

HIGH ACIDIC SULPHATE SALT PRODUCTION ON THE CAVE WALL IN THE YOSHIMI HYAKU-ANA HISTORIC SITE, CENTRAL JAPAN

Oguchi C.¹, Takaya Y.², Yamazaki, M.³, Ohnishi R.³, Thidar A.⁴ and Hatta T.⁵

¹ *Geosphere Research Institute, Saitama University, 338-8570, Saitama, Japan, ogchiaki@mail.saitama-u.ac.jp*

² *Research Facility Center for Science and Technology, University of Tsukuba, 305-8577, Ibaraki, Japan,*

³ *Department of Civil and Environmental Engineering, Saitama University, 338-8570, Saitama, Japan,*

⁴ *Graduate School of Science and Engineering, Saitama University, 338-8570, Saitama, Japan,*

⁵ *Japan International Research Center for Agricultural Sciences, 305-8686, Ibaraki, Japan,*

Abstract: Acidic sulfates such as aluminum sulfates and ferric sulfates are often observed on the wall of tuff or volcanic rocks in Japan. We investigated wall surfaces of an artificial cave dug from 1941 to 1945 in the Miocene tuff. The cave locates in the historic site of Yoshimi Hyaku-Ana which is ancient graves of 6-7 centuries. The cave was suffering from severe salt efflorescence and deterioration of its cause. Salts are much in dry winter but less in humid summer. We set up twelve investigation points for monthly monitoring of temperature and humidity. Fallen salts and debris at each point were also collected monthly from November 2008 to December 2009. Main salt minerals, detected by XRD, are hard and granularly effloresced alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) on the walls near the entrances, and gypsum was found on the inside walls in the humid summer. On the contrary, powdery effloresced halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), sodiumalum ($\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) were detected in the dry winter. Jarosite ($\text{KFe}_3(\text{SO}_4)_4 \cdot (\text{OH})_8$) minerals were observed on iron hydroxide stains on the walls in every season. Halotrichite, sodiumalum and epsomite damaged the walls most severely especially in the dry winter. The amount of salts and debris from the inner wall were greater than those from near entrances.

Keywords: alunogen, jarosite, sulphate, salt weathering, tuff, Yoshimi-Hyaku-Ana.

1. Introduction

Salt weathering due to sulphate salts causes sometimes severe deterioration on stone monuments and natural rock walls (Goudie and Viles, 1997; Winkler, 1994). Salt weathering itself is generally categorized into physical weathering but chemical reaction sure to be observed before the salt crystallization. These processes are sometimes investigated from the aspect of water-rock interaction. Seki and Sakai (1987) studied a decay of rock-cliff Buddha sculpted on Miocene tuff caused by sulphate salts of gypsum, thenardite (Na_2SO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Kuchitsu (1992) studied Japanese cultural important building made by brick covered with plaster and insisted that deterioration on the building occurred when evaporates such as apthitalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$), thenardite, trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) formed inside the building materials. Origin of sulphates of Seki and Sakai (1987)'s case was internal of rock, however, that of Ku-

chitsu (1992)'s case is external such as acid rain water with SO_4^{2-} ion.

Japan is volcanic country and Japanese cultural properties or historic sites are often sculpted on the tuff cliff. Thus, these cultural properties are suffering from sulphate attack. It is important to investigate sulphate mineral production for not only the purpose of characterization themselves but also aiming at conservation of stone monuments. In this study, monitoring of salt weathering and environmental condition as well as salt description were made at the Yoshimi-Hyaku-Ana Historic Site, central Japan.

2. Study Area

The Yoshimi-Hyaku-Ana historic site locates at the central Saitama Prefecture, central Japan (Fig. 1). The topography of Saitama Prefecture is largely divided by the western mountainous area neighboring the Kantō Mount Range of Paleozoic and Mesozoic systems and the eastern alluvial low-

lands formed by Arakawa River. The historic site exists on the branch of the Hiki hills, the Yoshimi hill, with an area of east-west length of 2.5 km and south-north length of 3 km at 50-80 a.s.l. According to the Matsumaru and Hayashi (1980), the hill composes of metamorphic rocks such as amphibolite, ultramafic rocks and crystalline schist in the center, sandstone, conglomerate, mudstone and tuff of Miocene Kosono formation in the northeast part, and tuff, mudstone and sandstone of Miocene Fukuda formation in the southwest part. Two faults are considered to run between the two members, which covered with Pleistocene Monomiyama conglomerate. The rocks are pale gray, fine tuffaceous mudstone and sandstone, which contains feldspars, quartz, volcanic glass and its altered clay minerals.

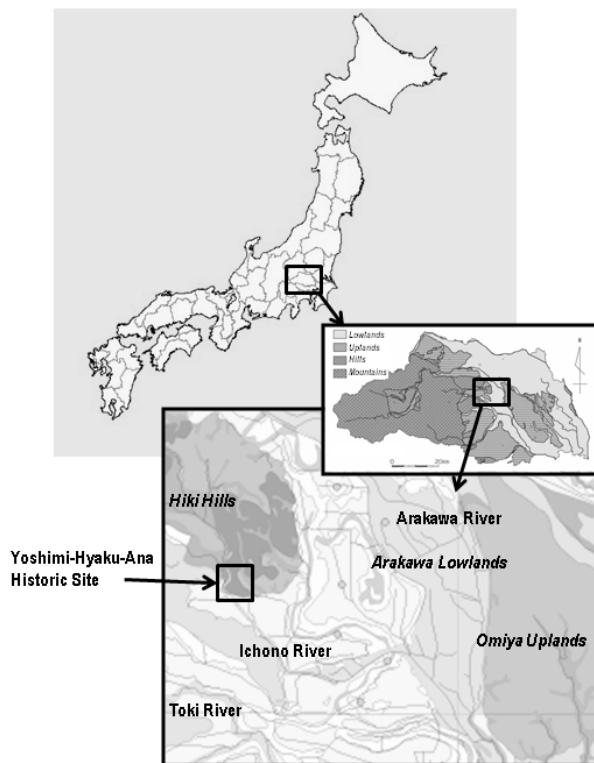


Fig. 1. Location of Yoshimi-Hyaku-Ana Historic Site.

The Yoshimi-Hyaku-Ana historic site is a graveyard of 6 to 7 century, which is one of the national cultural properties in Japan. The numbers of the graves exceed 200 (Kanaidzuka, 1986) and they distribute on the western slope of the Yoshimi Hill. The size of each grave is ca. 4 m in diameter and 2.2 m in height (Fig. 2). The entrance of each grave had a large stones to shut the inside and outside, although they disappeared anymore. At the foot of graveyard, there are larger artificial caves with a size of 4 m diameter. The caves were dug

by Japanese and Korean workers during World War II for purpose of Military use and occupy large areas under the Yoshimi Hill. A small river, Ichino River, flows in the west side of the Yoshimi Hill. The water level is 5 m below the artificial cave floor, and thus the caves have not experienced to be affected by river water.



Fig. 2 Overview of Yoshimi-Hyaku-Ana Historic Site (a) and artificial cave entrance (b).

Salts are observed on the both wall of the graveyards and military cave. However, much salts effloresced on the wall of military cave. Especially near the entrance of the artificial cave, much salt are observed. In the previous literatures, description of the salt efflorescence or evaporates were made (Horiguchi, 1975; Chiba et al., 1975; Kuchitsu and Ozaki, 1999; Horiguchi et al., 2000). Horiguchi et al. (2000) investigated salt types and identified them into alunogen, halotrihite, jarosite and gypsum. Kuchitsu (1999) also detected these minerals and considered the relationships between salt efflorescence and deterioration of the wall. However, these researches are not enough to consider quantitative amount of salt and debris formation.

3. Monitoring of Environmental Conditions

Figure 3 shows the plane map of the military cave. We set the twelve investigation points; Points 1-4 were located along the corridor A, Points 5-8 were located along the corridor B and Points 9-12 were

located the corridor C. The corridor B runs perpendicular to corridors A and C which run straight from two cave entrances to the inside. In each point salt collecting trays with a size of 21×9×3 cm were set and environmental data were collected in nearly one month interval from January 2008 to December 2008 (Jan 22nd, Feb 26th, Mar 27th, May 7th, Jun 6th, Jul 10th, Aug 11th, Sep 16th, Oct 21st, Dec 2nd). Environmental condition such as air temperature, air relative humidity, wall temperature was also measured on each monitoring dates using multi-environmental meter (Nihon Shintech Co. Ltd.; AHLT-100) and infrared thermometer (A&D Co. Ltd.; AD-5613A).

Environmental data are shown in figure 5. In February, temperature of all investigation points of the cave wall showed below 5°C (Fig. 5a). They increased and exceeded 20 °C in August. There were no variation of each point except for spring. Points 1 and 3 showed higher temperature during March to July, which might be caused by sunlight from the west. Air temperature near each point showed similar as wall temperature (Fig. 5b). The values of air temperature were by 2-3°C higher than those of

wall temperature. The reason of low temperature in June was rainy season in Japan. Relative humidity (RH) of each point varied especially in February and September (Fig. 5c). In February, the RH of the Points 1-4 were 38-45%, whereas those of the Points 11 and 12 were more than 60%. The values of points 5-8 showed around 50%. The Points 11 and 12 are close to the entrance 1 which is covered with branches of trees. In June, the RH of all points exceeded 80%. The cave wall contained much moistures and salts at all the investigation points difflorced. The RH decreased in mid summer to autumn. The RH values showed 70-80% in September and 60-70% in October. The variability of RH showed similar to February; Points 1-4 had higher RH, Points 9-12 had lower RH and Points 5-8 had intermediate RH values.

4. Monitoring of Salt Efflorescence and Salt Type Identification

General observation of each point is explained below and the pictures of representative points, Points 2 and 8, are shown in figure 4. Points 1-4 have many salts from December to June. The salts

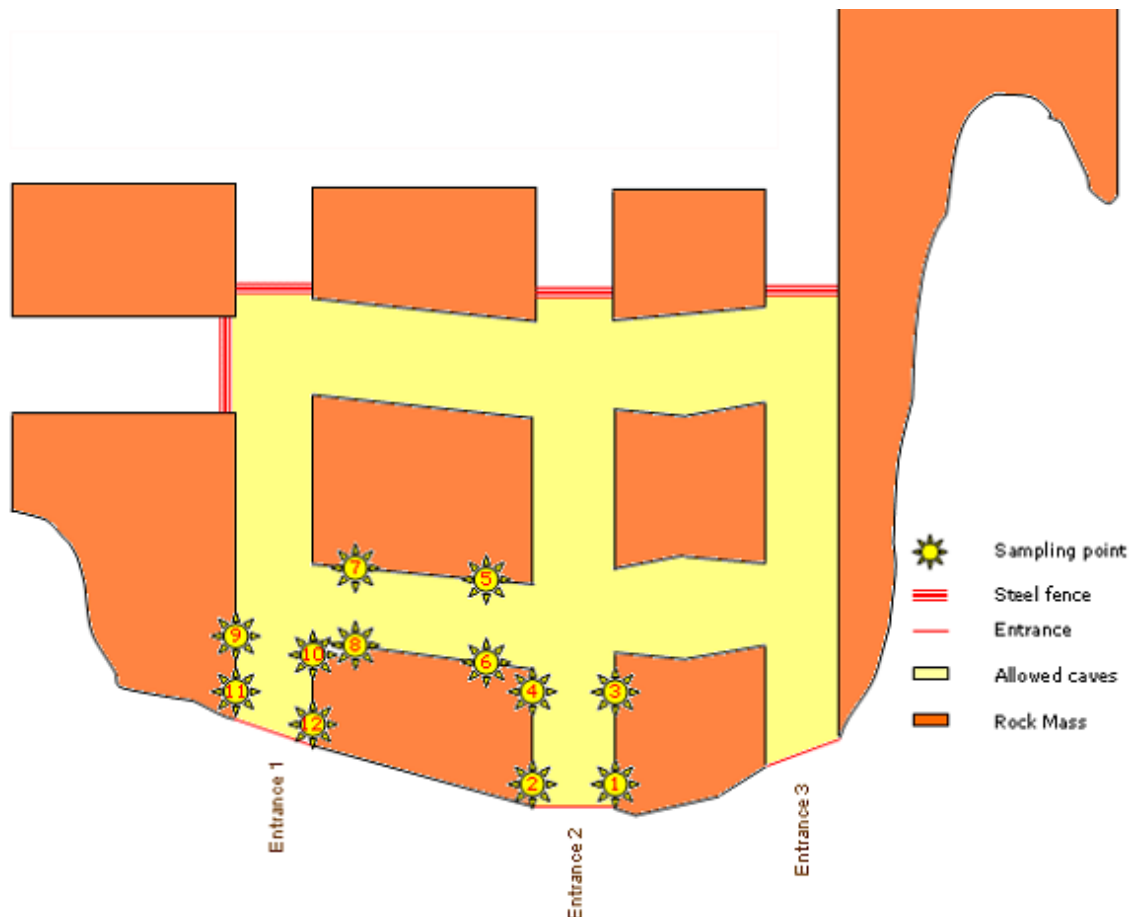


Fig. 3. Plane map of the artificial cave.

are white or yellow and their shapes are bubble scab with a diameter of 3-5 mm. In June the salts contain much moisture and in August most of salts were disappeared. The amounts of salts are larger in Point 2 than those in Point 1. Points 5-8 have less salts than points 1-4 and points 9-12. Changes in salt efflorescence are not clear, however, the amount of salts gradually increase from December to June. Powdery salts are observed in these points. Points locate next corridor to the points 1-4. These points shows intermediate characteristics of points 1-4 and 9-12. Points 11 and 12 are much salt efflorescence than the points 9 and 10.

Salts collected directly from the rock wall at each investigation point. They were identified using X-ray powder diffraction (Rigaku Co. Ltd.; RAD-X system). The operating conditions were X-ray target of $\text{CuK}\alpha$, tube voltage of 40 kV and tube current of 25 mA, scan speed of $2.00^\circ / \text{min}$ and $0.5^\circ - 0.3\text{mm} - 0.5^\circ$ slits.

Results are shown in figure 6. At Point 2, alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) and halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) was detected from January to July, then it disappeared but gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2) and albite ($\text{NaAlSi}_3\text{O}_8$) was identified.



Fig. 4. Salt efflorescence of the rock wall. (a) Point 2 and (b) Point 8.

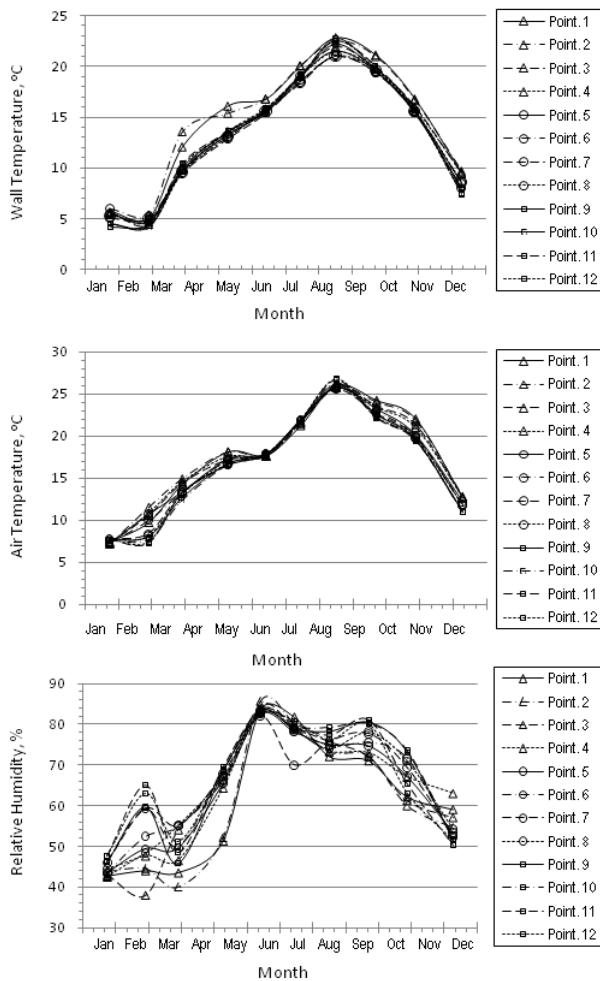


Fig. 5. Environmental condition of the investigation points. (a) Wall temperature, (b) Air temperature and (c) Air relative humidity.

Quartz and albite are originated by rock forming minerals. In December gypsum disappeared and alunogen and halotrichite come again. At Point 8, sodium alum ($\text{NaAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$), halotrichite and small amount of gypsum were detected from January to May. From June to October, jarosite ($\text{KFe}(\text{SO}_4)_2(\text{OH})_6$) and gypsum were dominant accompanied by small amount of quartz and albite. At Point 12, alunogen as well as small amounts of sodium alum and gypsum were detected from January to May. From June to September, gypsum and sodium alum as well as small amount of quartz and albite are identified.

5. Monitoring of Debris Production

Fallen salts and debris were collected using the tray set at each investigation point when every field work made. They were brought to the laboratory and the total weight of salts and debris of each point was measured. Then, the salt and debris were oven dried at 110 °C for 24 hours and weighed

again. After that enough distilled water pored and dissolved the salts. The solution was suction-filtrated using the 0.1µm filter paper and Büchner funnel. Finally, the remains were oven dried at 110 °C for 24 hours and weighed again, resulting net-weight of debris. Figure 7 shows the results. At the Points 1-3, there were much debris in May to August, but the Points 4 had little debris. Points 1 has extremely large amount of debris. Debris fallen in spring (from March to June) contains much moisture, whereas those fallen in summer (June to August) did not contain moisture. The debris amounts of Points 2 and 4 were comparatively stable throughout the year. There are few debris production from the cave wall along Points 2 and 4, whereas there are much debris production from the wall along Points 1 and 3. At Points 5-8, especially Points 6 and 8, had the largest amount of debris than another points. Salt weathering occurred and

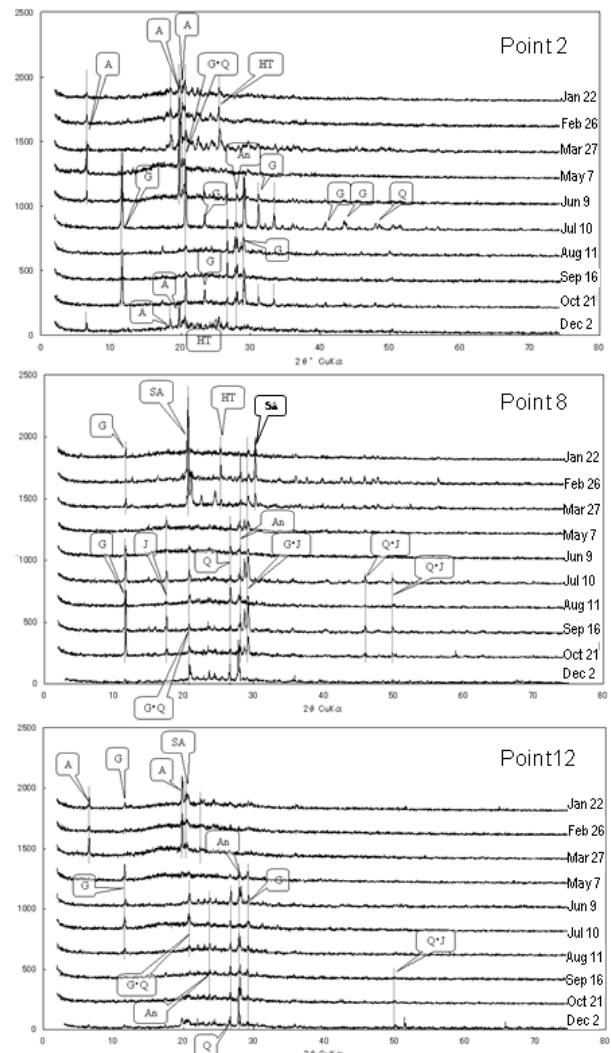


Fig. 6. X-ray diffraction of sampled salts. (a) Point 2, (b) Point 8 and (c) Point 12.

debris production are significant in winter and spring. Until June, they were stopped. The debris were fine powder, which was different from Points 1-4 and Points 9-12. Debris production of Points 9-12 started in the beginning of winter and the maximum production was between winter to spring. Debris were sporadically fell down during summer to autumn.

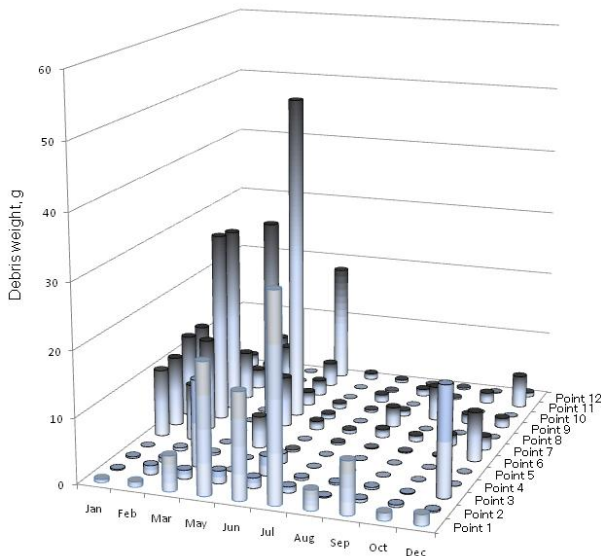


Fig. 7. Seasonal difference of debris production of each investigation point.

6. Discussion

Above these findings, it is confident that there are salt weathering occurred inside the Yoshimi caves, although the process is very slow. The types of salts were different from surrounding environments, reflecting the amount of debris production of each investigation points. There are much salt in humid summer and small amount of salt in dry winter. Especially at the Points 1-4, alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) crystallized from September and the peak period of the crystallization was February. Debris starts falling down from March. Thus, decrease of humidity plays an important role to crystallize of salt minerals and succeeding deflorescence occurred in the high humid season in summer.

Secondary, dominant salt type was different depending on the location of the cave. Points 5-8 are different from Points 1-4 and 9-12. Alunogen are dominant at the former location, whereas halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) and sodium alum ($\text{NaAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$) are dominant at the latter location. The differences of the characteristics of the efflorescence of these salts are that alunogen tends

to appear near the entrance of the cave, whereas the other salts occur at it inside of the cave. Alunogen is considered to prefer dryer condition rather than the other salts. Gypsum also occurred at Points 5-8, which complements to this interpretation.

Considering the relationships between salt type and debris production, there are time-lag when alunogen produce debris. Alunogen keeps itself on the rock wall for a long time, and then it falls down when the RH rise and the rock wall highly moisturized. However, halotrichite and sodium alum do not have time-lag to produce debris. As soon as they crystallize on the rock wall and they break the rock material powdery. In order to elucidate these phenomena, it will be necessary to consider more strict investigation.

According to Nordstrom (1982) compiled aluminium behaviour in natural water and insisted that alunogen are formed by evaporation under the strong acid environment. This assertion indicates that alunogen tends to occur near hot springs or secondary mineralization of mines. Actually the pH paper tests on salt debris solution showed around pH 2. The cave was artificially cut about 60 years ago and since then the direction of ground water movement gather to the tunnel caves.

The formation process of strong acid environment is often considered to be pyrite oxidation. Although pyrite was not detected from the rocks of the cave, pyrite might be contained in the rock mass of Yoshimi Hill, most of which is Miocene tuff and metamorphic rocks. When pyrite oxidizes, it produces much hydrogen ion. The ion has the ability to dissolve most of elements. Thus, water-rock interaction progresses and secondary minerals, salts, are formed. The origin of salts are considered to be cave opening, change in groundwater direction, dissolution and oxidation of pyrite, acid production and salt mineral formation. Salt type differs from its sensitive process of their environmental production, they damage to rocks by salt weathering.

7. Conclusions

Yoshimi-Hyaku-Ana Historic Site is suffering from severe salt weathering. The salts detected were sulphate minerals of alunogen, gypsum, jarosite, halotrichite and sodiumalum. These sulphates effloresced in different environmental conditions. Alunogen prefers to crystallise near the entrance of the artificial cave from dry winter to the

beginning of humid summer, whereas gypsum and sodiumalum prefer to effloresce inside of the cave with little environmental changes in the same season. Halotrichite prefers to crystallise more moisturized environment. These sulphates originated from tuff which contains pyrite that dissolved and produced strong acid. Seasonal debris production of this cave also monitored. Alunogen produced much debris when it disappeared in the beginning of humid summer. However, gypsum and sodiumalum produced powdery debris continuously when they crystallized.

Acknowledgements

We are grateful to Mr. Ota in Yoshimi archaeological centre for allowing us to field work. This study was supported by the Science Research Fund of the JSPS (No. 18680054).

References

- Goudie A. and Viles H., 1997. Salt Weathering Hazards, John Wiley & Sons, Chichester, 241p.
- Horiguchi M., 1975. Geology of Saitama Prefecture. Tsukiji Shokan, Tokyo, 258p (In Japanese).
- Horiguchi T., Nakata M., Shikazono N. and Honma H., 2000. Occurrence and formation process of alunogen and salt accumulation on the surface of tuff in Yoshimi Hills, Saitama Prefecture, Japan. *Journal of the Mineralogical Society of Japan*, 29, 3-16 (In Japanese with English abstract).
- Kanaidzuka R., 1986. Yoshimi no Hyaku Ana. Kyoikusha, Tokyo, 285p (In Japanese).
- Kuchitsu N., 1992. On the evaporites observed in the Museum Meiji-Mura, Aichi Prefecture, Japan. *Journal of Mineralogym Petrology and Economic Geology*, 87, 388-391 (In Japanese with English abstract).
- Kuchitsu N. and Ozaki T., 1999. The evaporates observed at the Yoshimi Caves Historic Site, Japan. *Journal of the Geological Society of Japan*, 105, 266-272 (In Japanese with English abstract).
- Matsumaru K. and Hayashi A., 1980. Neogene Stratigraphy of the eastern marginal areas of Kanto Mountains, Central Japan. *Journal of the Geological Society of Japan*, 86, 4, 225-242. (In Japanese with English abstract)
- Nordstorm D. K., 1982, The effect of sulphate on aluminium concentrations in natural waters: some stability relations in the system $Al_2O_3-SO_3-H_2O$ at 298 K. *Geochemica et Cosmochemica Acta*, 43, 681-692.
- Seki Y. and Sakai H., 1987, Salt crystallization decay of the rock-cliff Buddha sculpture and water-rock interaction at Daifukuji Temple, Tateyama, Chiba central Japan. *The Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists*, 82, 269-279 (In Japanese with English abstract).
- Tiba T., Saito Y. and Matsubara S., 1975. Acid Tuff from Yoshimi Hills, Saitama Prefecture, Japan. *Bulletin of National Science Museum, Series C (Geology)*, 1, 111-117 (In Japanese with English abstract).
- Winkler E. M., 1994, *Stone in Architecture* (Third ed.). Springer Verlag, Berlin, 313p.

