

The Changes of Specific Surface Area of Soils after Peroxidation and Its Implication for the Calculation of Critical Loads of Soil Acidification

Peroxidation 전후의 토양 비표면적 변화와 토양산성화 임계부하량 계산에의 의의

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ABSTRACT: Mineralogy and the exposed surface area are two of the most important factors controlling dissolution and weathering rates of soils. The mixture of inorganic and organic materials of various size distributions and structures that constitute soils makes the calculation of weathering rates difficult. The surface area of soil minerals plays an important role in most of programs for calculating the weathering rates and critical loads. The Brunauer-Emmett-Teller (BET) measurement is recommended for the measurement of specific surface area. However, BET values measured without organic matter removal are in fact those for all the N_2 -adsorbed surface areas, including the surfaces covered and aggregated with organisms. Surfaces occupied by organisms are assumed to be more reactive to weathering by organic activities. Therefore, the BET surface area difference before and after organic removal depicts the area occupied by organisms. The present study shows that the BET values after organic matter removal using H_2O_2 are larger than those without removal by 1.68 ~ 4.87 m^2/g . This implies that BET measurement without organic removal excludes the reactive area occupied by organisms and that the area occupied by organisms in soils is much larger than expected. It is suggested that specific surface area measurement for calculating weathering rates of mineral soils should be made before and after organic matter removal. The results of a column experiment are presented to demonstrate the potential retarding influence that this organic matter may have on mineral dissolution and weathering.

Key words: specific surface area, organic matter removal, weathering rates, potential retarding influence

요약: 광물조성과 노출표면적(exposed surface area)은 토양풍화속도 계산모델에 영향을 미치는 중요한 요인들이다. PROFILE 등 기존의 풍화속도 계산모델에서는 입도분석자료에 기초한 기하학적 계산값이나 N_2 -BET 비표면적 등을 그대로 노출표면적으로 적용하고 있다. 그러나, 토양은 광물과 유기물의 혼합체로써 노출표면적을 정확히 구하기는 상당히 어려운 것이 사실이다. 본 연구에서는 유기물의 영향에 의한 토양광물의 노출표면적변화를 토양 깊이에 따른 peroxidation 전후의 N_2 -BET

비표면적값을 통해 살펴보고, 토양칼럼실험을 이용하여 풍화속도의 차이를 살펴보았다. 실험결과 peroxidation 후의 N₂-BET 비표면적은 1.68~4.87 m²/g의 범위에서 증가하였으며, 깊이에 따라 증가하는 범위가 감소하는 경향을 보여주었다. 이는 부식산 등 토양표면에 농집되어 존재하는 다양한 형태의 유기산 등이 광물의 노출표면적을 감소시키고 있다는 것을 의미한다고 할 수 있다. 기존의 토양풍화속도 모델에서 토양광물 노출표면적변화 계산에 있어서 광물-유기산간의 결합에 의한 영향을 결합세기 측면에서 고려하고 정량화 하는 것이 향후과제라고 생각된다.

주요어 : 토양광물, 화학적풍화속도, 비표면적, 유기물 제거

Introduction

The specific surface area (SSA) of soils is one of the most important factors that control the chemical properties of soils, including cation exchange and weathering rates of base cations.

Weathering rates of base cations are calculated both in the laboratory and in the field on the basis of mineral dissolution rates. There are, however, several orders of magnitude in difference between dissolution rates determined in the laboratory and those based on field measurement (Velbel, 1993). These differences originate from the differences between conditions in the natural environment and laboratory; among them the SSA controls the concentration of reactive sites in mineral dissolution. This is one of the most important parameters in determining laboratory and field dissolution rates. It is also one of the hardest parameters to measure and poorly understood.

The relation between the variation of SSA and weathering rates of base cations has been studied by several previous workers (Holdren and Speyer, 1985, 1987; Anbeek, 1992; Hodson *et al.*, 1997a, b). Holdren and Speyer (1987) were concerned with variations in mineral dissolution rate with grain size. Anbeek reanalyzed the data of Holdren and Speyer and differentiated between the weathered surfaces of grains and the surfaces that are exposed by grinding. Hodson *et al.* (1997a,b) carried out a study on the surface roughness and found no correlation between porosity as determined by scanning electron microscope (SEM) observation and the SSA from N₂-BET experiment but suggested correlation between the SSA and the

topography of grains.

However, these studies have focused on the variation of SSA or on the variation of SSA with grain size or surface roughness without consideration on the effects of organic matter on the weathering rates in the field. Organic matter is very important for the chemical weathering rates of base cations in soils; as the soil ages, organic matter such as humus and fulvic acid are concentrated in the top soils. As a result, fresh mineral surfaces that are exposed are blocked and coated or intercalated by organic matter (Theng, 1999). Therefore, the concentration of reactive sites from mineral surfaces is decreased. On the other hand, it has been reported that organic matter significantly enhances the weathering rates by producing both inorganic and organic acids (Webley, 1963; Kutuzova, 1969; Berthelin, 1971; Williams and Rudolf, 1974; Avakyan *et al.*, 1981; Vandevivere *et al.*, 1994). Vandevivere *et al.* (1994) measured a 200-fold increase in Si release rate from a Ca-rich plagioclase in an acid producing bacterial culture compared to an abiotic control. Similarly, Berthelin reported 200-fold increase in Al concentration from granitic sand reacting in an acid producing microbial culture (about pH 3) compared to an abiotic control.

If the above results can be applied to field conditions without any correction, the weathering rates measured in the field should be much higher than those measured in the laboratory due to the effect of organic matter. However, the results reported are opposite. Weathering rates in the field are much lower than those determined in the laboratory.

The context and significance of this current

work on SSA are provided by the current interest in weathering rates as a fundamental part of the research in critical loads in relation to acidification of soils. Base cation weathering rates are increasingly recognized as playing an important role in the neutralization of acid deposition, and the supply of nutrients to soils (Nilson and Grennfelt, 1988; Marschner, 1995). The role of organic matter in buffering and acid neutralizing capacity (ANC) production was studied through the use of a column experiment. The present study examined these differences of weathering rate in a view of the differences of SSA between before and after organic matter removal of soils.

Materials and Methods

The soil samples used in the analysis were taken from Kimjae and Pyeogchang area in southeastern and eastern parts of Korea, respectively. Kimjae soils are developed from granite and Pyeogchang from limestone.

The soil samples were taken from the upper soil horizons in order to examine the maximum effects of organic matter in relation to the SSA. All the soil samples were air-dried and fractionated through a 2 mm sieve after gentle crushing with a pestle, without grinding because of aggregation by clay minerals. After sieving, samples were mixed well and sub-sampled for use in X-ray diffraction (XRD) analysis and the column experiment.

The mineral identification and quantification were undertaken by XRD procedures, using a Rikagu Geigerflex X-ray diffractometer with Ni-filtered Cu K α radiation at 40 kV/30 mA in a step-scanning mode.

The organic matter in the soil samples was oxidized by adding 20 mL of 30% H $_2$ O $_2$ to about 1 g of dry soil in a 100 mL centrifuge tube. This mixture was heated in a water bath to 80°C and continually stirred and then centrifuged once the effervescence had subsided. The supernatant was decanted and the procedure repeated five more times. Although peroxidation

might cause crystals of micaceous and smectite clay to exfoliate and decompose (Drosdoff and Miles, 1938; Douglas and Fiessinger, 1971), these effects were not taken into consideration because the present study is not focused on the exact measurement of the SSA of soils but on the difference of SSA before and after organic removal of soils and its implication for weathering rate calculation.

The BET equation was adopted to measure the SSA of the soils before and after organic matter removal. The SSA is based on the adsorption of nitrogen gas at 77 K (Brunauer *et al.*, 1938). N $_2$ -BET adsorption at 77 K was determined using a Quantachrome monosorb MS-18 instrument on soil samples that had previously been outgassed at 110°C for 24 hrs.

Frequently BET measurements are reported on the basis of repeat analysis carried out on a single weight. Surface area is presented as a mean of these repeat measurements from the single sample. In this analysis, because the SSA value is the slope of the line in the plane of gram (X-axis) and m 2 (Y-axis), the SSA was determined as the slope after repeat (triplicate) measurement of N $_2$ -BET. This method can reduce the deviation that the instrument might have, even after the calibration with the standard materials.

In order to examine the potential impact that organic matter coating may have on mineral grain dissolution, ANC production and base cation weathering rates, a column experiment was undertaken. The column used consisted of a small chromatograph column and peristaltic pump. The column was filled with a small sub-sample of the soil (before and after OM removal). The column was treated with an acid input and the effluent monitored at a flow rate of 2 mL/min. The pH of the input solution was held at 3 by adding nitric and sulfuric acid. The pHs of both the input solution and the column effluent were measured using an Orion model 920A.

Results and Discussion

Soil Mineralogy

Mineral identification were carried out on the basis of results from ethylene glycol intercala-

tion and heating up to 550°C after Mg saturation. There are no expanding clays in both site after ethylene glycol intercalation. The XRD patterns of the Kimjae soils are given in Figure 1. The soils are mainly composed of (in the order of decreasing abundance) quartz, kaolinite,

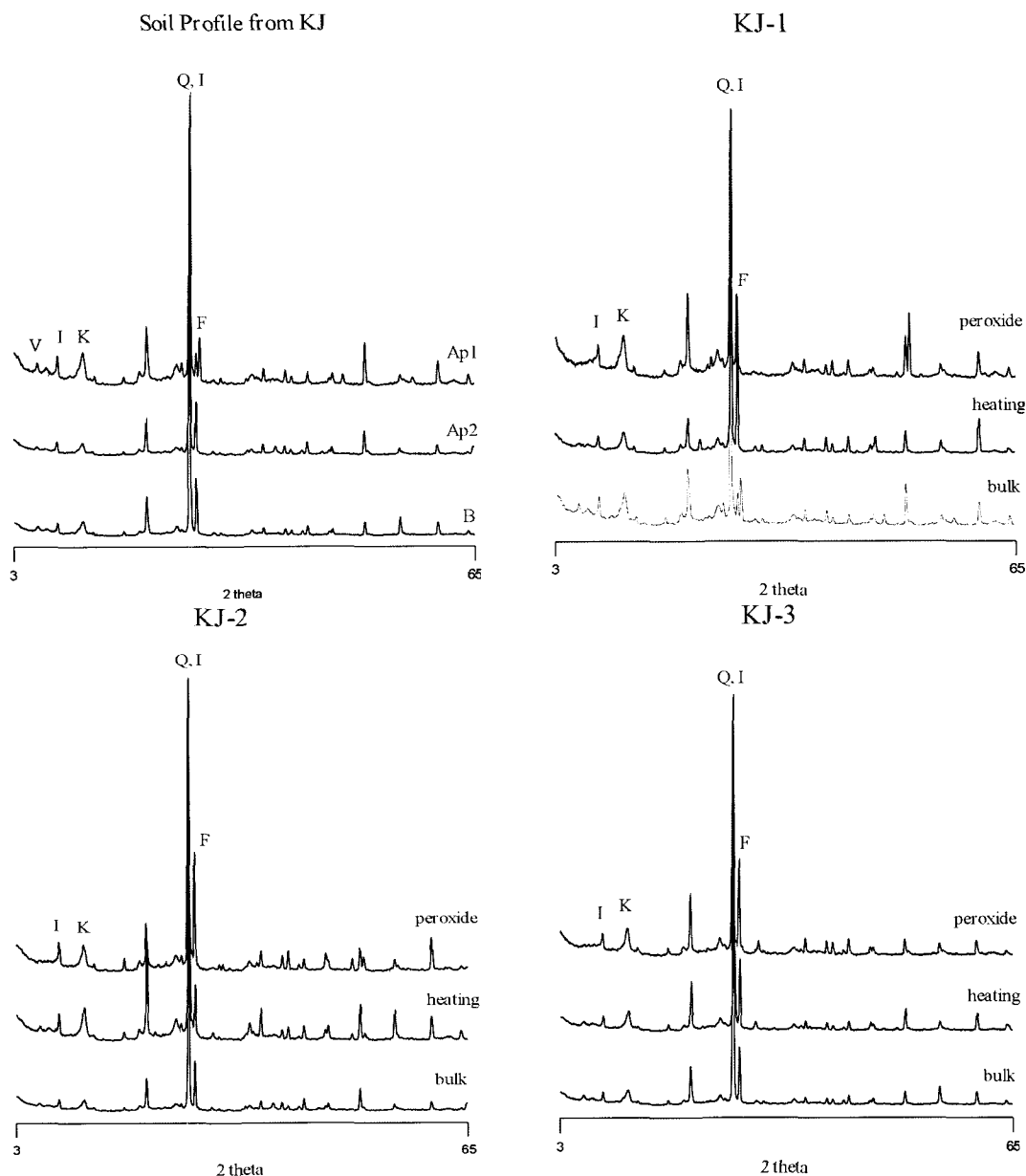


Fig. 1. The XRD patterns of the Kimjae soils; bulk soil samples of the profile (KJ), XRD patterns of peroxide treated and heated samples up to 550°C (KJ-1, KJ-2, KJ-3).

feldspar, illite, and vermiculite. The Ap1 horizon (the uppermost mineral horizon) has more vermiculite and mixed layer phase than the deeper mineral horizons. The results of XRD of the Kimjae profile soils after peroxidation are shown in Figure 1. It shows an agreement with

the result of Douglas and Fiessinger (1991) that 14 Å clay mineral is decomposed toward 10 Å after peroxidation. The XRD patterns of the Pyeongchang soils comprise of quartz, illite, vermiculite, kaolinite, and feldspar (Figure 2). As with the Kimjae soil, after peroxidation, the

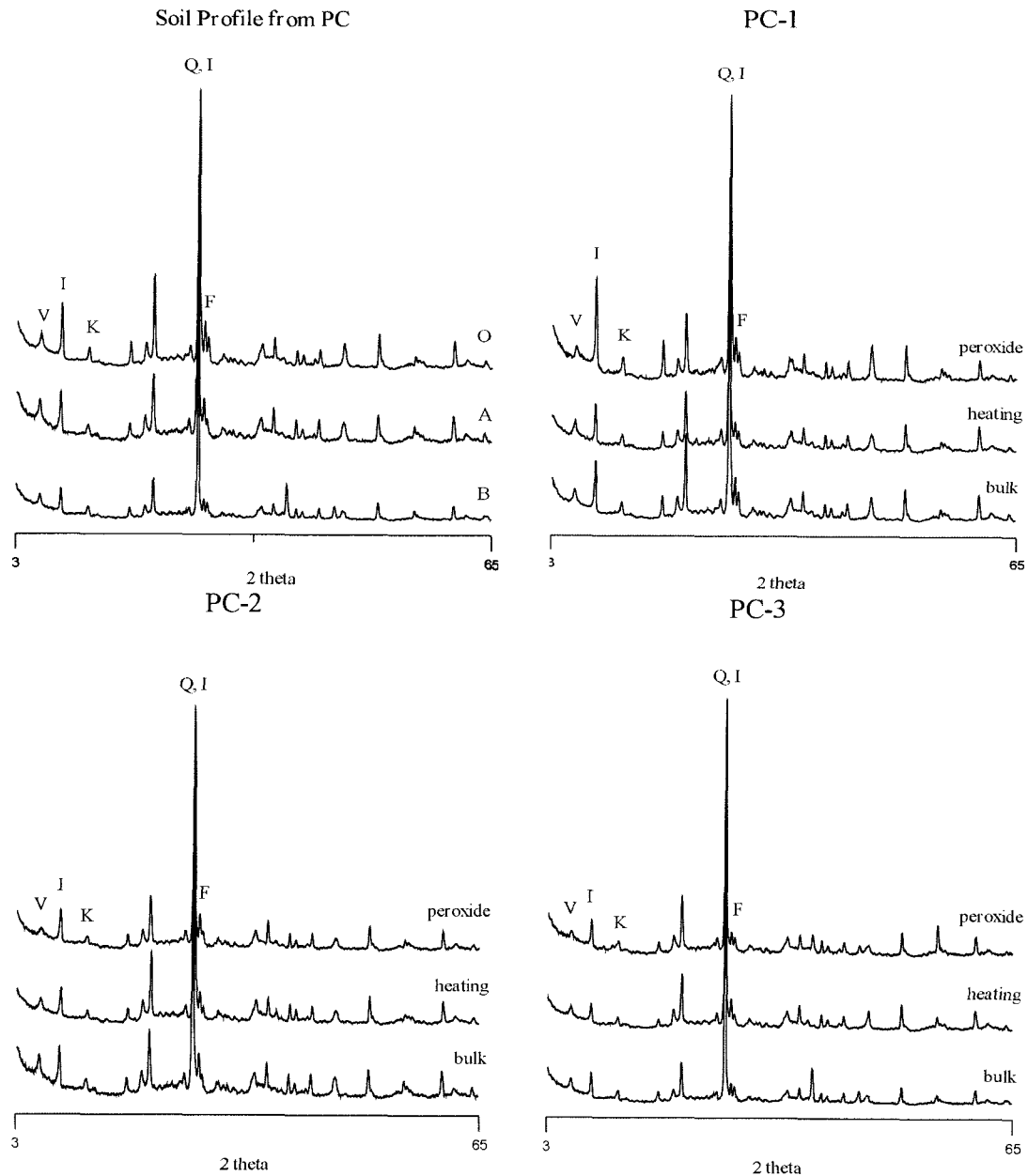


Fig. 2. The XRD patterns of the Pyeongchang soils; bulk soil samples of the profile (PC), XRD patterns of peroxide treated and heated samples up to 550°C (PC-1, PC-2, PC-3).

14 Å phase was affected. However, It is interesting that in this case some 14 Å phase was not decomposed to 10 Å. It is assumed that the degradation effect of peroxidation varies with the degree of hydration, interlayer charge and types of interlayer cations of clay minerals.

Specific Surface Area

The results of SSA measurements before and after peroxide treatment are shown in Figures 3 and 4. Both Figures show an increase in the SSA after peroxide treatment. This result is the same as that of Theng et al. (1999) and many previous workers. This observation has been explained by the blocking of micropores or the coating of clay aggregates by the organic matter, or by the decomposition of clay minerals that are vulnerable to peroxides. A simple formula for the differences of SSA (ΔSSA) between before (SSA_b) and after (SSA_a) organic matter removal of soils can be written as follows:

$$\Delta SSA_{OM} = SSA_a - SSA_b$$

These values can be applied for the consideration of the retardation of chemical weathering rates by organic matter in natural environment. The high values of ΔSSA_{OM} suggest that the blocking, coating or aggregating of organic matter might affect the reactive sites of mineral. As Table 1 illustrates, the SSA increases vary from 5 to 30% across the sample used. The increasing effects of the SSA lessen with depth

Table 1. The summarized results of SSA measurements

	SSA before peroxidation (m ² /g)	SSA after peroxidation (m ² /g)	ΔSSA (m ² /g)	%increased
KJ-1	15.709	20.400	4.691	29.9
KJ-2	14.680	17.975	3.295	22.4
KJ-3	14.971	17.710	2.739	18.3
PC-1	23.732	28.603	4.871	20.5
PC-2	26.613	31.372	4.759	17.9
PC-3	33.549	35.230	1.681	5.0

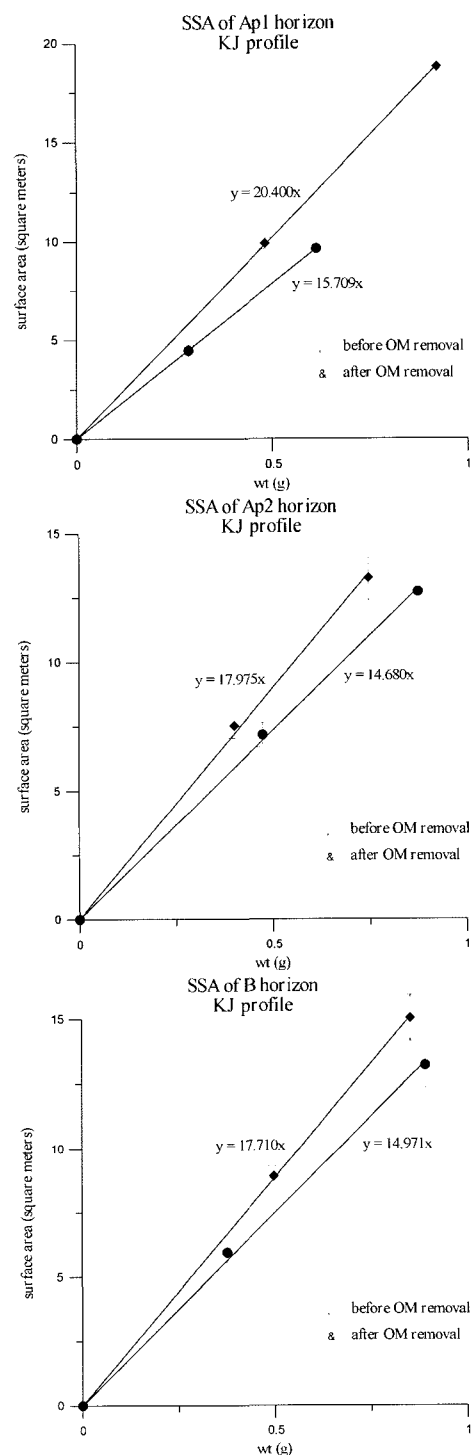


Fig. 3. The results of SSA measurements before and after peroxide treatment of Kimjae profile soils. The slopes of fitted lines are SSA (m²/g).

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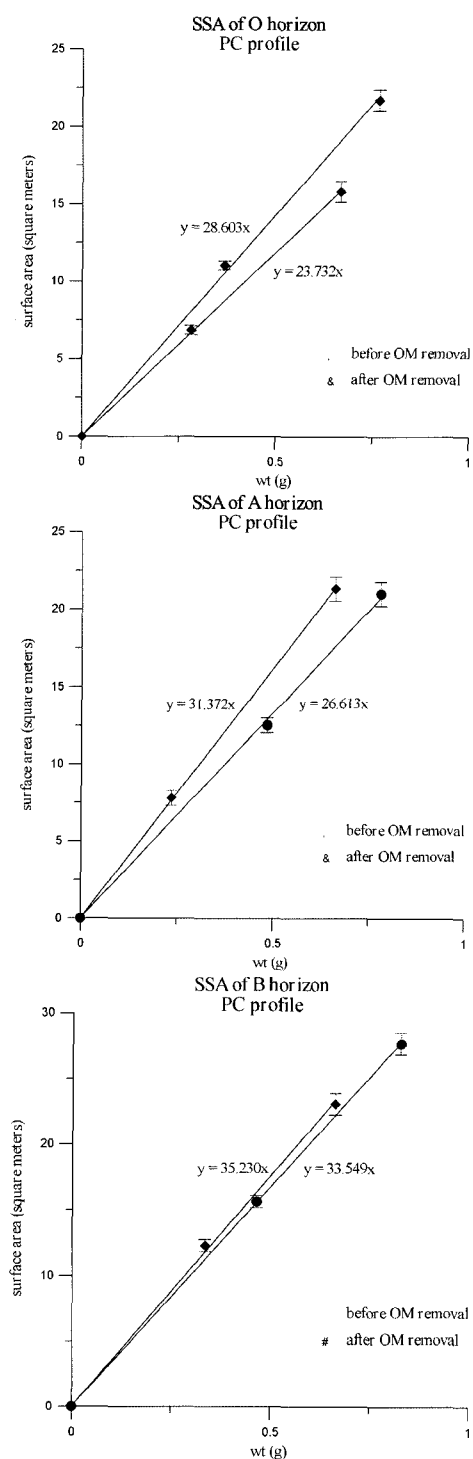


Fig. 4. The results of SSA measurements before and after peroxide treatment of Pyeongchang profile soils.

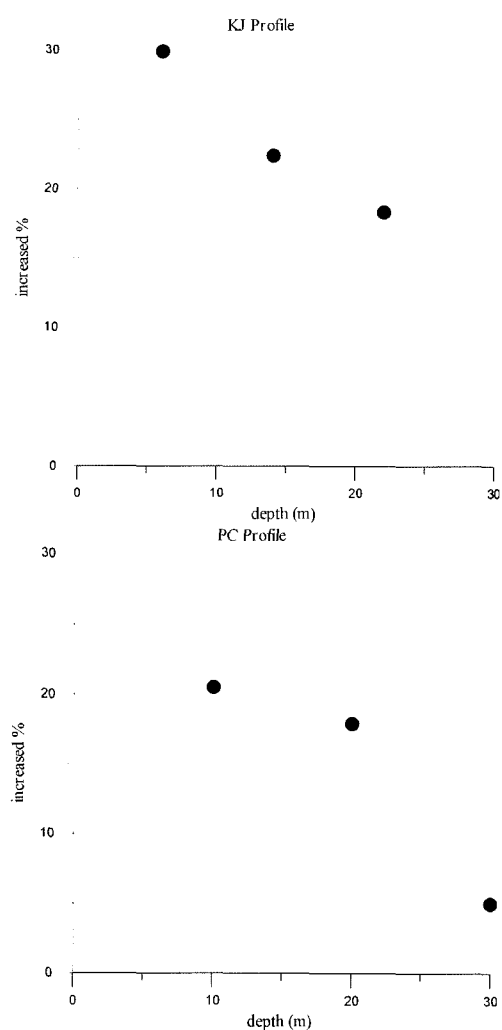


Fig. 5. Increased percentage after peroxidation treatment with depth.

in both soil profiles as shown in Figure 5. This is attributed to the lower organic matter content of soils with depth.

Acid Neutralizing Capacity

Figure 6 shows pH changes before and after organic matter removal in the column leaching experiment. This figure suggests that the ANC as reflected by changes in the pH of soil sample after peroxide treatment is much higher than that before treatment.

The kinetic curve of pH before organic

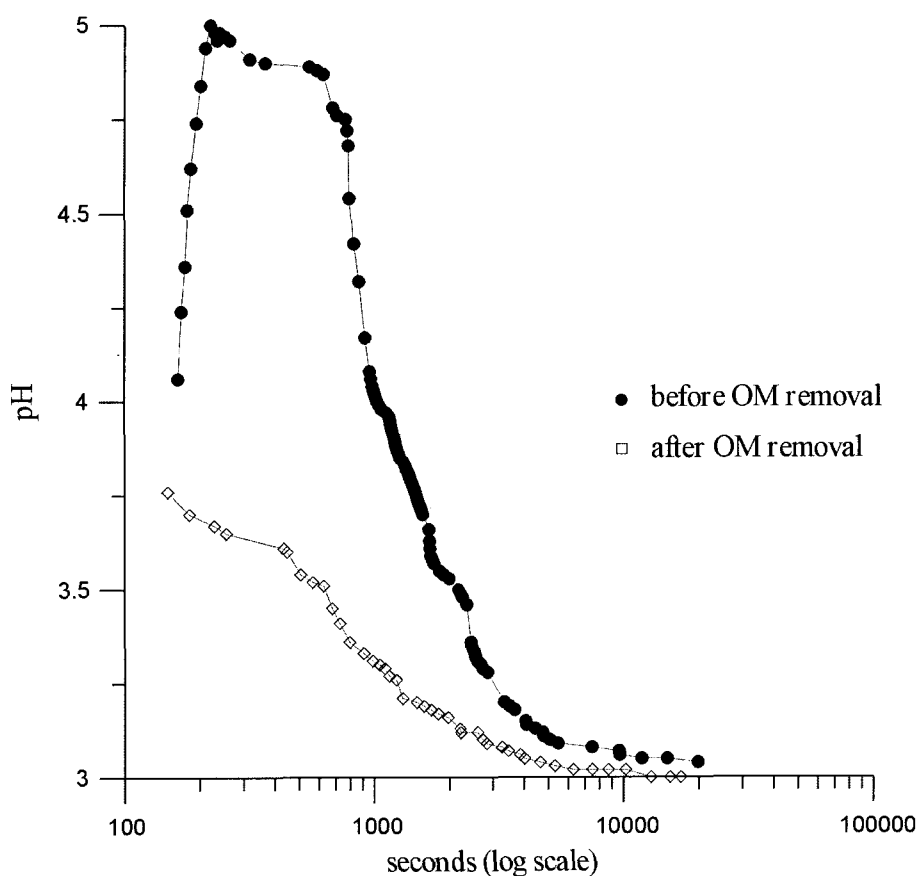


Fig. 6. Column leaching experiment for soil of Ap2 horizon of Kimjae showing the differences in pH changes with time before and after peroxidation treatment. The flow rates of input solution is 2 mL/min.

matter removal slightly increased from pH 3 up to pH 3.75 and then did not resist acid attack, slowly declining for 600 sec. The edge appeared at around 700 sec. The kinetic curve of pH after organic matter removal first increased to ~ pH 5 in 250 sec and then resisted hydrogen ions at ~ pH 5 to 750 seconds. The pH edge, then, appeared around 1000 seconds. After that, the pH curve approached tangentially to the pH 3 in more than 11000 sec, a noticeably slower decline than observed prior to the OM removal. The above results suggest that fresh surfaces exposed by peroxidation react with attacking hydrogen ions and consume them. That is, the ability to produce ANC through the dissolution of mineral over a greater surface area is increased by organic matter removal. The in-

creased consuming quantity of hydrogen ion by organic matter removal over the duration of the experiment was $0.9939 [\text{H}^+] \text{ M} \cdot \text{sec}$ as calculated by the differences in the kinetic curves of pH.

Conclusion

The work reported here has illustrated that organic matter coatings are related with reduction of the surface area of soil minerals, comparing the N_2 -BET surface areas before and after peroxidation. It is possible that increased mineral surface is influenced not only by organic matter removal but also by other mechanism such as exfoliation of micaceous minerals. The exact quantitative mechanism needs

further study.

Through the use of a column experiment it has been shown that peroxidation increased the reactive surface area available for mineral dissolution reactions. The reduction of fresh mineral external surface will have direct consequences for the ability of soils to buffer acidic inputs. However, due to the limited number of samples available in the current study the magnitude of this effect has yet to be fully quantified. Database for the calculating models of soil weathering rates might be established only after integration of the examination on various types of soil samples.

The nature of the temporal dynamics of organic matter coatings has not been considered. However it would seem reasonable to suggest that the older the soil, the greater the opportunity for organic coatings on mineral grains to have developed. This is important in the context of the soils of much of East Asia in which concern over the impact of acid deposition and soil acidification is growing.

Studies have been instigated to examine how Δ SSA varies between soils of different ages and organic matter content. This should complement existing studies examining the relationships between soil exchange capacities, surface area, grain size and organic matter by Theng and co-workers (Theng *et al.*, 1999). Further consideration should also be given to the relative role of organic acids as an enhancement to dissolution in the early phase of mineral exposure versus organic matter coatings as an inhibitor over much longer periods of exposure, particularly within existing modeling frameworks.

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