

# Nanoscale Characterization of Biotite Alteration at pH 7 in the Presence of Ammonium

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## INTRODUCTION

Biotite is a mineral belonging to the class of phyllosilicates, which is arranged in a T-O-T structure with high negative charge in tetrahedral layers because of the substitution of a quarter of the tetrahedral Si by Al. This charge is compensated by K ions in interlayer positions. Its octahedral layers are composed mainly of divalent cations (Fe, Mg) leading to a trioctahedral disposition.

Previous studies (e.g., Köhler et al., 2003; Oelkers et al., 2008) have advocated the influence of pH on mica dissolution: at low and high pH the dissolution rate tended to be higher, while reaching a minimum around neutrality. It is generally accepted that for acidic media hydronium ions play a pivotal role in mineral dissolution, acting as proton donors. While for basic conditions, those associated with mineral dissolution are hydroxyl ions.

Ammonium is a weak acid that in neutral environments, where the concentration of hydronium is very low ( $<10^{-7}$  M), contributes to the overall acidity of the solution. In such conditions ammonium ions could act as the main proton donors instead of hydronium ions, aiding in the mineral alteration processes. The ammonium ion is a frequent byproduct of organic matter maturation in sedimentary environments and in some basins its concentration may reach up to 0.1 M (Collins, 1975). Hence, this ion probably plays a (relevant) role during dissolution processes in early diagenetic environments. This hypothesis is supported by results obtained in flow-through experiments on smectites (Lamarca et al, 2014). But those experiments did not provide mechanistic insight of the processes occurring at the mineral-water interface.

One-way of achieving this is by direct observation at the nanoscale, of dissolving surfaces. Unfortunately, smectites particles are difficult to observe by microscopy techniques.

Therefore, as a first step to better understand the surface processes involved during ammonium induced phyllosilicate alteration we have opted to characterize by atomic force microscope (AFM) the processes occurring during batch alteration of biotite in the presence of ammonium. Based on the characterization procedure established during this study and previous ones (Cappelli et al., 2013; Cappelli et al., 2015), we will be able to study in the future the surface processes that control smectite dissolution mediated by  $\text{NH}_4$ .

## Materials and Methods

Batch experiments were carried out with alteration reactors in which, 50 mL of solution were placed in contact with samples of Bancroft biotite plates of 5x5x1 mm approximately, and heated in an oven at constant temperature of  $50 \pm 1$  °C.

Alteration solutions were composed of ammonium acetate at two different concentrations ( $10^{-4}$  and  $10^{-1}$  M) buffered to pH = 7 with ammonia. In order to establish a reference experiment, one alteration run was done using only Milli-Q water.

Initial and final pH values (Table 1) of the reacting solutions were measured using combination electrodes (Crison) standardized against pH 4.01 and 7.00 buffer solutions ( $\pm 0.02$  pH units).

Ammonium concentrations were determined using a Metrohm 883 Basic Ion Chromatography Plus with a Metrosep C3 column with 3.5 mM nitric

acid as eluent.

Ex situ AFM experiments were carried out to characterize the surface topography of the (001) face of biotite plates altered in the presence of  $\text{NH}_4$ . Measurements were done with a Nanoscope III (Bruker) using contact mode. Prior to AFM characterization the reacted biotite samples were extracted from their reactors using plastic clips. The sample was abundantly rinsed with Milli-Q water and subsequently dried with dry nitrogen. This treatment was also done for unreacted samples to ensure this procedure did not cause artefacts on the biotite surface. Once the AFM measurements were finished, samples were returned into their respective reactors.

## RESULTS AND DISCUSSION

The evolutions of pH during the experiments are shown in table 1.

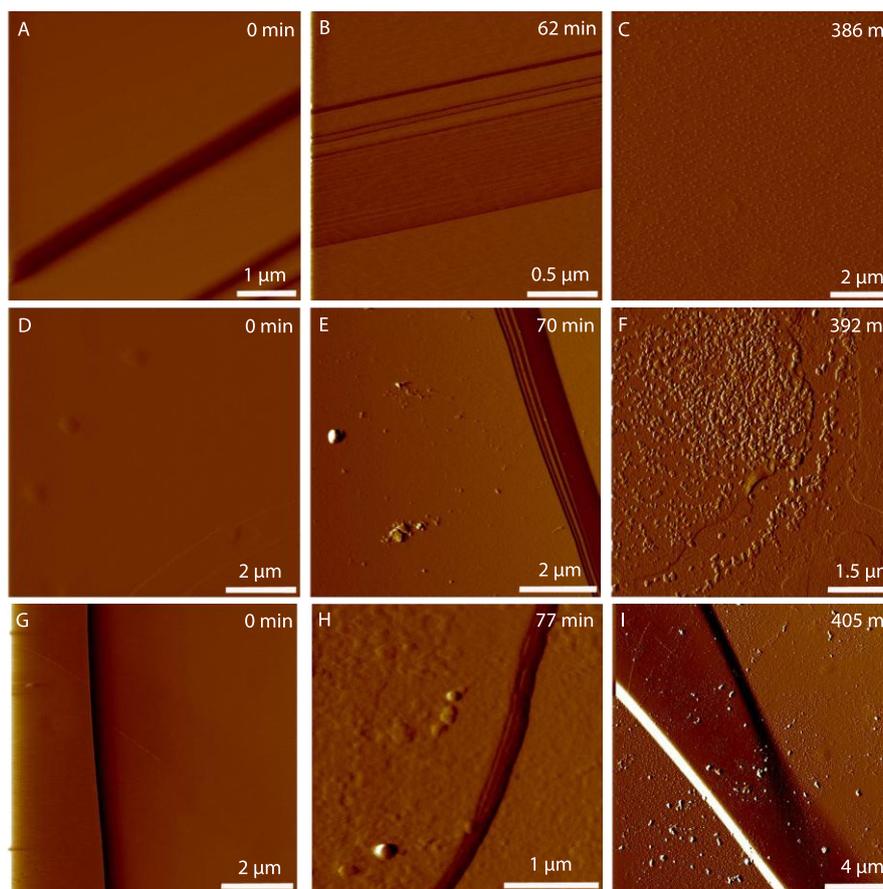
Sample	Initial pH	pH (1 hour)	pH (6 hours)
Milli-Q	5.68	-	5.88
$10^{-4}$ M	6.98	6.96	6.81
$10^{-1}$ M	7.04	7.02	6.95

Table 1. Evolution of pH during experimentation time.

The evolution of the biotite alteration was studied qualitatively by monitoring the characteristic topographic features of the basal surface, i.e. terraces and step edges, as a function of reaction time. Fig. 1 shows a series of AFM images of the biotite basal (001) surface at different reaction times. Freshly cleaved, unaltered surfaces are dominated by well-defined edges separated by smooth terraces. After ~1 h of reaction the Milli-Q sample remained identical to the initial appearance, whereas the other two samples already showed signs of alteration: surface precipitates are observed for both samples. In the case

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**fig 1.** Variations of surface morphologies on (001) biotite surface as the experiment progresses. It shows the three series of alteration, A-B-C corresponding to Milli-Q water, D-E-F to  $10^{-4}$  M  $\text{NH}_4$  and G-H-I to 0.1 M  $\text{NH}_4$ .

of  $10^{-1}$  M sample these precipitates are more developed and deposited homogeneously across terraces and steps. Nevertheless, for the  $10^{-4}$  M sample only localized formation of a secondary phase(s) is detected. On the other hand, no evidence of step retreat or etch pit formation is observed.

Noteworthy, after 6 h of interaction of biotite with Milli-Q water we found that precipitates had also formed on the surface, although much smaller in size compared to those observed for the other samples at the same time.

Finally, the comparison between the other two samples shows that at lower ammonium concentration, the coating of precipitates has significantly increased with respect to the previous stage, but still remains lower than that presented by the 0.1 M experiment. Furthermore, significant swelling phenomenon starts to appear in the last sample.

Similar coatings were already described by Pachana et al. (2012) who concluded

that the biotite alteration process at low pH (ca. 1) is dominated by the formation of etch pits, while at higher pH values (5.7) the coating becomes dominant process and almost no dissolution features are detected. Consistent with these data, we did not observe the generation of etch pits on the (001) surface of biotite.

At present the origin of the dissolution front has not yet revealed itself, i.e. no step retreat or layer swelling was observed. Most likely this is a direct consequence of the short reaction times employed in this works. Long duration experiments should resolve this caveat.

PHREEQC software was used to model the equilibrium of alteration solutions with micas. The model output suggests solutions may be supersaturated in Fe oxyhydroxides, which might be our main candidates for coating material.

#### CONCLUDING REMARKS

Our experiments seem to suggest that the presence of ammonium in near

neutral conditions has a significant effect on the alteration process of phyllosilicates.

It seems clear that an increase in ammonium concentration in the alteration solution leads to a higher development in both, particle size and the homogeneity of the coating surface.

In order to precisely quantify the effect of ammonium ion on dissolution-precipitation process, we will extend the sampling time and the temperature of alteration, completing the current study.

In addition confocal Raman spectroscopy and/or microprobe analysis will be undertaken to determine the precise nature of the formed precipitates.

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