

# A geochemical signature of acidification leading to loss of Ca in the forested ecosystem of Yakushima, a world heritage site

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## Abstract

A geochemical study was undertaken to elucidate the influence of acid rain on the aquatic and soil-vegetation ecosystems of the forested island of Yakushima, a world heritage site in southern Japan. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of rainwater in Yakushima is almost identical to that of seawater, and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of terrestrial plants and plant-available components in soil are also close to that of seawater and rather independent of the underlying bedrock, indicating that enormous amounts of precipitation containing high concentrations of sea salt exert a significant influence on the material transport between plants and soil. On the other hand, stream waters are characterized by low pH (av. 6.5), low Ca and  $\text{HCO}_3$  contents, high Na and Cl contents, and Na/Cl and Mg/Cl ratios close to those of seawater, but have distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios dependent on the bedrock geology in each drainage basin (i.e., widely distributed granite or the sedimentary rock around it). These results indicate that rainwater also strongly controls dissolved species in Yakushima stream waters and the chemical weathering of Ca-minerals (i.e., plagioclase), though providing sufficient amounts of Ca and Sr into stream water, can not fully neutralize rain acidity due to overload of atmospheric H inputs.

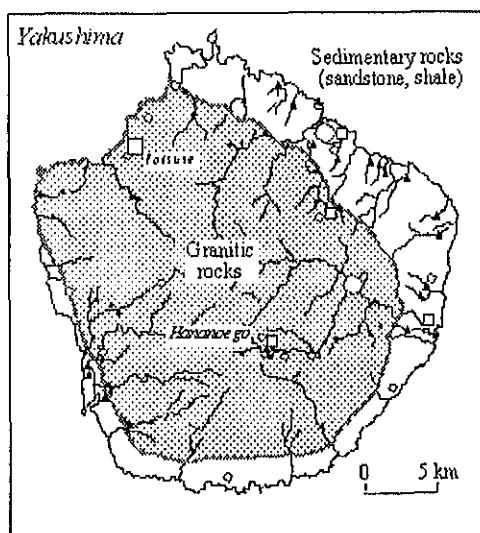
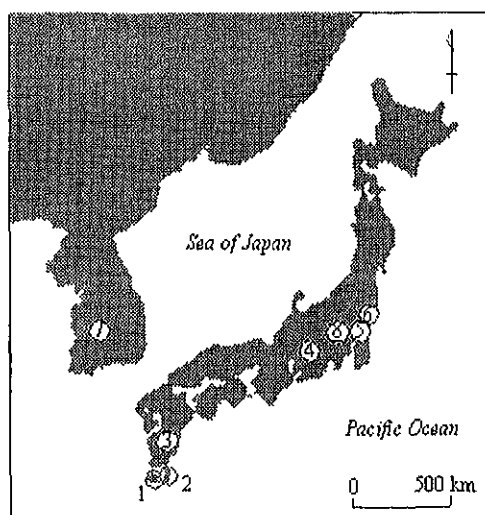
The Ca content in the soil-column at a site called Yotsuse, is 1 tenth that in the bedrock granite, while the concentrations of Al and Ti and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increase monotonically toward the surface. This pattern indicates that aeolian minerals, which are resistant to chemical weathering, are deposited on the upper soil, where plants absorb nutrients. The deficiency of Ca in the soil pool due to chemical weathering of granitic rocks and the large amount of acid wet deposition with high seasalt component and dry deposition of aeolian minerals, both

of which are depleted in Ca, lends support to the view that the forested ecosystem of Yakushima is sensitive to acidification, particularly with respect to Ca, which is indispensable for plant growth.

## INTRODUCTION

The influence of acid rain on terrestrial ecosystems in Japan is of increasing concern because rains of around pH 4.7 fall on the Japanese islands (TAMAKI et al., 1991). However, acidification of rivers and impoverishment of soils and forests in Japan are not so severe as those in Scandinavia, Central Europe, and North America, despite similar rain acidity among these areas. The effects of acid rain on biogeochemical cycles are thus so complex that an integrated approach which considers entire ecological systems as single interacting units is required to understand them. It is particularly important to elucidate processes regulating the flow of matter within and between ecosystems (LIKENS and BORMANN, 1995). Nutrients in soil-vegetation systems are ultimately derived from the atmosphere and bedrock. Ca, K, and P are essential for plant growth and increased acidification results in decreased availability of these nutrients in soil pools (LAWRENCE et al., 1995). Chemical weathering of bedrock is known to play an important role, not only in providing nutrient elements, but also by neutralizing acid. Sensitivity to acid rain is low in areas of carbonate rocks, which are high in Ca, while it is high in areas of granitic rocks, which are low in Ca (SHILTS, 1993). Sr isotopes have recently been reported to be powerful tracers which are useful for determining the source and flow of Ca in soil-vegetation systems (e.g., MILLER et al., 1993; ÅBERG, 1995) and in aquatic system (e.g., WICKMANN and ÅBERG, 1987).

The island of Yakushima (YKI), in southern Japan, was nominated to be a world heritage site in 1993 in recognition of its unique and irreplaceable forested ecosystem. However, stream acidification and tree die-back on this remote island made acid rain impacts all too obvious. This study was undertaken to elucidate the geochemical response of the aquatic and soil-vegetation systems of this island to atmospheric inputs, particularly the flow of Ca, by using Sr isotope analysis.



### GEOLOGY AND SAMPLES

YKI is located at 70 km south of Kyushu (Fig. 1). This small island, 132 km in circumference around and 503 km<sup>2</sup> in area, consists of deeply forested mountains with many cliffs and waterfalls owing to

enormous amounts of precipitation; Mt. Miyanoura, the highest point on the island, is also the highest peak (1935 m) in the Kyushu region. The island is composed mainly of Miocene granites of the ilmenite series containing orthoclase megacrysts with maximum lengths of 14 cm, plagioclase, quartz, and biotite, with small amounts of chlorite, apatite, zircon, tourmaline, muscovite, ilmenite, and pyrrhotite (SATO and NAGAHAMA, 1979). These minerals intrude the Kumage Group, of Paleogene age, which is mainly composed of sandstone and shale and is distributed around the periphery of the island. They are sometimes unconformably overlain by terrace deposits, talus deposits, and alluvium of Quaternary age, mainly along the eastern and southern coasts. A pyroclastic flow deposit, called Akahoya, locally covers these rocks.

Fig. 1 Location of studied areas (upper); 1: Yakushima, 2: Tanegashima, 3: northern Kagoshima, 4: Naegi, 5: Tsukuba. 6, 7, and 8 are the Joban area, Yatsugatake area, and the Okchon belt in Korea, where the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of land plants are compared with those of Yakushima (Fig. 5). Geology and sampling sites of the Yakushima (lower); Solid circles, solid triangles, and open triangles are the sampling points of stream waters on the drainage geology of granite, sedimentary rocks of the Kumage group, mixture of the both rocks, respectively. Open circles and open tetragons are the sampling sites of land plants and rain waters, respectively. Large open tetragon indicates the Yotsuse site. Two large open circles are the location of rainwater monitoring and sampling in TAMAKI et al. (1991).

We collected stream water, bedrock, soil, plants, and rainwater at several sites (Fig. 1). Stream waters in YKI were sampled at different locations chosen in consideration of their basin geology. For comparison, we collected stream waters from several areas with various geological conditions, the island of Tanegashima close to YKI (sedimentary rock), northern Kagoshima (granitic rock, sedimentary rock, and volcanic rock mostly of andesite composition), Naegi in the Chubu district (granite), and Tsukuba in Ibaraki prefecture (granite and gabbro). Their locations are also shown in Fig. 1. The water samples were filtered through 0.22 μm pore

size Millipore filters; pH and alkalinity were measured immediately after sampling. At the Yotsuse site of northwestern YKI, where the granitic bedrocks are deeply weathered, we collected plants and soils at various depths. Because of the severe topographical and climatological situation of YKI, many difficulties arise in the systematic collection of rainwater. We collected six rainwater samples at three sites in YKI (Fig. 1) with different season (June 1992, September 1993, and April 1996) and duration of sampling (one day to one year). They were used only for the determination of Sr isotopic ratios because the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios would not be changed significantly during the sample preservation.

All analyses were made using equipments installed at the Chemical Analysis Center and the Institute of Geoscience, University of Tsukuba. The concentrations of cations and anions in stream waters were made determined by Jarrell Ash ICAP-757V ICP-OES and Yokokawa IC7000 ion chromatography, respectively. The chemical compositions of rocks and soils were determined by Phillips PW1404 X-ray fluorescence analyser, and Sr isotope measurements by Finnigan MAT 262RPQ multicollector mass spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of NBS987 throughout the analysis was  $0.71024(\pm 0.00001)$ .

## RESULTS

### *Aquatic system*

The mean electrical conductivity, pH, and dissolved species composition of stream waters from YKI and the other studied areas are summarized in Table 1. Fig. 2 shows the frequency of pHs of stream waters. As shown in Fig. 2, stream waters from areas except YKI are neutral to slightly alkaline, although there is a tendency that stream waters in granitic basin are slightly acidic compared to those in sedimentary or volcanic rocks basin; This difference is consistent with that granite is composed of minerals (i.e., quartz and K-feldspar) resistant to chemical weathering. However, one remarkable feature is that the YKI stream waters are more acidic, with pH

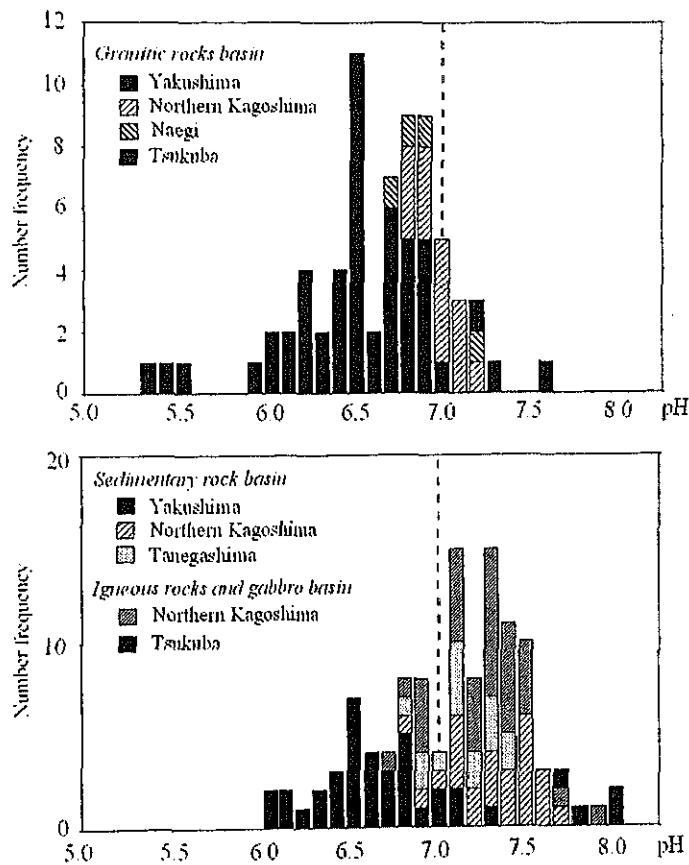
in the range from 5.5 to 7.1 (average 6.5), and no notable dependence of their pH or dissolved ion composition on the drainage basin geology was observed.

Fig. 3 shows the relation between Cl and major cations (Na, K, Ca, and Mg) of stream waters studied. It is notable that the ratios of Na and Mg versus Cl for YKI stream waters are similar to those of seawater. Although the Ca/Cl and K/Cl ratios of YKI stream waters deviate from those of seawater, the values are still closer to seawater ratios compared to those for stream waters from other areas. These results strongly suggest that wet precipitation on YKI contains significant amounts of sea spray components, which in turn control the chemical composition of dissolved elements in YKI stream waters. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of YKI rainwaters were highly uniform of  $0.7092 \pm 0.0001$  independent of location, season, and duration of sampling. The similarity of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of YKI rainwaters ( $\sim 0.7092$ ) to that of seawater (0.70917) (e.g., DIA et al., 1992) supports the above conclusion and demonstrates that the major source of Sr in YKI rains is sea salt. The concentration of Cl in YKI stream water whose watershed is small tends to decrease with elevation (Fig. 4). This altitude effect is further observed in other dissolved cations from their relatively constant ratios with Cl as seen in Fig. 3. This pattern is qualitatively consistent with previous studies of rainwater chemistry (BERNER and BERNER, 1987), which shows that seasalt component decreases with distance away from the coast.

If all Cl in YKI stream water is assumed to be derived from sea salt, the non-sea salt fractions of Na, K, Ca, Mg, Sr, and  $\text{SO}_4$  can be calculated easily (Table 1). It is evident that despite low concentrations, Ca and K in YKI stream waters are largely of non-sea salt origin. However, this does not necessarily mean that the non-sea salt Ca and K are derived from chemical weathering of bedrocks, because dissolved elements in rain, particularly Ca in inland rain, are largely of non-sea salt origin (BERNER and BERNER, 1987). We estimated the non-sea salt

component in YKI rain from data of TAMAKI et al. (1991), who published the average elemental composition of wet precipitation over 2 years at 2 YKI sites with different altitudes (40 m and 475 m). According to their data, (1) the YKI rains have the Na/Cl and Mg/Cl ratios very close to seawater but the Ca/Cl and K/Cl ratios are higher than those of seawater (Fig. 3), and (2) their Cl concentration is low in the 475 m site than in the 40 m site (Fig. 4), the pattern being consistent with that in YKI stream waters.

Fig. 2. Frequency of pH of stream waters from areas with granitic watershed (upper) and from areas with the Kumage clastic sedimentary rocks, volcanic rocks mostly of andesite composition, and gabbro (lower).



The non-sea salt fraction in YKI rain calculated from the data of TAMAKI et al. on the basis of Cl content is 50 and 58% for Ca and 27 and 45% for K, but is negligible for Na and Mg. If this is the case, then it is possible to estimate the non-precipitation

fractions of cations in YKI stream water. If 50% Ca and 30% K in YKI rain is assumed to be of non-seasalt origin, it is calculated that 79% of the Ca and 63% of the K in YKI stream water, both elements being essential for plant growth, are derived not from precipitation but rather from the bedrock. However, the bedrock contribution is calculated to be only about 11% for Na and 13% Mg. Thus the non-precipitation component, a component of stream water (largely bedrock) which is originated from sources except precipitation, is enriched in Ca and is comparable to stream water in other areas; the average order of dominance of the cations in YKI stream waters not contributed by precipitation was Ca (1.14 ppm) > Na (0.69 ppm) > K (0.41 ppm) > Mg (0.10 ppm).

Dissolution of silicate minerals is suggested by the relatively high concentrations of Si in YKI stream waters (4.1 ppm on average) (Table 1). Therefore, the K and Mg in the non-precipitation component in YKI stream water is likely to be attributed to the dissolution of K-feldspar and biotite, while Ca and Na in it is to that of plagioclase. Petrographic observation shows that plagioclase is altered into sericite and biotite into chlorite, while the weathering of K-feldspar is weak and quartz is not altered. The plagioclase weathering sometimes occurs in the core part enriched in Ca. This is consistent with that the molar Ca/Na ratio of the non-precipitation component in YKI stream water (ca. 0.49) is slightly higher than the Ca/Na ratio of plagioclase in YKI granite (0.2-0.3). It is therefore likely that the relative enrichment of Ca and Na in the

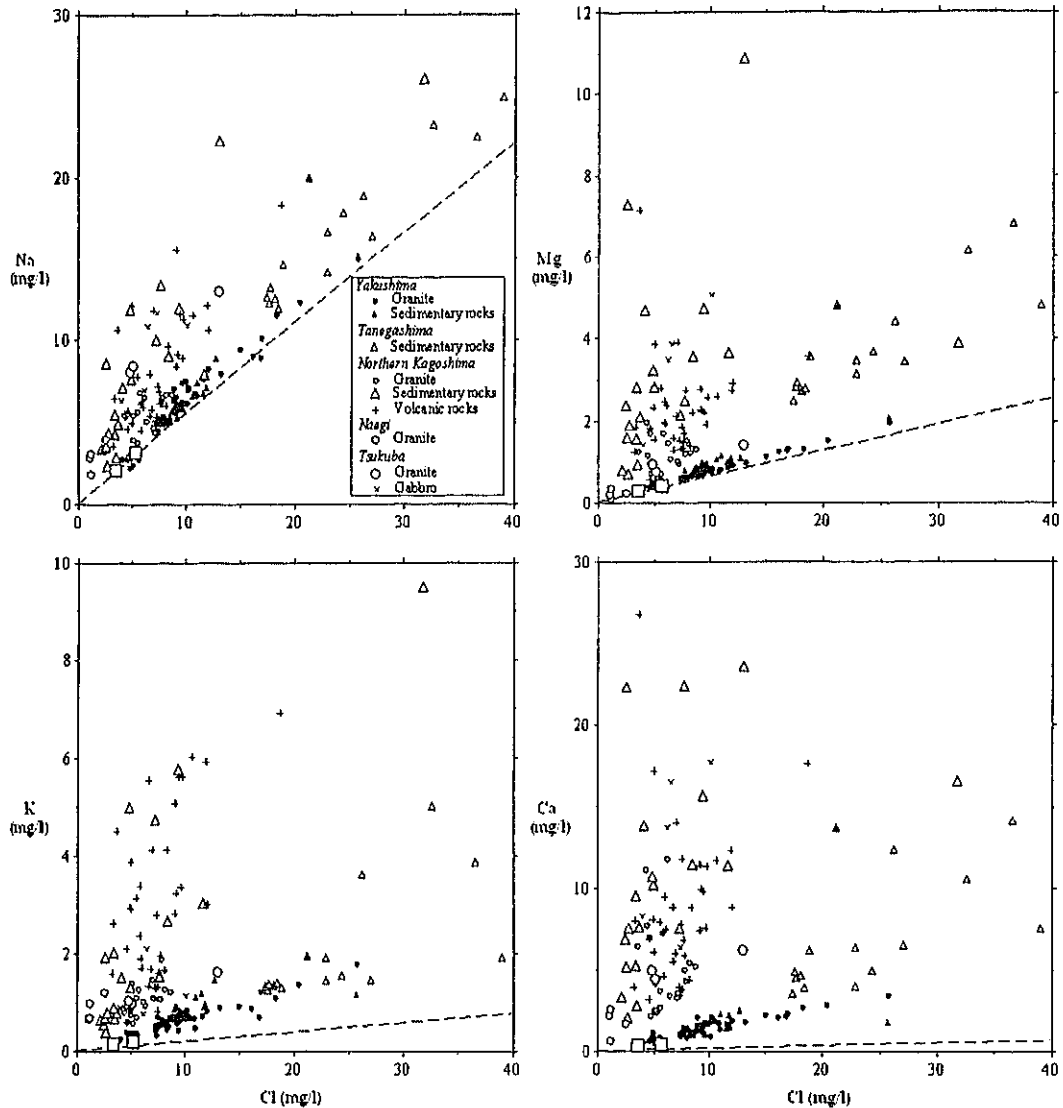


Fig. 3. Concentrations of the major cations (Na, Mg, K, Ca) versus Cl in stream waters in Yakushima and other areas with different bedrock geologies. Dotted lines indicate seawater ratios. Two large open tetragons indicate the averaged compositions of rainwaters at two sites in Yakushima taken from TAMAKI et al. (1991).

non-precipitation component in YKI stream water is caused by the selective dissolution of Ca-rich plagioclase which is sensitive to chemical weathering.

The significant incorporation of bedrock Ca into stream water is consistent with Sr isotope data which show that YKI stream waters have distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios depending on the bedrock in each drainage basin. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of stream waters in YKI averaged  $0.7084 \pm 0.0002$  in drainage basins underlain by granitic rocks and  $0.7120 \pm 0.0015$  in drainage basins underlain by Kumage clastic sedimentary rocks (Fig. 5). On the other hand, despite limited data, the

$^{87}\text{Sr}/^{86}\text{Sr}$  ratio of granite in YKI lies mostly in a narrow range of  $0.7082 \pm 0.0002$ , while clastic sedimentary rocks in the Kumage group have more elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.711-0.719. Calcium containing minerals are generally enriched in Sr (FAURE, 1986), and the Sr in YKI stream water is largely of non-sea salt origin (Table 1). Therefore, we conclude that, similar to the situation for Sr, the Ca in YKI stream waters is essentially derived from bedrocks.

TAMAKI et al. (1991) give the ranges and average concentrations of  $\text{SO}_4$  and  $\text{NO}_3$  in precipitation at 29 sites in Japan, from 1.43 to 5.85 ppm (average 2.64 ppm) and from

0.40 to 2.81 ppm (0.96 ppm), respectively. The calculated nss-SO<sub>4</sub> fractions of these anions lie in the range from 67% to 95%. Of these, precipitation at 2 sites in Yakushima contains 1.71 and 2.42 ppm SO<sub>4</sub>, 0.50 and 0.67 ppm NO<sub>3</sub>, and 67% and 71% nss-SO<sub>4</sub> fraction. In contrast, the mean concentrations of SO<sub>4</sub> and NO<sub>3</sub> in YKI stream waters are 2.94 and 0.49 ppm, respectively (Table 1). Sulfur isotopic ratios of rain and stream waters from YKI ( $\delta^{34}\text{S}_{\text{CDT}}$ : 10~14‰) are distinctly lower than that of seawater (20.3‰) (MINARI et al., 1996). According to TAMAKI et al., (1991), the annual mean pHs of precipitations at two YKI stations are both 4.7. These data strongly indicate that the YKI rains, and by extension the YKI stream waters, contain significant amounts of anthropogenic S and N, which lower their pH values.

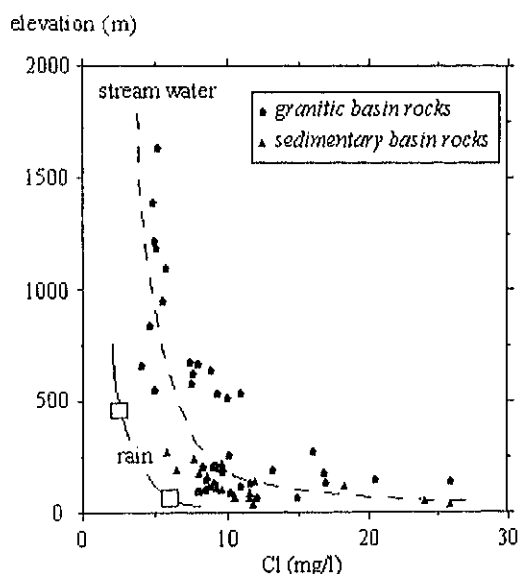


Fig. 4. The concentration of Cl of stream waters in Yakushima versus elevation. Stream water samples from small drainage areas are plotted to minimize the effects due to the elevation where rain water falls. The concentration of Cl of rain water at two sites in Yakushima are taken from TAMAKI et al. (1991).

#### Soil-vegetation system

Similar to the situations for other elements, the Sr in terrestrial plants is ultimately derived from two sources, the atmosphere and bedrock. Along with a wide variation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  (1986), even fewer measurements have shown that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of

precipitation varies areally and temporally due to the different degree of the contribution from multiple sources (i.e., seaspray, terrestrial dust etc.) of differing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (ANDERSEN et al., 1990, HERUT et al., 1993; NAKANO et al., 1993a). Given different isotopic ratios of Sr between the two sources, it is possible to estimate the relative contribution of their Sr into land plants by comparing the variation of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and using the calculation method by GRAUSTEIN (1988). GRAUSTEIN (1988) estimated that ca. 60-80% of the Sr in Spruce and Aspen in the Tesuque watershed, New Mexico, is derived from precipitation. Likewise MILLER et al (1993) document that ~53% of the Sr of vegetation in a forest ecosystem in the Adirondack mountains, New York, has an atmospheric origin. Further, NAKANO et al. (1992, 1993b) have shown the regional variation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of land plants in Japan and Korea probably due to the areal heterogeneity of atmospheric  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Fig. 5).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of terrestrial plants on YKI are variable depending on the underlying bedrock, 0.7085-0.7091 for terrestrial plants growing on granitic bedrock and 0.7091-0.7096 for those growing on sedimentary bedrock (Fig. 5). However, this difference is small compared to the difference in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of stream water or aquatic plants, and as a whole the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of YKI terrestrial plants falls in the narrow range of  $0.7090 \pm 0.0006$ . As these ratios are distinct from values of terrestrial plants from other areas in Japan and Korea and are so close to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater, it is likely that the YKI plants contain significant amounts of rainwater Sr of sea salt origin. In order to estimate the contribution of the rainwater Sr into vegetation, it is required to determine the isotopic ratio of exchangeable Sr in soil released by the bedrock weathering. We simply assume the value to be correspondent to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of bedrock as GRAUSTEIN (1988) did. Calculations based on end-member  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of rain water

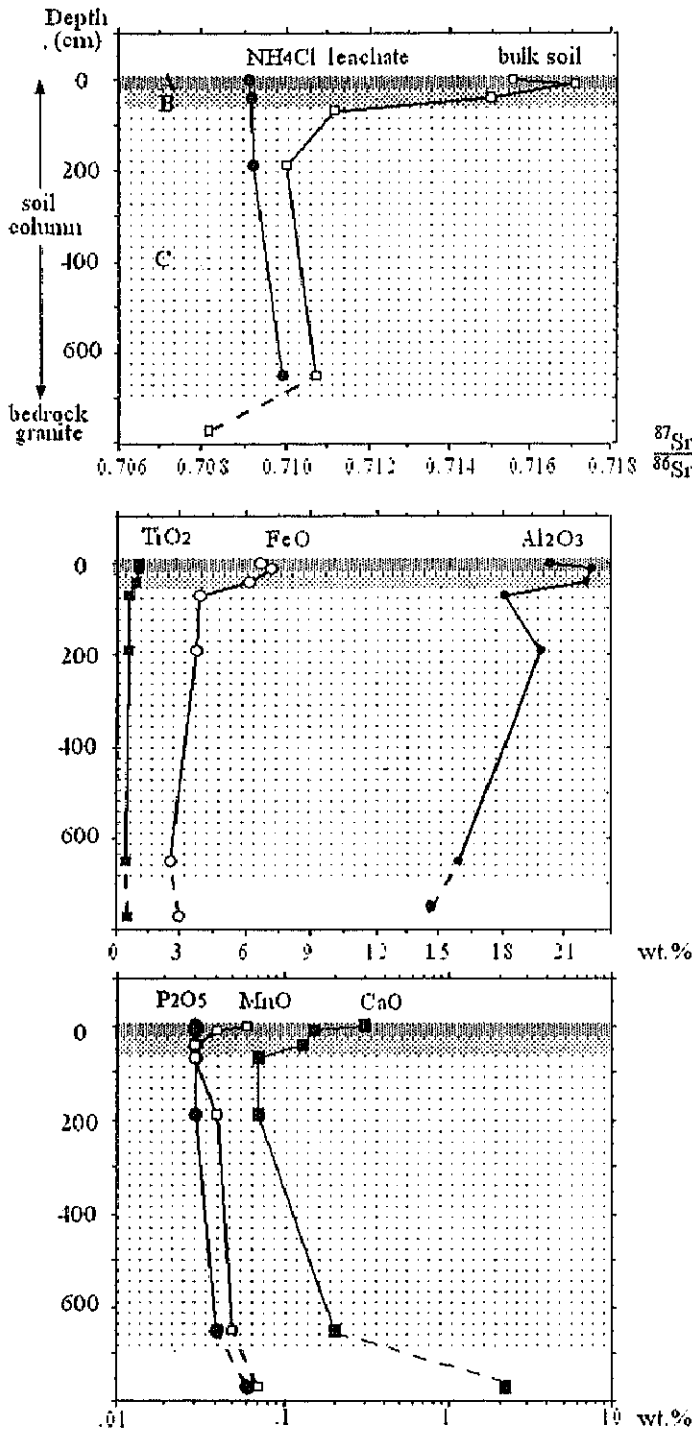


Fig. 5. Frequency of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of stream water versus drainage basin bedrock type (upper) and land plants growing on granite or Kumage clastic sedimentary rock (lower). The Sr isotopic data of land plants in other areas are taken from NAKANO et al (1992) for the Joban area, NAKANO et al (1993b) for the Okchon belt in Korea, and unpublished data of YOKOO and NAKANO for the Yatsugatake area.

and of bedrock granite show that 30-100% of the Sr in the YK1 plants growing on granite substrate appears to have been derived from atmospheric sources. This value is similar to, but is more scattered than, values (ca. 50-80%) of previous studies by GRAUSTEIN (1988) and MILLER et al. (1993). The variation is likely to be ascribed to a spatial heterogeneity of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in soils, along with an invalid assumption of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the Sr lost during the chemical weathering of bedrock granite. It is notable that there are two sites (Yotsuse and Hananoego sites) where the vegetation contains significant, atmospheric contribution (>90%).

We evaluated the depth profiles of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of soils at the Yotsuse site (Fig. 6). This site forms a 7 m high cliff, which is composed of soils on weathered granite. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of bulk soil decrease from 0.715 to 0.708 with depth, while those of 1 M NH<sub>4</sub>Cl leachates from the A- and B-soil horizons (exchangeable Sr) lies in a narrow range ( $0.7092 \pm 0.0001$ ) independent of depth. This leachate  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is the same as that of terrestrial plants at the Yotsuse site, demonstrating that soil leachates correspond to plant-available components, and additional plant-available Sr in the Yotsuse soil is derived largely (>90%) from rainwater Sr of sea salt origin.

Similarly, the elemental composition of the Yotsuse soil changes systematically with depth. The Ca concentrations in these soils are 1 tenth those in granitic bedrock (Fig. 6). Likewise, Mn and P are also more depleted in the B- and C-soil horizons than is the

underlying fresh granite. In contrast, the concentrations of Al, Fe, and Ti increase monotonically toward the surface, in part due to the chemical weathering of granitic bedrock. We ascribe the depletion of Ca to the dissolution of plagioclase. This is consistent with that the non-precipitation Ca component in the YKI stream waters is largely of bedrock origin. However, the high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the upper soil demonstrates that the soil contains exotic minerals whose  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are higher than those of the underlying granitic minerals. Previous studies demonstrate that water-insoluble aeolian minerals originating from the deserts of central Asia, Kousa minerals, occur widely in soils and sediments of the northwestern Pacific region. These Kousa particles are composed of quartz, illite, and kaolinite and are low in Ca and high in Al, Fe, and Ti. They have high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of around  $0.719 \pm 0.0003$  (TAYLOR et al., 1983; MIZOTA et al., 1992), similar to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the A-soil horizon at the Yotsuse site. These values are identical to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of water-insoluble minerals from deserts in China (NISHIKAWA et al, unpublished data). Therefore, we suggest that this chemical zonation in the soil column was primarily caused by mixing of Kousa minerals and weathered granite. The increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the soil toward the surface indicates the recently increased contribution of Kousa minerals in the A-soil horizon.

### DISCUSSION

YKI is known to have enormous precipitation of 4000 mm/year in the coastal zone and 8000-10000 mm/year in the mountainous zone. The unique topography of YKI, with jagged mountains facing the coast, provides favorable conditions for cloud formation of water vapor evaporated from the surrounding seawater; this water vapor may condense to rain by cooling due to adiabatic expansion as it rises up along the mountain slopes. This process seems to be the primary control on the chemical composition of YKI rain and stream water,

which are similar to diluted seawater. It is likely that the evaporated water vapor is not acidic, but rather alkaline due to high sea salt content. Incorporation of anthropogenic  $\text{SO}_4$  and  $\text{NO}_3$  into YKI rains is indispensable for the formation of acid rains with pH similar to those measured in other areas of Japan. According to TAMAKI et al (1991), the deposition of H through precipitation is high at two YKI sites ( $0.081$  and  $0.127 \text{ g/m}^2 \cdot \text{year}$ ) due to large amounts of precipitation compared to at other 27 sites over the Japanese islands ( $0.005$  to  $0.055 \text{ g/m}^2 \cdot \text{year}$ ). The significant amounts of acid precipitation thus formed have been input to the ecosystem in YKI and would accelerate the chemical leaching of base cations from bedrocks.

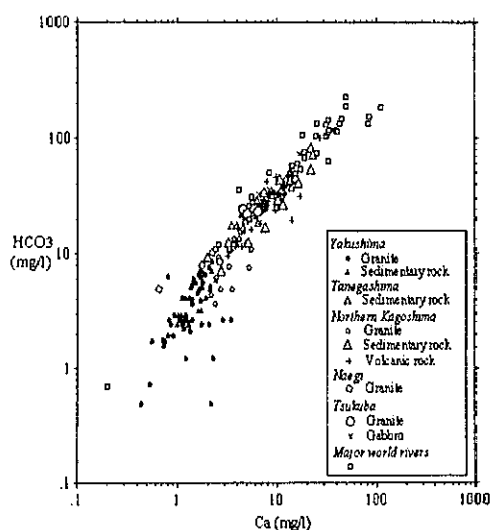


Fig. 7 Relation between the concentration of Ca and  $\text{HCO}_3$  in stream waters from Yakushima and other areas. Data on major river waters in the world taken from BERNER and BERNER (1987) are also shown for comparison.

The increase of pH from precipitation (av. 4.7) to stream water (av. 6.5) in YKI is largely attributable to the dissolution of Ca-minerals such as plagioclase. Stream waters are generally dominated by Ca and  $\text{HCO}_3$ , and there is a good correlation between Ca and  $\text{HCO}_3$  (Fig. 7). This is caused by the chemical weathering of Ca minerals (i.e., plagioclase and carbonate)



during which H is consumed and Ca and HCO<sub>3</sub> are produced. It is notable in Fig. 7 that the concentration of Ca and HCO<sub>3</sub> tends to be lower in stream waters from granitic basin than those from volcanic and sedimentary rock basins, which is consistent with that granitic rock has a low capacity to neutralize acid. Further, despite a wide distribution of granitic rocks over YKI, YKI stream waters are more depleted in the concentrations of Ca and HCO<sub>3</sub><sup>-</sup>. The low concentration of Ca and HCO<sub>3</sub> and high concentration of H in YKI stream waters is therefore explained by assuming that chemical weathering is not sufficiently achieved at a rate to compensate the overloading of atmospheric H inputs. As a result of the chemical leaching of Ca-minerals, the soil pool becomes depleted in Ca and enriched in secondary minerals high in Al and Ti (Fig. 6). In addition, as determined from Sr isotope data, fine-grained aeolian minerals originating from Asian deserts are deposited on YKI. As these Kousa particles are composed of water-insoluble minerals resistant to chemical weathering, their deposition may also increase the susceptibility of the soil to acidification and depletion of nutrient bases.

The Sr isotope profile in Fig. 6 further demonstrates that silicate minerals of Kousa origin and secondary minerals of granitic origin in YKI soils do not interact significantly with plants, but rather rainwater exerts dominant control on the cycling of elements between the plant and soil pools. The concentration of Ca at the Yotsuse site is slightly higher in the upper A-soil horizon, which is enriched in organic matter, than in the underlying soils (Fig. 6), suggesting that plant-available elements in soil are mainly absorbed onto organic matter rather than onto the cation-exchange sites of clay minerals. Granite is generally poorer in base cations and more resistant to chemical weathering than are other rocks. Moreover, base cations are extensively leached out of areas of strongly weathered granite. In such areas, wet precipitation is the major external source of nutrient cations to the

soil-vegetation system, and the forested ecosystem accordingly becomes more sensitive to acidification.

The source of anthropogenic S and N in YKI ecosystem has not yet been determined. However, the majority of these elements may be derived from Asia and/or Japan as atmospheric gases. As most SO<sub>4</sub> and NO<sub>3</sub> are transported to YKI with air masses, their concentrations would be high in mountainous areas. In contrast, the sea salt contribution to YKI ecosystem is likely to decrease with elevation (see Fig. 3). In addition, the deposition of H through precipitation would be high in mountainous area due to increasing amounts of precipitation. As a result, under similar soil conditions, the acid rain impact in mountainous areas at high elevation would be greater than that at lower elevations. The die-back of trees occurring to the east of Mt. Kuromi (1500 m high) appears to support this supposition.

## CONCLUSIONS

YKI rainwaters contain dissolved cations highly enriched in seasalt component and significant amounts of anthropogenic S and N leading to the lowering of rainwater acidity. However, despite having the average rain acidity in Japan, YKI receives 3 to 4 times deposition of atmospheric H to the average in Japan due to enormous precipitation amounting to 4000 to 8000 mm/year. The significant contribution of acidic rainwater onto the ecosystem in YKI is indicated by low pH, Ca, and HCO<sub>3</sub> and high seasalt component in the stream waters and Sr isotopic ratios of soil waters and land plants close to marine value. Sr isotope data further suggest that the depletion of Ca in the soil pool in the granitic substrate is attributable to the selective weathering of Ca-plagioclase and the recent accumulation of water-insoluble Kousa minerals, and those secondary minerals are not vitally exchanged base cations with plants. It is implied from these data that the unique forested ecosystem of YKI becomes more sensitive to the acidification of atmospheric inputs.

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Table 1. Electric conductivity, pH, and concentration (mg/l) of dissolved ions in stream waters from drainage basins with different bedrock types and the concentrations (mg/l) and fractions (%) of the non-seasalt components of Ca, Mg, Na, K, Sr, and SO<sub>4</sub> (italics).

Bedrock in the basin (area)	E.C.	pH	Si	Cl	NO <sub>3</sub>	HCO <sub>3</sub>	Ca	nss-Ca %	Mg	nss-Mg %	Na	nss-Na %	K	nss-K %	Sr	nss-Sr %	SO <sub>4</sub>	nss-SO <sub>4</sub> %
Granite (Yakushima)	36.8	6.45	4.22	9.82	0.52	3.54	1.46	<i>1.25</i> <i>85.2</i>	0.76	<i>0.11</i> <i>15.8</i>	6.16	<i>0.74</i> <i>11.5</i>	0.66	<i>0.46</i> <i>69.6</i>	0.014	<i>0.010</i> <i>71.4</i>	2.79	<i>2.32</i> <i>82.8</i>
Sedimentary rock (Yakushima)	45.0	6.62	3.93	10.91	0.53	4.05	1.49	<i>1.26</i> <i>84.0</i>	1.00	<i>0.27</i> <i>28.1</i>	6.77	<i>0.69</i> <i>10.2</i>	0.86	<i>0.64</i> <i>74.1</i>	0.016	<i>0.012</i> <i>72.8</i>	3.13	<i>2.60</i> <i>82.8</i>
Sedimentary rock (Tanegashima)	110.5	7.14	6.54	24.13	2.99	26.41	7.16	<i>6.65</i> <i>91.9</i>	3.84	<i>2.24</i> <i>57.3</i>	16.71	<i>3.27</i> <i>19.6</i>	2.04	<i>0.92</i> <i>87.9</i>	0.054	<i>0.044</i> <i>80.4</i>	10.28	<i>8.39</i> <i>87.4</i>
Granite (N. Kagoshima)	49.7	7.04	8.70	5.94	0.72	14.23	5.08	<i>4.95</i> <i>96.9</i>	1.12	<i>0.72</i> <i>61.0</i>	5.17	<i>1.87</i> <i>33.9</i>	1.04	<i>0.92</i> <i>87.9</i>	0.039	<i>0.036</i> <i>91.2</i>	5.04	<i>3.75</i> <i>94.4</i>
Sedimentary rock (N. Kagoshima)	91.7	7.38	10.69	6.71	3.00	33.83	10.73	<i>10.59</i> <i>98.5</i>	3.18	<i>2.73</i> <i>83.7</i>	8.46	<i>4.73</i> <i>55.7</i>	3.05	<i>2.91</i> <i>93.0</i>	0.087	<i>0.084</i> <i>96.3</i>	13.95	<i>12.24</i> <i>96.7</i>
Volcanic rock (N. Kagoshima)	92.6	7.25	17.66	7.93	2.66	29.63	8.95	<i>8.78</i> <i>97.8</i>	2.34	<i>1.82</i> <i>74.8</i>	8.53	<i>4.11</i> <i>45.7</i>	3.09	<i>2.93</i> <i>93.3</i>	0.051	<i>0.048</i> <i>93.3</i>	9.55	<i>6.52</i> <i>93.8</i>
Granite (Naegi)	25.6	6.88	5.59	1.47	0.50	7.93	1.81	<i>1.78</i> <i>97.8</i>	0.22	<i>0.12</i> <i>50.0</i>	2.98	<i>2.16</i> <i>72.6</i>	0.89	<i>0.86</i> <i>96.7</i>	0.013	<i>0.012</i> <i>94.8</i>	2.13	<i>2.06</i> <i>95.6</i>
Granite (Tsukuba)	75.9	7.39	12.90	7.64	2.89	23.40	5.24	<i>5.07</i> <i>97.0</i>	1.06	<i>0.55</i> <i>54.2</i>	9.86	<i>5.61</i> <i>59.2</i>	1.23	<i>1.07</i> <i>88.1</i>	0.046	<i>0.043</i> <i>93.4</i>	3.71	<i>3.35</i> <i>90.3</i>
Gabbro (Tsukuba)	150.2	7.91	13.45	7.62	3.63	67.69	15.96	<i>15.80</i> <i>99.0</i>	4.13	<i>3.63</i> <i>87.9</i>	9.60	<i>5.36</i> <i>55.3</i>	1.34	<i>1.19</i> <i>86.5</i>	0.077	<i>0.070</i> <i>96.0</i>	4.50	<i>4.13</i> <i>90.9</i>