dosimat 605, Metrohm) were connected to a personal computer by a Microlink MF18 interface (Biodata, Manchester, UK). The burettes contained

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