Mineralogical Study of the Granite Weathering in the Seoul Area:
Water-Rock Interaction in the Namsan Granite

남산 화강암의 풍화 및 광물-물 반응에 관한 연구

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ABSTRACT : The weathering of the Namsan granite was studied in terms of sorption process. The Namsan granite consists mainly of quartz , alkali feldspar, plagioclase ($Ab_{85}An_{15}$-Ab_{100}) and biotite with small amounts of sericite, magnetite and ilmenite.

The kinetic factors for altering the granite body are the proton and hydroxyl ions derived from the reaction of water and mineral. There are two different types of pH variation curves for rocks of different mineral assemblages, when powdered granite was dispersed in distilled water under ambient condition. The sorption-process proceeds by three steps for fresh granite; (1) the initial rapid pH-rise to 10 by the uptake of proton by negatively charged mineral surfaces, (2) the gradual pH-down, and (3) the stable pH tail between 7.1-7.5. For somewhat weathered granites, the sorption proceeds; (1) the initial rapid pH-down to 4.8, (2) the slight pH-rise and slow pH-down, and (3) the stable pH tail between 5.0-5.3. The reaction rate is controlled by the density of adsorbable sites, the solubility of the mineral, pH of the system and the formation of amorphous gel and gibbsite. Amorphous gel floates on the surface of the solution while stirring the powdered granite and then is transformed into gibbsite in an hour or so. The pH saturation values for -325 mesh fresh granite from 5 m depth is about pH 10 when rock/water ratio is over 10g/200 ml.

요약 : 남산 화강암의 풍화를 물과 광물의 흡착작용의 관점에서 연구하였다. 순수한 증류 수만으로도 광물-물의 흡착반응이 일어나며, 그 반응속도는 암석/물의 비율에 따라 수초-수 시 간 이내로 매우 빠르다. 광물과 물이 반응할 때 가장 영향을 미치는 것은 광물의 표면의 결합 상태와 물의 수산이온농도이며, 암석/물의 비율은 용액의 수산이온농도를 좌우한다. 광물 입자 의 크기는 반응속도에 큰 영향을 미치지만 암석/물의 비율이 약 7g/200 ml 이상이 되면 큰 변 화를 보이지 않는다. 풍화를 받지 않은 화강암은 양의 pH edge(최대 pH 10)를 보이며 pH 7.1 ~7.5으로 하강하는 양상을 보인다. 그러나, 풍화를 받아서 점토 광물이 섞인 화강암은 음의 pH edge(최소 pH 4.8)를 보이며 pH 6을 넘지 않는다. 흡착반응 동안에 젤이 수면 위에 생성된 후 이것은 후에 깁사이트로 변하고, 암석/물의 비율이 높을수록 그리고 pH 변화가 클수록 많이, 그리고 빨리 형성된다.

INTRODUCTION

The crust of planet Earth has large surface area which is in contact with water or its vapor The processes taking place at mineral-water in terfaces consist of two fundamental mechanisms

chemical species attachment to and detachment from mineral surfaces. Both processes are called adsorption and desorption, respectively.

The behavior of ions in aqueous system is readily predictable if the structure of mineral is known. The common silicate minerals have surfaces of oxygen, hydroxyl or equivalent chemical species. The outer exposed nonbridged surface has some remnant charge and it can attract counterions near the surface forming complexes in solution. The mineral-water interaction will be discussed on the basis of surface complexation theory to predict the behavior of ions.

Surface functional group theory is useful in interpreting mineral-water interactions when the structure and solubility of mineral is well known (Davis and Kent, 1990). The study of water itself reacted with mineral is another approach to decode the natural system (Kharaka et al., 1988; Ball and Nordstrom, 1991).

Though silicate dissolution was already observed in the early to mid 1800's by some investigators (Hochella and White, 1990), it has been in just the last decade that means have been developed to directly study mineral-water interfaces. With the progress of theories and cognate experimentals including models (Sposito, 1983; Davis and Kent, 1990), we are now on the horizon where we can glean the small indentures to decipher mineral-water interactions.

The alteration of the Namsan granite was studied in terms of the water-rock interaction in this study.

EXPERIMENTALS

Sample Preparation

The granite samples were taken along the profile from the newly excavated sites (Fig. 1). All samples were analysed by X-ray diffraction (XRD) before chemical experiment. A computerized Rigaku Geigerflex RAD3-C with a scintillation counter was used for XRD.

The samples used in sorption experiment were crushed using tungsten carbide ball-mill for 60 minutes. After milling, the powdered samples were fractionated with 60, 80, 120, 230 and 325
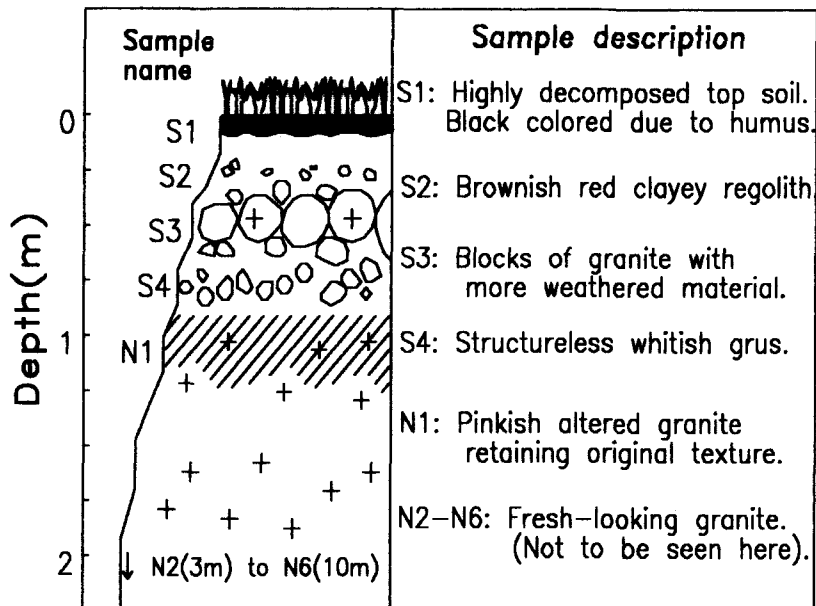

Fig. 1. Weathering profile of the Namsan granite and sampling sites.

mesh sieves shaking with hands.

When dispersing the granite in distilled water, the powdered sample was taken into Pyrex beaker with pertinent aliquot of water and stirred using magnetic bar coated with teflon under ambient condition. The pH meter is an Orion model 920A equipped with an auto temperature control probe. The pH value was obtained immersing the electrode bulb 3cm below water surface stirring the solution. The electrode was continuously submerged when measuring pH values to evade fluctuation. The reacted solution was filtered using Whitman No. 100 and analysed by AAS. Bulk chemical compostions of granite were analysed by XRF for major elements.

PETROLOGY AND MINERALOGY OF THE GRANITE

The Namsan granite is part of the so called Seoul granite, which is widely distributed in the mid area of Korean peninsula. It intruded the Precambrian gneiss complex in the Jurassic age according to K-Ar dating (Park, 1972). The rock has generally medium- to coarse-grained texture excluding the aplitic parts in places, and has four joints systems; N12W/10NE, N35E/68SE, N76E/74SE and N60E/80NW (Lee, 1993). Modal compositons are plotted in the granite field (Kim et al., 1994). The Namsan granite consists mainly of quartz, plagioclase, orthoclase, microcline and biotite with small amounts of muscovite, chlorite, apatite, sphene, and opaque minerals.

Quartz grains are subhedral to anhedral ranging 5-12mm in diameter. They contain many inclusions of tiny muscovites and/or rarely euhedral plagioclase. Plagioclase grains are subhedral to euhedral ranging 2-8mm in diameter. They usually exhibit normal, reverse or oscillatory zoning when traced by WDX (Kim et al., 1994). Myrmekitic intergrowth of albite and quartz is occasionally observed along the contact between potash feldspar and plagioclase. Potash feldspar

usually shows perthitic texture. The perthite sometimes has small inclusions of plagioclase, quartz and biotite, thus forming poikilitic texture. It also has many unidentified tiny particles which are assumed to be clay minerals.

Biotite has euhedral or subhedral form up to 3 mm long and shows deep maroon to pale green even in one grain under the polarized microscope. Biotite is sometimes altered to clay minerals thus resulting in changes of color and shape. A small amount of muscovite is included in the Namsan granite. It usually occurs as inclusions in feldspars. Magnetite, ilmenite, rutile and zircon occur as accessory minerals in the Namsan granite.

WEATHERING PROFILES OF GRANITE

Textural Change of Granite

The weathering profile of the Namsan granite is very simple because there is no significant structural and mineralogical variations in the original granite body except some faults and joints. Manganese and iron oxides and hydroxides are precipitated on the surface or along the fissures of altered rocks in some area.

Major Chemical Change of Granite

The degree of alteration of granite can be estimated by chemical analyses of rocks. The chemical analyses of samples from vertical section delineate systematic variations. The bulk chemical changes of the Namsan granite are shown in Fig. 2.

The SiO_2 content increases toward the surface indicating that Si is very immobile. The enrichment of SiO_2 is mainly due to the stable nature of quartz and the resistant Si framework in feldspar and mica.

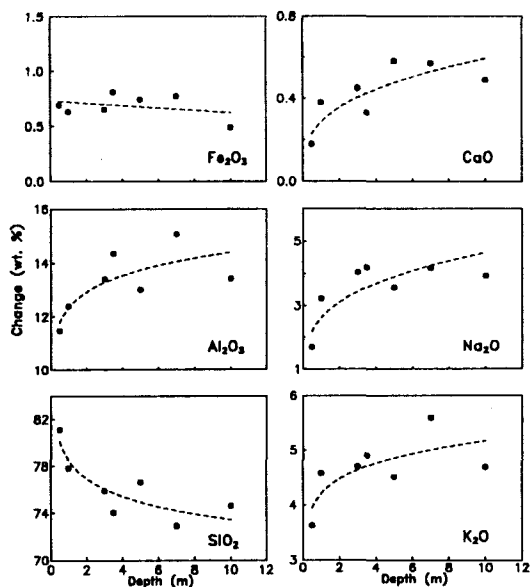The Al_2O_3 content decreases toward the surface. The Al depletion in many geological envi-

Fig. 2. Bulk chemical variation of the Namsan granite along the vertical profile.

Fig. 3. Weathering index determined by XRD for the Namsan granite.

ronments is controversial to many investigators (Jeong, 1992) because it has been considered to be relatively immobile in terms of ionic potentials (Blatt et al., 1980; Velde, 1985). But the concept of ionic potential took little account about the formation of other complexes in a certain pH condition. The slight enrichment of Fe_2O_3 in the surface suggests the formation of iron oxides and/or hydroxides.

The CaO content shows rapid decreasing tendency toward the surface. It indicates the selective dissolution and removal of Ca in plagiclase in the form of hydrated ion. As the hydration energy of Ca ion overcomes the adsorption strength of smectite and other clays, the Ca ion is easily removed by the circulating waters (Blatt et al., 1980). The Na_2O content also decreased suddenly near the surface. This is mainly due to the wide stability field of albite and the relatively easy hydration nature of Na ion when once decomposed. Na is also rather soluble than adsorbable in the interlayer of clays. Furthermore, the interlayer Na of clays are not stable when the flow rate is high enough to hydrate it.
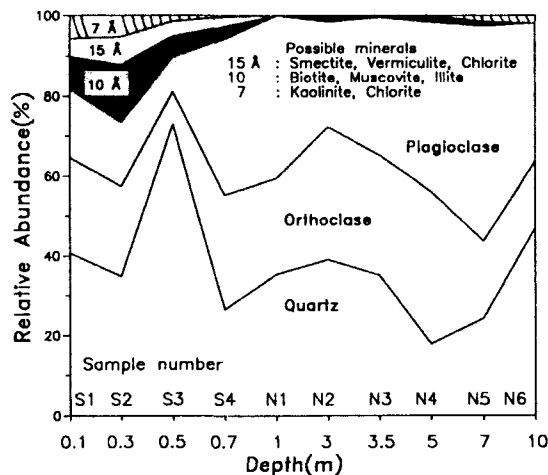
In terms of the ionic potentials, Ca, Na, and K are very soluble but it is only true of when these ions are free in the solution.

Mineralogical Change of Granite

Quartz usually resists alteration when exposed to surface environments. Feldspars exhibit milky white colors when they are altered. Biotite also has reddish rinds when it is somewhat disintegrated. Even the fresh-looking feldspars are significantly altered when observed under the polarized microscope. The feldspar alteration are traced about 50m down the ground.

The degree of alteration of the granite can be roughly traced by XRD (Fig. 3). As quartz is the most stable phase, the intensity of (101) peak was used as an internal standard to estimate the weathering index. The high intensity ratios of 14-15Å phases to quartz toward the surface indicate the formation of smectite or vermiculite. The 10Å phase near the surface may be illite, but it is confused with biotite. The 7Å phase also increases toward the surface indicating that kaolinite has been formed near the surface. The granite is deeply altered to the depth of roughly one meter from

the surface.

Quartz from the Namsan granite shows no prominent fractures. Sometimes quartz exhibits black color indicating that it was exposed to some radioactivity within the granite (Nassau, 1978).

Plagioclase is considerably altered even at deeper part of the profile. The zoned plagioclase shows compositional variation from $Ab_{85}An_{15}$ to Ab_{100} when traced by EPMA. The zone boundaries or fissures of plagioclase look isotropic under the plane polarized microscope. It may be due to the fine-grained nature of clay minerals. The zone boundaries and fissures have been the pathways of groundwater for mineral-water reaction. The perthite usually shows that the Na-rich parts are more altered than K-rich parts (Kim et al., 1994).

Biotite shows various degrees of K-depletion even in a single grain. Biotite is usually transformed into vermiculite (Velde, 1985). Muscovite lost small amount of K, hence the illitic components are not significantly produced.

WATER-ROCK INTERACTION IN THE GRANITE

Each mineral has characteristic surface reactive sites. When the mineral is dispersed in distilled water, the reactive surface functional group reacts with ions present in water. The negatively charged sites attract proton from the water molecule if there is only pure water. The hydroxylated sites play amphoteric roles. As Na, K and Ca ions are considered to be conservative ones, they do not affect the pH of the system (Drever, 1988).

The Sorption Process of Granite

Two types of pH variation curves are distinguishable; one with positive pH edge (Fig. 4) and the other with negative pH edge (Fig. 5).

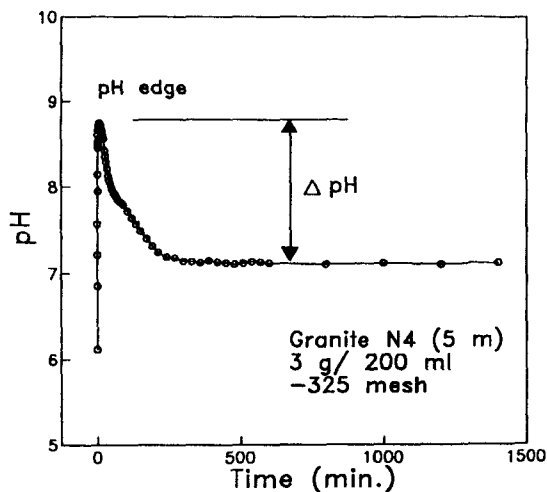The sorption process having positive pH edge takes place in three steps; (1) the initial rapid pH-

Fig. 4. pH variation curve for the fresh Namsan granite.
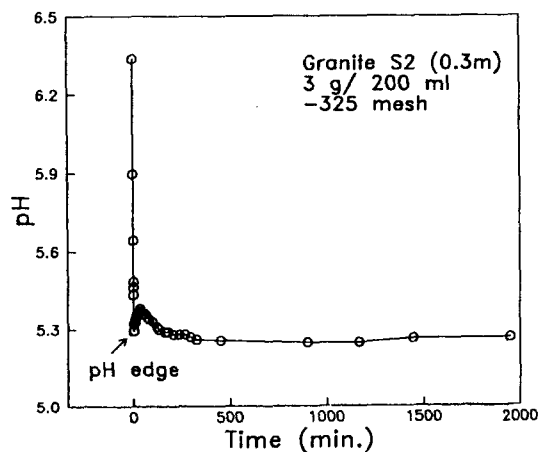

Fig. 5. pH variation curve for the intensely altered Namsan granite.

rise, (2) the slow pH-down, and (3) the stable pH tail. The initial pH-rise indicates that the total number of negative surface functional group, i.e., exposed oxygens outnumbers the positive one. This reaction takes place very rapidly resulting in steep gradient toward alkaline side. If the powdered granite is dispersed in distilled water, there takes place a reaction between minerals and water by which the pH of water changes giving characteristic variation curves depending on the

mineral assemblage of rocks.

When all the negative surfaces are exhausted by uptaking the protons available, the environment of solution is populated with OH, and this induces the release of proton from hydroxyls in the octahedral layer of biotite or muscovite. The reactions at pH maxima take place in a very restricted time because the dissolution rate is very slow compared with the sorption process itself. If Si-O and Al-O continue uptaking the proton to form silanol ($\equiv$SiOH) and aluminol (= AlOH), the proton is depleted in the solution. All these processes are dependent upon the bulk mineral compositions of initial rocks. Because the Namsan granite has a small amount of biotite, the decrease of [OH$^-$] proceeds very slowly.

The tails of the pH variation curves having positive pH edge converge to pH 7.2–7.7 in all sizes of rocks and rock/water (W/R) ratios. As the surface dissolution rate is controlled by the solubilities of minerals, the pH tails indicate that the surface reaction proceeds under saturated ion condition.

The sorption reaction showing negative pH edge (Fig. 5), which is observed in a somewhat altered granite containing clay components, proceeds differently from that of positive pH edge. The initial rapid pH-down suggests that the rate of dissociaton of proton from hydroxyl attached on the mineral is faster than the rate of adsorption on the surface. The tails having negative pH edge converge to near 5.0–5.3 in all rock/water ratios.

Rock/Water Ratio and Depth Effect on the Sorption

The pH edges for samples from 0.3, 1 and 5m depths show various parabolic relationships between R/W = 0.5–50 g/ 200 ml (Fig. 6). These parabolic relationships indicate that the rates and process of mineral-water interaction are critically affected by the content of water and original rock compositions. The critical pH saturation is about

10 g/200 ml for the fresh granite. In natural systems, CO_2 is almost always present, so the HCO_3^- is produced as an anion rather than OH$^-$. This retards the pH rise associated with mineral alteration (Drever, 1988). The effect of CO_2 on the pH variation curve has not been made in present
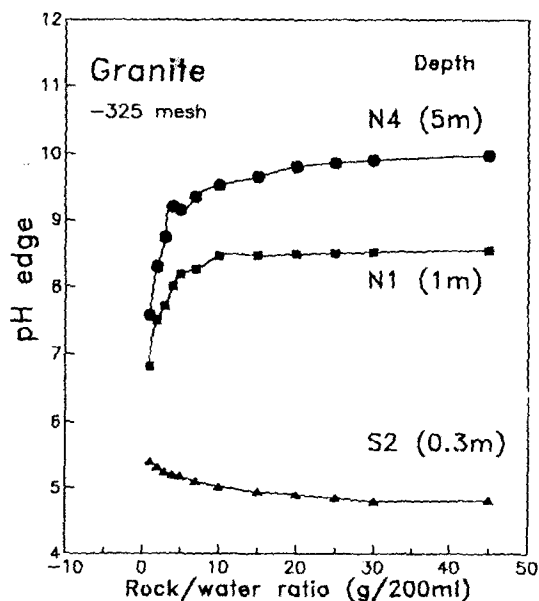

Fig. 6. pH edges varition curves for the Namsan granite at various depths.
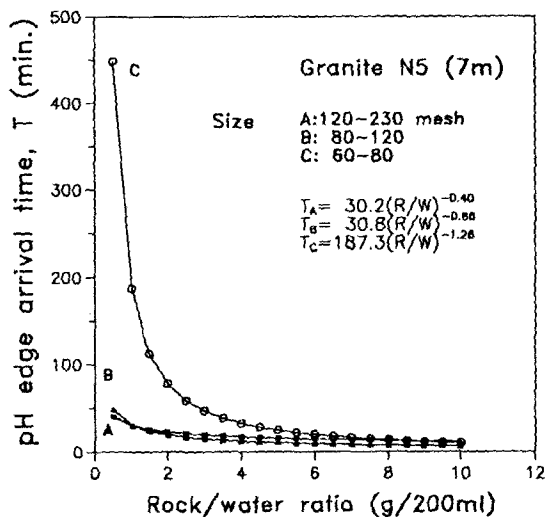

Fig. 7. Size effect of the water-rock reaction for the Namsan granite.

study.

Size Effect on the Sorption Process

The arrival time to the pH edges decreases exponentially as R/W increases (Fig. 7). The arrival time to the pH edges is very slow for 60-80 mesh samples at low R/W compared with those of 80-230 mesh, indicating that the smaller sizes react much faster than the larger ones.

Dissolution of Minerals

Sodium and potassium are released while stirring the granite in distilled water. This fact was proved by the AAS analysis of the water after each run of sorption experiment. It indicates that the interplaced cation inside the crankshaft is hydrated by water molecule and eventually dissociated from its site. The exact quantitative analysis was not carried out in this experiment. The dissolution of minerals suggests that the newly formed surface acts like an initial intact surface and the newly formed phase affects the system. This is like an alteration process in natural environment.

Formation of Gibbsite

An amorphous material floates on the solution forming white accumulations which are very sticky while stirring the granite in distilled water. It is transformed into gibbsite in an hour or so (Fig. 8). The amount of gibbsite increases as rock/water ratio and pH augments.

Just after the pH rises up to maximum pH edge, it falls slowly down to near pH 7.5-7.7 for the fresh granites. The activity of $Al(OH)_4^-$ species also increases if the pH is higher than 7, but it decreases if the system passes pH maxima (Drever, 1988). At this point the supersaturated Al species begins precipitating gibbsite. The activity of silica, which is very important in pre-
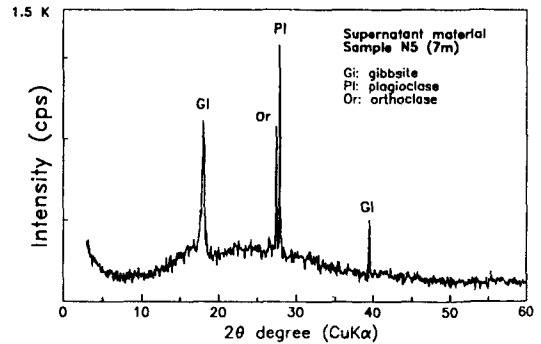

Fig. 8. XRD pattern of gibbsite formed during the water-granite reaction.

cipitating kaolinite or smectite, does not increase while the pH of the system is below 9 (Helgeson, 1969; Garrels and Christ, 1965). This expains why the interior part of feldspar releases Al and Si by a drop of water, and the released species precipitates outside the grain where the pH is dropped by the decreased R/W, hence causing Al depletion in the weathering profile (Fig. 2).

As for the negative pH edge, gibbsite is also formed. But in this case, aluminum species attracts one or three hydroxyls from each water molecule to form gibbsite because the predominant species is $Al(OH)_2^+$ or Al^{3+} (Drever, 1988), thus lowering the pH. This process will go on as long as the system retains low pH.

DISCUSSION AND CONCLUSION

The alteration of rocks was studied in the view points of mineralogical, chemical changes and surface functional group. The former two show the general phenomenon what we see in the field and laboratory, whereas the third explains why such process should take place.

The degree of alteration can be roughly traced using the XRD by which we can know about the weathering depth and common mineral composition. The chemical analyses of bulk rocks also can be used as general indicator of degree of alteration in the profile, but they are not suffi-

cient for describing the exact aleration process of each mineral.

Quartz does not show significnat alteration in both thin section and XRD. Feldspars are easily altered where structural and/or chemical changes are especially recorded. Zone boundaries and fissures are considerably disintegrated in every specimen examined.

The sorption process on the basis of surface functional group can be successfully applied to the study of mineral-water interface reaction. The acidity which has been considered as a main factor for altering the mineral in natural environment is not primary constraint. The solubility dependence on the pH condition and the formation of a new phase should be traced in determining the exact alteration mechanism of minerals. Furthermore the dissolution rate should be taken into account in terms of the pH varition.

If the ground water flow rate is assumed to be about 2-8 m/yr (Back and Hanshaw, 1971), which sweeps about 4-64 m^2/yr, and the average surface area of the granite powder ranging 80–325 meshes (roughly 100 μm) to be the order of 10–16 m^2/g, the sorption process could be roughly extended to natural environment because the solution was stirred at least about 100-200 rpm, which is equivalent $0.5^{-1} \times 10^8$ rotations per year, in conducting sorption experiment and most processes take place within several hours.

Gneiss complex intruded by the Namsan granite shows the acidity near pH 3.5 in sorption experiment. The proton derived from the gneiss affects significantly the alteration of the granite body. It is often found that the boundaries between granite body and gneiss complex are widely decomposed hence making a deep valley in most cases.

ACKNOWLEDGEMENTS

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