

Influence of Fe(II), Fe(III), and Al(III) isomorphous substitutions on acid-base properties of edge surfaces of *cis*-vacant montmorillonite: Insights from first-principles molecular dynamics simulations and surface complexation modeling

PENGYUAN GAO^{1,2,3}, XIANDONG LIU^{4,5,†}, ZHIJUN GUO^{1,2}, AND CHRISTOPHE TOURNASSAT^{3,6,*}

¹Radiochemistry Laboratory, School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

²Frontiers Science Center for Rare Isotopes, Lanzhou University, Lanzhou 730000, China

³Institut des Sciences de la Terre d'Orléans, Université d'Orléans, CNRS, BRGM, OSUC, Orléans 45071, France

⁴State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China

⁵Frontiers Science Center for Critical Earth Material Cycling, Nanjing University, Nanjing 210023, China

⁶Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, U.S.A.

ABSTRACT

Knowing the influence of isomorphous substitutions on the acid-base properties of smectite edge surfaces is an important aspect of the detailed understanding of clay minerals' interfacial properties with implications in the modeling of adsorption processes. We investigated the intrinsic acidity constants of Fe(II)/Fe(III) and Al(III) substituted edge surface sites of montmorillonite with a *cis*-vacant structure, which includes four crystallographic orientations perpendicular to [010], [0 $\bar{1}$ 0], [110], and [$\bar{1}$ $\bar{1}$ 0], using the first-principles molecular dynamics (FPMD) based vertical energy gap method. Fe(II) and Fe(III) substitutions resulted, respectively, in a significant increase and decrease in pK_a values of amphoteric groups directly associated with Fe octahedra. In addition, Fe(II) substitution increased the pK_a values of the neighboring silanol sites, while Fe(III) substitution had a weak influence on these sites. The Al-substituted tetrahedra had amphoteric sites with higher pK_a values than the non-substituted Si tetrahedra, and they increased significantly the pK_a values of the sites bridging the tetrahedral and octahedral sheets on surfaces perpendicular to [010] and [110]. The acid-base properties of substituted and non-substituted surface sites of *cis*-vacant montmorillonite were used to build a state-of-the-art surface complexation model, which successfully reproduced the best available experimental acid-base titration data. This model was further used to predict acid-base properties of dioctahedral smectites (montmorillonite, beidellite, and nontronite) according to their *cis*- or *trans*-vacant structures and their layer chemistry. According to these predictions, these smectites exhibit very similar overall pH buffering properties despite significant differences in structure and chemistry. A detailed analysis of the acid-base properties as a function of crystallographic directions demonstrated, however, that these differences should have a large influence on the adsorption of ionic species.

Keywords: First-principles molecular dynamics, surface complexation modeling, clay, *cis*-vacant, *trans*-vacant, montmorillonite, Fe(II)/Fe(III) isomorphous substitution, Al(III) isomorphous substitution, pK_a