

# Heterogeneous Reactions of Gaseous HNO<sub>3</sub> and NO<sub>2</sub> on the Clay Minerals Kaolinite and Pyrophyllite

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Airborne clay mineral particles have long atmospheric lifetimes due to their relatively small size. To assess their impact on trace atmospheric gases, we investigated heterogeneous reactions on prototype clay minerals. Diffuse reflectance infrared spectroscopy identified surface-adsorbed products formed from the uptake of gaseous nitric acid and nitrogen dioxide on kaolinite and pyrophyllite. For kaolinite, a 1:1 phyllosilicate, HNO<sub>3</sub> molecularly adsorbed onto the octahedral aluminum hydroxide and tetrahedral silicon oxide surfaces. Also detected on the aluminum hydroxide surface were irreversibly adsorbed monodentate, bidentate, bridged, and water-coordinated nitrate species as well as surface-adsorbed water. Similar adsorbed products formed during the uptake of NO<sub>2</sub> on kaolinite at relative humidity (RH) of 0%, and the reaction was second order with respect to reactive surface sites and  $1.5 \pm 0.1$  for NO<sub>2</sub>. Reactive uptake coefficients, calculated using Brunauer, Emmett, and Teller surface areas, increased from  $(8.0 \pm 0.2) \times 10^{-8}$  to  $(2.3 \pm 0.4) \times 10^{-7}$  for NO<sub>2</sub> concentrations ranging from  $0.56 \times 10^{13}$  to  $8.8 \times 10^{13}$  molecules cm<sup>-3</sup>. UV-visible spectroscopy detected gaseous HONO as a product for the reaction of NO<sub>2</sub> on wet kaolinite. The uptake of HNO<sub>3</sub> on pyrophyllite, a 2:1 phyllosilicate, resulted in stronger signal for nitric acid molecularly adsorbed on the silicon oxide surface compared to kaolinite. Monodentate, bridged, and water-coordinated nitrate species bound to aluminum sites also formed during this reaction indicating that reactive sites on edge facets are important for this system. The uptake of NO<sub>2</sub> on pyrophyllite,  $\gamma_{\text{BET}} = (7 \pm 1) \times 10^{-9}$ , was significantly lower than kaolinite because NO<sub>2</sub> did not react with the dominant tetrahedral silicon oxide surface. These results highlight general trends regarding the reactivity of tetrahedral silicon oxide and octahedral aluminum hydroxide clay surfaces and indicate that the heterogeneous chemistry of clay aerosols varies with mineralogy and cannot be predicted by elemental analysis.

## 1. Introduction

Airborne mineral dust impacts tropospheric photochemical cycles by providing reactive surface sites for heterogeneous reactions and by altering photolysis rates by scattering or absorbing solar radiation.<sup>1-4</sup> A global modeling study by Bian and Zender found the former to be the dominant mineral factor perturbing global O<sub>3</sub> and OH burdens, with heterogeneous uptake accounting for a 0.9% decrease in O<sub>3</sub> and a 5.1% decrease in H<sub>2</sub>O<sub>2</sub>.<sup>2</sup> Bauer and co-workers predicted that heterogeneous reactions on mineral dust were responsible for a 5% decrease in global tropospheric ozone, due primarily to the irreversible uptake of HNO<sub>3</sub> on mineral aerosols.<sup>3</sup> In this study, African dust emissions over the tropical Atlantic were predicted to have the largest regional effect, decreasing ozone levels by 10–20%.<sup>3</sup> East Asia also experiences intense dust storms. A study by Tang et al. simulated a 20% decline in near-surface ozone and a 95% decrease in nitric acid levels in this region.<sup>4</sup> Although the direct uptake of O<sub>3</sub> on dust does not affect global ozone levels significantly, this reaction may become important during dust storms.<sup>3,4</sup>

These atmospheric models, however, treat mineral dust as a single component despite regional variations in mineral aerosol composition due to differences in source region soil mineralogy.<sup>5</sup>

Laboratory experiments routinely demonstrate that mineral composition affects heterogeneous reactions and their corresponding uptake coefficients.<sup>6,7</sup> This suggests that including such mineral distinctions in atmospheric models might improve accuracy, especially on a regional scale. Long-range transport also affects the composition of airborne dust clouds through mineral fractionation which occurs as large-diameter particles, often quartz and carbonate minerals, experience faster rates of gravitational settling compared to fine-grained micas and clays.<sup>8,9</sup> Therefore, while coarse-mode minerals impact regional atmospheres, small grain size particles (diameter < 2 μm) such as clays are expected to have a more global impact since they comprise an increasing fraction of mineral aerosols undergoing long-range transport.

The term “clays” is commonly used to describe a broad group of aluminum phyllosilicate minerals which are formed primarily through the chemical weathering of silicate rocks. Clay particles are generally fine-mode, often having hexagonal platelet structures due to their layered silicate crystal structure.<sup>10</sup> Airborne clay components consist of individual platelets, aggregates of platelets, and platelets coating larger quartz particles.<sup>8,11</sup> Wind tunnel experiments suggest that composite particles may be fractured by impactions at high wind velocity, introducing the potential to increase the number of individual platelets suspended in the atmosphere.<sup>12</sup> Clay minerals are an important constituent of mineral aerosols emitted from most major arid source regions.<sup>8</sup> For instance, African dust measured

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