

Mineralogical Change of Acid Sulfate Weathering of Hydrothermally Altered Pyritic Andesite

열수변질 안산암 기원의 함황광물과 특이산성토적 풍화에 따른
광물학적 변화

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ABSTRACT : Oxidation of pyrite has caused a serious environmental problem such as the acidification of soil and surface water. The mineralogical change of acid sulfate weathering of hydrothermally altered andesite which contained 11.8% of pyrite and was exposed in atmosphere by lay out works for a residential area and a golf course was studied using X-ray diffraction (XRD) and electronmicroscopes. Ferrihydrite, jarosite, and an unidentified water soluble phase were observed as weathering products of the andesite. Under electronmicroscopes, ferrihydrite showed aggregate of platy microcrystals; jarosite was platy morphology; water soluble phase was columnar. Morphology of fresh pyrite in the andesite changed from pyritrohedron to cubic in its frequency with increasing its particle size. The drainage water was acidic (pH 3.5) and in an equilibrium state with both ferrihydrite and jarosite.

Keywords : XRD, electronmicroscopes, pyrite, jarosite, ferrihydrite.

요약 : 황철석의 산화에 의한 토양 및 지표수의 산성화는 심각한 환경문제를 야기하여 왔다. 특이산성토의 이차광물과 화학적 특징은 풍화과정을 반영하고 있다. 택지 및 골프장 조성과정에서 지표에 노출된 11.8% 황철석을 함유한 열수변질 안산암의 풍화에 따른 광물학적 변화를 X-선 회절, 전자현미경 (SEM, TEM), 배수의 화학분석을 통하여 연구하였다. 수용성 염, ferrihydrite, jarosite가 풍화과정의 이차 광물로서 관찰되었다. 전자현미경하에서, ferrihydrite는 미세입자들의 입단, jarosite는 판상, 수용성 염은 기둥모양을 나타내었다. 안산암 내에 존재하는 황철석은 입자의 크기가 증가할수록 정육면체 형태/육각기둥 형태의 비가 증가하였다. 배수는 강산성 (pH 3.5)이었으며 ferrihydrite, jarosite와 화학적 평형을 이루고 있었다.

주요어 : XRD, 전자현미경, 황철석, 자로사이트, 웨리하이드라이트

Introduction

Acid sulfate soils are sulfur rich soils with pH below 4.0 in water and are worldwide in distribution (Bloomfield and Coulter, 1973). A potential acid sulfate soil can be defined the material with a potential to be developed to an acid sulfate soil by aeration. Potential acid sulfate soils contain significant amount of sulfides, mainly pyrite (cubic FeS_2). Most of them are sedimentary origin and a few case has been reported as metamorphic and igneous origin (Bloomfield and Coulter, 1973).

A reduced environment with a continuous supply of sulfate and iron ions in the presence of easily decomposable organic matter and sulfate reducing bacteria is considered important ingredient in the formation of sedimentary origin sulfide (Arora *et al.*, 1977). Hydrothermal origin pyrite is formed by reaction between existing iron in geologic formation and sulfide in hydrothermal solution at the late stage of magma evolution.

The acidity in an acid sulfate soil is generally attributed to oxidation of sulfides at some stage of weathering (van Breemen, 1973). When sulfide containing sediments or geologic formations are aerated, oxygen (O_2) will start to oxidize sulfide. The oxidation process produces a significant amount of sulfuric acid (H_2SO_4) (McKibben and Barnes, 1986). The rate at which pyrite oxidizes depends on the O_2 concentration in the reaction medium. The produced acidity leads a drop in pH of soil. The acidity produced by the oxidation of pyrite has caused several environmental problems such as acidification of soil and surface water and resulting increased available heavy metal concentration in soil and water.

The secondary minerals reflect weathering history and current solution chemistry (Carson and Dixon, 1983). The oxidation process of pyrite may lead formation of jarosite [$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$] in presence of alkaline cations such as potassium (K) (Carson and Dixon, 1983), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in presence of calcium carbon-

ate (Ritsema and Groeneberg, 1993), and Fe oxides (Harmsem and van Breemen, 1975). The acid history of acid sulfate soils is reflected in weathered layer silicates too. Mineral deterioration in acid environment as opposite direction of reduction environment was also reported by Lynn and Whitting (1966).

As meteoric water percolates through soil and unconsolidated rock, its chemical composition is modified by precipitation-dissolution, oxidation-reduction, and adsorption/ion exchange with mineral and amorphous surfaces. Understanding of mineralogical change by weathering of potential acid sulfate soil may give us an important clue to solve the acidification of soil and surface water. The objective of this study was to examine the mineralogical change of the acid sulfate weathering of a hydrothermally altered andesite which was exposed in atmosphere by lay out for a residential area and a golf course.

Materials and Methods

Study Site and Sampling

The sampling site was located at Samho-ri, Ungsang-myon, Yangsan-si, Kyongsangnam-do, Korea. The sampling site has been layed out for a residence area and a golf course (about 83.3 ha). After laying out, the site was landscaped with grass and tree. The planted grass and tree were killed several days after landscape. We visited and examined the site to see the reason why grass and tree were killed. There were oxidation of pyrite and resulting acidification of soil which killed grass and tree. Pyrite was originated from a hydrothermal alteration of andesite (Korea Institute of Geology, Mining and Material, 1962) which was covered with a soil, Bongsan series (2 - 20 m in thickness), before the lay out. Samples of the hydrothermally altered andesite (Fig. 1.), and sediments and water in drainage ditch were collected and stored in air-tight polyethylene bags and bottles, respectively. All samples were also

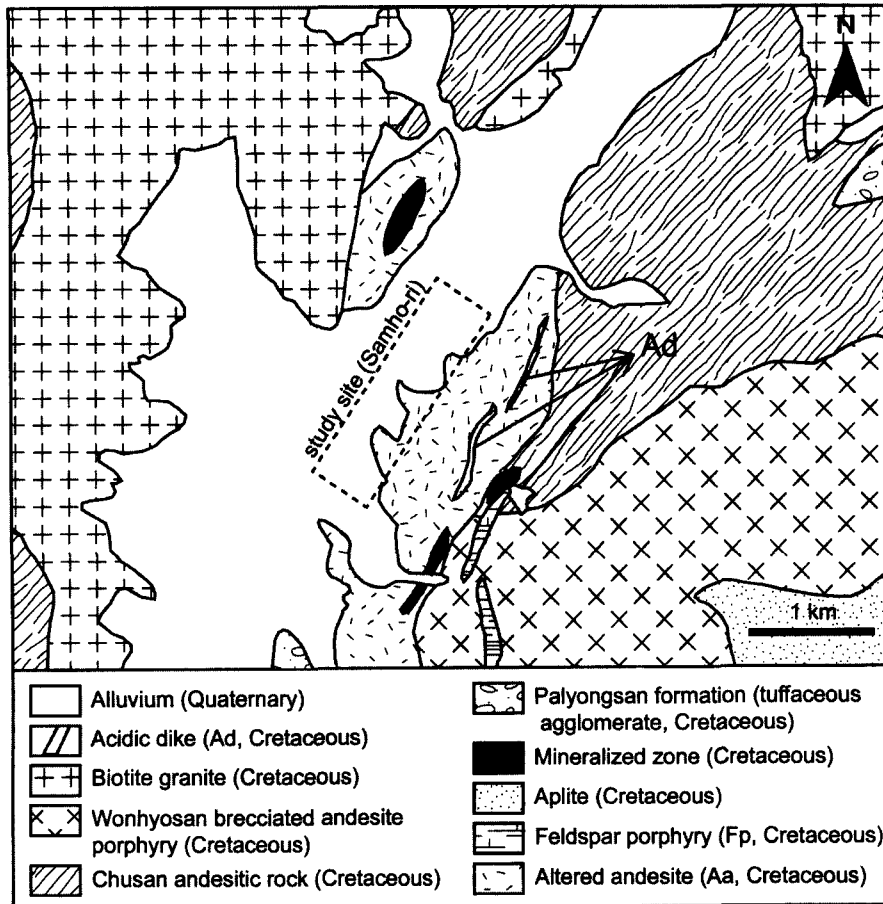


Fig. 1. Geologic map of the study site and surrounding area. The box with dash line in the map was the construction site for a residence area and a golf course. This was reconstructed based on Geologic map for Yangsan by Korea Institute of Geology, Mining, and Material (1962).

stored at 4 °C in a refrigerator.

Analysis of Samples

Total sulfur concentration of the andesite was determined using an infrared analysis with a Carbon and Sulfur Analyzer (Leco Co.). The pH and Eh of the drainage water were determined with an Orion pH meter model 720A. Mineralogical and morphological analysis of andesite, yellow coating, and sediments were conducted with a Philips X-ray Diffractometer (XRD), a Hitachi S-570 scanning electron microscope (SEM), and a Hitachi S-800 transmi-

tion electron microscope (TEM).

Results and Discussion

Results

The andesite contained 6.5% of S. The calculated pyrite content of the andesite was 11.8%. In the calculation, it was assumed that all S existed as pyrite. The surface of andesite showed pale yellow coating as a sign of weathering. Water soluble phase was also observed in cracks of weathered andsite. Yellowish red colored sediments in drainage ditch were observed (Fig. 2).

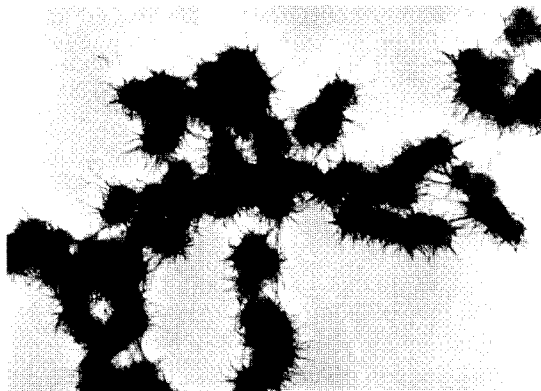


Fig. 5. TEM micrograph of ferrihydrite showing aggregate of platy and needle shaped microcrystals.

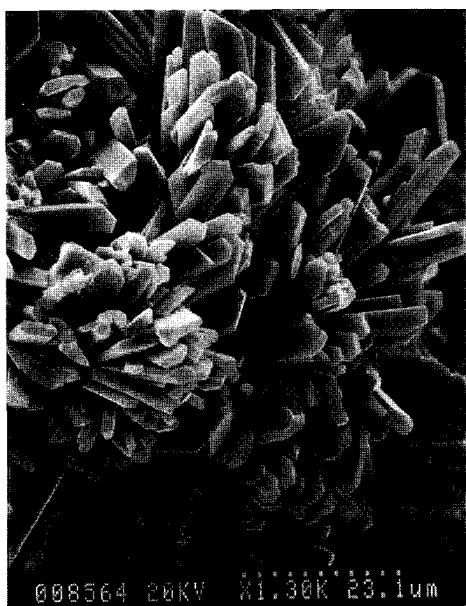


Fig. 6. SEM micrograph of water soluble phase in the crack of weathered andesite. It shows hexagonal and rectangular columns.

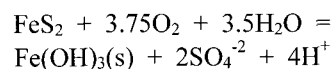
micrograph of the water soluble salt showed hexagonal and rectangular prisms (Fig. 6). Its appearance was similar with zeolite but the solubility in water differentiated from zeolite.

Discussion

The change in crystal morphology of pyrite

(pyritohedron to cubic) with increasing its size may be due to change in periodic bond chain during crystal growth: flat face at early stage and stepped face at late stage (Hartman and Perdok, 1955).

The acidity of drainage water (pH 3.5) might be due to the oxidation of pyrite (McKibben and Barnes, 1986):



The pH and Eh values of drainage water (3.5 and 583.4 mV) indicated that both ferrihydrite and jarosite in the sediment was in an equilibrium with drainage water (Fanning and Fanning, 1989). For 583.4 mV of the system, jarosite can be formed at pH between 2.5 to 5.5 and ferrihydrite can be formed at pH higher than 2.2. It also indicated that oxidation of pyrite and dissolution of K-bearing minerals such as K-feldspar and mica occurred at the same time. The produced acidity by pyrite oxidation may accelerate the dissolution of K-bearing minerals too. The formation of the water soluble phase could not be explained in this study. However, morphology of the water soluble phase suggested that it was probably magnesium sulfate, epsomite.

Conclusions

Jarosite, ferrihydrite, and an unidentified water soluble phase were observed as weathering products of the hydrothermally altered andesite. Micrographs of jarosite, ferrihydrite, and water soluble salt showed thin plates, aggregate of platy and needle shape microcrystals, and hexagonal and rectangular columns, respectively. The drainage water was strongly acidic, pH 3.5, due to oxidation of pyrite and was an equilibrium with both jarosite and ferrihydrite.

Acknowledgements

This study was supported by Korea Science and

Engineering Foundation (KOSEF). The authors express thank to Mr. J.S. Lee at National Institute of Agricultural Science and Technology for his assistance in electronmicroscopic analysis.

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2000년 5월 6일 원고접수, 2000년 6월 7일 게재승인.