Sulfide Ore Smelting at the Naganobori Copper Mine Recorded on Speleothems from the Ogiri No. 4 Pit on the Akiyoshi-dai Plateau, Yamaguchi, Japan

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(Received on November 30, 2013; accepted on March 3, 2014)

At the Naganobori Copper-Mine site, Akiyoshi-dai, Yamaguchi, southwestern Japan, the mining of copper ores dates back from the end of the 7th century to the beginning of the 8th century. The copper ore smelting was considered to be performed near the mine. Although copper ores in the oxidizing zone should have been used in the early stages, but later the sulfide ores in the enriched and primary zones, it has not yet been clarified as to when the smelting of the sulfide ores was started. The environmental change information for the past two thousand years was extracted from two growing stalagmites in the Ogiri No. 4 pit. Their fluorescent annual microbanding information was used for dating. The sulfate concentration was almost constant from 100 to 1400 A.D., and then clearly increased, suggesting that the extensive smelting of the sulfide ores had started. The concentration gradually increased, reached a maximum in the early stages of the 1700s, and then increased again from 1900. The magnesium concentration changed, almost synchronizing with the sulfate concentration. The possible reduction of the biomass by acid rain or leaching of the magnesium ions from the soil was suggested. The records extracted were in good agreement with those partially extracted from ancient documents, ancient picture maps and topographical maps. The copper used for the Great Buddha of Nara casting has the high possibility of being smelted using copper ores from the oxidizing zone.

KEY WORDS: sulfide ore smelting; acid rain; vegetation change; stalagmite; Naganobori copper mine.

1. Introduction

At the Naganobori Copper-Mine site, Akiyoshi-dai, Yamaguchi, southwestern Japan, the mining of copper ores dates back from the end of the 7th century to the beginning of the 8th century. There are some records that the copper was transported from “Naranobori” to Nara, the town of the emperor of Japan, and used for the Todaiji Great Buddha erection. In this mine site, the excavations have been done from 1989 to 19991) and the area has been designated as one of the Special Historic Sites of Japan in 2003.2) The copper ore smelting was considered to be performed near the mine. Although copper ores in the oxidizing zone should have been used in the early stages, but later using the sulfide ores in the enriched and primary zones, it has not yet been clarified as to when the smelting of the sulfide ores was started. SOx, generated by the smelting of the sulfide zone copper ore, might locally increase the acid precipitation, resulting in the change in vegetation from forest to grassland.

One of the features characteristic of the karst areas is secondary deposits, such as speleothems in the limestone caves. Some of them are found in the natural limestone caves connected to the copper mine tunnels. Especially, the bamboo shoot form speleothem, or stalagmite, offers the potential to recover accurately dated, detailed records of both climatically and anthropogenically driven vegetation changes as far back into prehistory times.3,4) The vegetation change in the Akiyoshi-dai karst plateau, designated as the Akiyoshi-dai Quasi-National Park, could be clarified using the carbon isotope ratios of a stalagmite developed in the grassland area when the yearly burning of the dead grass on the Akiyoshi-dai Plateau started about 400 years ago for agricultural use.5) We now present a chemical approach to interpreting past vegetation changes based upon the plant-derived Mg2+ together with the C isotope ratios and their causes based on sulfide-ore smelting-derived SO42− preserved in the stalag-
mites of the Ogiri No. 4 pit in the Naganobori copper-mine site, Mito, Mine City, and discuss the relation with human activities and the vegetation in this area.

2. Study Area and Sampling

2.1. Geological Setting of the Study Area

The Naganobori Copper Mine is situated at the eastern margin of the Akiyoshi-dai limestone plateau, belonging to the Akiyoshi Terrane (Fig. 1). The terrain is a late Permian accretionary complex in the Inner Zone of Southwest Japan, and the sediments around the Akiyoshi-dai consist of the Carboniferous to Permian Akiyoshi Limestone Group, Tunemori Formation (mainly massive mudstone), and Ota Group (mainly siliciclastics). The mine is composed of Cu skarn deposits associated with the intrusion of the Hananoyama granite porphyry into the Akiyoshi Limestone Group during the late Cretaceous in age. The Hananoyama granite porphyry is a stock that was formed by igneous activities related to an accretion of the Shimanto Terrane from the Cretaceous to Paleogene in age, and is exposed about 500 to 600 meters in diameter around Mt. Hananoyama west of Naganobori. The mine consists of several ore deposits, such as the Eboshi, Hananoyama, Ogiri, etc., and they occur at the contacts between the limestone of the Akiyoshi Limestone Group and slate of the Ota Group, or are embedded in the limestone. Each ore deposit is small-scaled, and forms a lens-shaped or tabular body about 5 to 6 meters wide, 50 to 80 meters long in the strike direction and approximately 130 meters in maximum length in the dip direction. The main ore minerals of the mine are chalcopyrite (CuFeS₂), pyrite (FeS₂), pyrrhotite (Fe₇S₈–FeS) and arsenopyrite (FeAsS), with subordinate amounts of bornite (Cu₅FeS₄), cobaltite (Co₆S₈), sphalerite (ZnS), galena (PbS), and magnetite (Fe₃O₄). As gangue minerals, hedenbergite, garnet, iron wollastonite, quartz, calcite and fluorite also occur.

Oxidations of these primary sulfide minerals by groundwater in the near-surface environment resulted in the secondary enrichment of the primary ore deposits proceeded by the addition of some Cu-bearing secondary minerals, such as native copper, malachite (Cu₂(OH)₂CO₃), cuprite (Cu₂O), azurite (Cu₃(OH)₂(CO₃)₂) and limonite (FeO(OH)·nH₂O). Because these secondary ore minerals are composed of oxides, carbonates and hydroxides, and are distributed near the surface or as cave-filling ore deposits, those were easily mined and refined prior to the mining of the primary sulfide ore deposits during the early stage of the development of the Naganobori Copper Mine.

2.2. Historical Records of the Study Area

In the area 1.6 km EW and 2 km NS, 16 quarries and 13 smelter remains are distributed (Fig. 1(I)). It is still uncertain when Naganobori Mine development was started. The earthenware from the early to middle Yayoi Period (300 B.C. to 250 A.D.) has been excavated from this area, therefore, there is the possibility that the start of the mine devel-

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Fig. 1. Index and geological maps of the Naganobori Copper Mine. I: Index map for ore deposits of the Naganobori Copper Mine. 1: Kayagaba-yama, 2: Ogiri, 3: Hakushiki, 4: Hananoyama, 5: Naganobori (Imori), 6: Eboshi, 7: Oda, 8: Sanjin, 9: Kameyama, 10: Futatsumabu, 11: Tsuzugamori. A–G: Ancient and modern smelting sites. O: Ogiri No.4 pit. II: Geological map and geological cross-section around Mt. Hananoyama. (Online version in color.)
opment dates back to 100 B.C. The 3rd year in Jinki (in 726) is the oldest for the beginning of the Naganobori development at present. Numerous unearthed mokkans (wooden plates for official messages) in the 2nd to 5th years in Tenpyo (in 730–733) showed that the government office, i.e., the “Naganobori Copper Mine office”, prospered in the same period. The Naganobori Mine supplied a large quantity of smelted copper for erection of the Great Buddha of Nara.10) Many archeological studies have clarified that Naganobori Mine was presumed to have been started from the 7th century based on the unearthed Sue-ki (Sue ware, a type of unglazed pottery) which has the form of the end of 7th century. “Rokusyo” (patina), described in “Shoku-Nihongi” (the second of the six classical Japanese history texts) published in the 2nd year of Mommu Tenno (in 698), is also presumed to be collected from the Naganobori Mine.9) The chemical analysis proved that copper and lead collected from the Naganobori Mine were used to make Honcho-Junisen (the twelve coinages minted in Japan) including “Wado Kaichin” (the Japanese first circulated coinage).11) Copper was produced by the smelting of copper ores in an oxidizing zone using circular low-shaft furnaces in this period.12) Archeological records indicate that the Naganobori Mine has been operated for over 200 years from the end of 7th century.10) The “Nagato-koku copper mine” referred in the historical record in the 5th year of Jogan (in 863) is presumed to be the Naganobori Mine.

The copper smelting was stopped at the Naganobori Mine in the 11th–12th centuries. It was restarted from the Muromachi Period in the 15th century, and the site was moved to the entrance of the Ogiri-dani valley area. The oxidizing smelting of copper sulfide ores should have been done in this period, because a small blast furnace made in the ground and platy smelting slag were unearthed. The Yamaguchi Kokushoji Temple, referenced in an old document, is presumed to participate in the copper smelting at Naganobori Mine. The Ouchi and Mori Families also participated in the smelting in the 16th century.

The mine development prospered by the Mori Family in the 17th century, accordingly the Naganobori Mine became the leading copper mine in the Yamaguchi area.13) The Naganobori Mine was changed to private management in 1637, managed by the merchants from Kyoto and Osaka. Speiss production was increased in the Hakusan and Kitabirayama areas from 1727. The mining was stopped in this area at the end of the 18th century. The Naganobori Mine has been redeveloped by modern technology in the 1880s. The Hananoyama smelter site was established in the 38th year in Meiji (in 1905). The copper production output was 18 tons in 1906, 129 tons in 1908, and 142 tons in 1912. The copper mining continued until 1960. The Naganobori Mine was closed in 1962 as ground water filled the gallery and the shaft.

2.3. Collection of Stalagmite Samples

The Naganobori copper mine was working along the small valley of Ogiri-dani and around Mt. Kayagaba-yama, the upper hill of Ogiri-dani, from the Nara period (710–794) to the Heian period (794–1185). The pith mouths currently called the Takinoshita and Ogiri mining remains were distributed around the southern side of the ridge extending northeastward of Mt. Kayagaba-yama, and one of them is the Ogiri No. 4 pit, where a part of the limestone cave serves as a mining tunnel. The surface is covered by a groove of mixed trees and partially by an artificial plantation of cedar. Two growing stalagmite samples were collected at the deepest part 50 m from the entrance. One of them is a 21-cm tall O-1 stalagmite (Figs. 2(a), 2(b)). A clear black layer existed 23.80–24.55 mm from the top of the growing part, and this part is considered to have grown later. The point of the drip water may have been artificially changed. The other sample was located 1 m from the O-1 stalagmite and is 15-cm long (Fig. 2(c)). The position of the drip water has been unchanged and therefore there was no discontinuity.

2.4. Collection of Drip Water Sample

The drip water at the site O-1 was collected using a 20 L polyethylene tank. The field measurements and water treatments were done in similar ways as already mentioned.14,15)

![Fig. 2. Examined stalagmite samples collected from the Ogiri No. 4 pit. (a) Growing stalagmites before collecting samples. (b) Cross-section of the O-1 stalagmite, showing the clear hiatus. (c) Cross-section of the O-2 stalagmite. (Online version in color.)](image-url)
3. Analytical Procedures

3.1. Chemical Analysis of Water

All chemicals were of analytical grade. Deionized water prepared by a Milli-Q SP system (Millipore) was used throughout. The Mg$^{2+}$ and Ca$^{2+}$ concentrations in the water were determined by atomic absorption spectrophotometry (AA-7000, Shimadzu, Kyoto). The Cl$^{-}$ and SO$_4^{2-}$ concentrations were determined by ion chromatography (ICS-90, Dionex, Sunnyvale, USA). The alkalinity was determined by titration and the equivalent points were detected by the Gran method. The reproducibility of the measurements had a relative standard deviation within 2%. The chemical equilibrium calculations for the CaCO$_3$–H$_2$O–CO$_2$ system were performed using the computer program PHREEQC.

3.2. Chemical Analysis of Stalagmites

For the extraction of sulfate ion from the carbonate fraction, the carbonate samples were dissolved in water using an H$^+$ type cation-exchange resin. A weak-acid H$^+$ type cation-exchange resin (Muromac MAC-3, Muromachi Technos, Tokyo) was used. The sulfate ion concentration was determined by ion chromatography using the ICS-90 instrument from Dionex. The reproducibility of the measurements had a relative standard deviation within 5%. The cations in the carbonate fraction were analyzed after dissolving the stalagmite samples with acetic acid. The calcium and magnesium concentrations were determined by atomic absorption spectrophotometry in a way similar to that mentioned above, the strontium concentration by ICP-MS using a 7500 cx Agilent instrument at the Kyushu Environment Evaluation Association. The reproducibility of the measurements had a relative standard deviation within 2%.

3.3. Stable Isotope Composition Analysis

The carbon isotope compositions were determined by an IRMS mass spectrometer (Finnigan MAT DeltaS) at Tohoku University. The carbon isotope compositions are given as δ values in parts per thousand relative to the VPDB international reference material in the delta notation. The analytical precision for δ$^{13}$C was ±0.1‰.

3.4. Determination of Average Growth Rates of Stalagmites

The seasonal concentration variation of fulvic acids, a type of humic substance, can form annual fluorescence bandings in the stalagmites. The fluorescence intensities of the stalagmite sample were observed in similar ways as already mentioned.

4. Results and Discussion

4.1. Average Growth Rates of the Stalagmites

The annual banding could be clearly observed in the stalagmites from the studied caves. The distribution of the annual banding widths was almost constant everywhere for the stalagmites. The average annual growth rates were determined to be 38 μm/y for the O-1 stalagmite, and 40 μm/y for the O-2 stalagmite.

In the case of the O-1 stalagmite, there was a black layer, and the stalagmite continued to grow on it (Fig. 2(b)). The average growth rate showed that the stalagmite began to newly grow on the black layer around A.D. 1390 and recorded environmental information for the recent 620 years. The reason for the change in the growing point is not clear but might be due to human activities because the copper smelting started again in the 15th century, once disrupted in the Heian period. The other stalagmite sample (O-2) was found to record environmental information for the past 2000 years (Fig. 2(c)).

4.2. Stable Carbon Isotope Ratio

It has been reported that the stable carbon isotope ratio of C3 plants that grow in a forest (e.g., trees and most shrubs) is ~−32 to −22‰, and that of the C4 plants, such as Miscanthus sinensis and Cyperus microiria that grow in grasslands, is −16 to −10‰. The average value of the carbon isotope ratio of plants and that of carbonate (δ$^{13}$C = +2.7 ± 1.0‰ for Akiyoshi Limestone) were recorded in the stalagmites. Therefore, the variations in δ$^{13}$C of the speleothems can be used to reflect changes in the nature and extent of the vegetation cover, because the carbon of HCO$_3^−$ ions produced by the dissolution is supplied from CaCO$_3$ and CO$_2$. The isotopic fractionation when a stalagmite precipitates from drip water containing HCO$_3^−$ is about +3‰, and therefore, the forest vegetation shows −12 to −7‰, while the grassland vegetation is −4 to −1‰ in the stalagmite.

The stable carbon isotope ratios of the O-1 stalagmite for the past 620 years are shown in Fig. 3(A). From the top, the δ$^{13}$C values significantly increased from −4.1‰ to +0.6‰, and then decreased from −1.0‰ to −6.2‰. Just above the black layer at 23.80 mm from the top, the δ$^{13}$C value was −1.9‰. On the contrary, at 24.55 mm and below the hiatus, the ratio was −11.1‰, which is not shown in Fig. 3. The drip water forming the stalagmite was fed from a hillside area. Over 620 years ago, the stable carbon isotope ratio of −11.1‰ revealed forest vegetation. At the beginning of the 1400s, the stable carbon isotope ratio was high (δ$^{13}$C = −2‰), suggesting a drastic change in the grassland vegetation probably due to local acid deposition of SOx produced by the sulfide ore smelting. It was suggested that at that time the surface had been covered by grass around Mt. Kayagabayama, the upper hill of the Ogiri-dani valley. This value then started to decrease, which might suggest the gradual recovery of the forest until the late 1800s. However, the variation in the sulfate did not support this, which will be discussed later. It was found that Pleioblastus chino var. viridis, characteristic of grassland, is one of the C3 plants. Miscanthus sinensis grasslands can be dominated by dwarf bamboo, such as Pleioblastus chino var. viridis, because dwarf bamboo can extensively grow by receiving its nutrient supply through rhizomes and overwhelm the Miscanthus sinensis. Therefore, the vegetation may have been grassland predominant with Pleioblastus chino var. viridis, which is the vegetation characteristic to that of the present Akiyoshi-dai Plateau. As mentioned above, since Pleioblastus chino var. viridis, which represents a grassland together with Miscanthus sinensis, is a C3 plant, it does not become a necessary and sufficient condition which presumes grassland vegetation only by a stable carbon isotope ratio, but the higher isotope ratio in the second half of the 18th century may be ascribed to the recovery of the vegetation predomi-
nant with C3 because the copper mine was closed. The stable carbon isotope ratio became high again from the middle of the 19th century, the time of the copper mine redevelopment and the resulting extensive copper ore smelting in the Meiji Era, suggesting the vegetation change from a forest to grassland predominant in Miscanthus sinensis. The recent stable carbon isotope ratio reflects the present forest vegetation.

On the other hand, from the O-2 stalagmite, it was possible to read the record for about 2000 years. As shown in Fig. 3(B), the stable carbon isotope ratio of around −9‰ revealed forest vegetation. The O-2 stalagmite had been grown near the O-1 stalagmite (about 1 m in distance), but the recorded information is somewhat different. The catchment areas of the two drip waters may be somewhat different depending on the geological and topographic situation. As discussed later, the vegetation may have been changed from forest to grassland predominant with Pleioblastus chino var. viridis, but it is difficult to estimate the time of the vegetation change.

4.3. Trace Constituent Contents in the Stalagmites

Ichikuni reported the relationship between the trace constituent contents of the terrestrial carbonate and those of the corresponding mother liquid.33 When a stalagmite grows as a result of calcite precipitation, the ions contained in the drip water coprecipitate. A SO\textsubscript{4}\textsuperscript{2−} ion is substituted for a CO\textsubscript{3}\textsuperscript{2−} ion during the precipitation process of calcite according to the ion-exchange equilibrium as follows:34,35

\[
\text{SO}_4^{2−}(aq) + \text{CO}_3^{2−}(s) ⇌ \text{CO}_3^{2−}(aq) + \text{SO}_4^{2−}(s) \quad (1)
\]

where \(D_{SO4}\) is a distribution coefficient expressed by the activity ratios in the solid and solution phases. The seasonal changes in the chemical properties of the drip water of the O-1 stalagmite, shown in Table 1, were relatively small and therefore \(D_{SO4}\) was calculated to be 3.4 \times 10\textsuperscript{−5} using PHREEQC\textsuperscript{17} and the average analytical values in Table 1. This value was in fairly good agreement with that obtained for the stalagmites from Saikai City, Nagasaki Prefecture,36 (5.2 \pm 2.0) \times 10\textsuperscript{−5}, suggesting that the sulfate in the stalagmite was coprecipitated according to the ion-exchange equi-

\[
D_{SO4} = \left(\frac{\text{SO}_4^{2−}}{\text{CO}_3^{2−}}\right)_s / \left(\frac{\text{SO}_4^{2−}}{\text{CO}_3^{2−}}\right)_\text{aq} \quad (2)
\]

![Fig. 3. Variation in δ\textsuperscript{13}C and the trace constituents. (A) O-1 stalagmite, (B) O-2 stalagmite.](image)
librium. In this study, we introduced $D^a_{SO_4}$ proposed by Takano et al., as follows:

$$D^a_{SO_4} = \left(\frac{\text{SO}_4^{2-} \, \text{mole fraction}}{\left[ \left( \frac{\text{SO}_4^{2-}}{\text{HCO}_3^-} \right)_{aq} \right]} \right) \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

As shown in Table 1, the pH and temperature of the drip water were almost constant, and therefore, the $D^a_{SO_4}$ values can be a measure of the past sulfate concentrations in the drip waters. The $D^a_{SO_4}$ was determined to be 0.0045 for the O-1 stalagmite, which enabled us to estimate the past SO$_4^{2-}$ concentrations of the drip water (Fig. 3(A)). A drastic change in the SO$_4^{2-}$ concentration was observed. In this area, the source of Cl$^-$ in the drip water is considered to be sea salt, and the SO$_4^{2-}$ concentration derived from sea salt [ss-SO$_4^{2-}$] was calculated to be 1.5 mg/L based on the Cl$^-$ concentration in Table 1 as follows:

$$[\text{ss-SO}_4^{2-}] = [\text{Cl}^-] \times \left(\frac{[\text{SO}_4^{2-}]_{aq}}{[\text{Cl}^-]_{aq}}\right) \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

where [Cl$^-$]$_{asc}$ = 19.4 g/kg and [SO$_4^{2-}$]$_{asc}$ = 2.7 g/kg. Throughout the examined period, the SO$_4^{2-}$ concentration was fairly higher than [ss-SO$_4^{2-}$] = 1.5 mg/L, suggesting the constant but small contribution of the natural oxidation of the sulfide ores. In addition, it was found that the calculated SO$_4^{2-}$ concentration of the past drip water had increased in the 15th century. An unusually high SO$_4^{2-}$ concentration was recorded around the 17th century. According to excavated historical records and/or the ancient documents, the Mori Clan focused on mine development in the 17th century, and then the mine was closed again in the second half of the 18th century. The highest SO$_4^{2-}$ concentration was observed from the 17th century to the beginning of the 18th century, suggesting that the sulfide ores were extensively used for the smelting. The following decrease in the SO$_4^{2-}$ concentration was due to the close of the mine. The increase in the sulfate concentration by redevelopment using modern technology from the beginning to the middle of the 20th century is clearly recorded. At present, acid deposition by long distance transport from East Asia cannot be ignored.

When calcium carbonate precipitates, divalent cations in the drip water are also taken into the calcite lattice by ion-exchange. The ion-exchange equilibrium of Ca$^{2+}$ and Mg$^{2+}$ is expressed as follows:\cite{33,39}

$$M^{2+}(aq) + Ca^{2+}(s) \rightleftharpoons Ca^{2+}(aq) + M^{2+}(s) \ldots \ldots \ldots \ldots (5)$$

$$D_M = \left(\frac{M^{2+} / Ca^{2+}}{\left[ M^{2+} / Ca^{2+} \right]_{aq}} \right) \ldots \ldots \ldots \ldots (6)$$

where $D_M$ is the distribution coefficient expressed by the activity ratios in the solid and solution phases. In the case of Mg$^{2+}$ ion, the value of 0.032 was obtained using the Mg$^{2+}$ content at the surface of the O-1 stalagmite and the average values of the drip water (Table 1), and was in fairly good agreement with the values for the stalagmites from Saikai City, Nagasaki Prefecture,\cite{15} suggesting that Mg$^{2+}$ in the stalagmite was coprecipitated according to the ion-exchange equilibrium and recorded the Mg$^{2+}$ concentration in the past drip water. Under a climax condition, it can be expected that the amount of Mg$^{2+}$ supplied by the fallout and chemical weathering is equal to that removed by the runoff, i.e., the Mg budget is balanced, as in the similar case for phosphate.\cite{56} However, the Mg$^{2+}$ concentration of the drip water will change with the biomass variation because the chlorophyll of plants is a Mg$^{2+}$ complex. The change in the (Mg$^{2+}$/Ca$^{2+}$) molar ratio of the stalagmite can be a measure of that in the biomass and does not include the effect of the chemical weathering of limestone. Sr$^{2+}$ is also expected to be coprecipitated in the calcite according to the ion-exchange equilibrium. The $D_{Sr}$ value is almost similar to that of $D_{Mg}$.\cite{30} The average contents of Mg$^{2+}$ and Sr$^{2+}$ of Akiyoshi Limestone are 1810 and 182 mg/kg, respectively,\cite{37} and the chemical weathering of the limestone will give Mg$^{2+}$ and Sr$^{2+}$ with the same (M$^{2+}$/Ca$^{2+}$) ratios in the drip water. The average weight ratio of (Sr$^{2+}$/Mg$^{2+}$) of living plants is reported to be about 35.\cite{38} The change in biomass will give a constant value of (Sr$^{2+}$/Mg$^{2+}$) if the source of Mg$^{2+}$ and Sr$^{2+}$ is plants. The concentrations of Sr$^{2+}$ gradually increased from around 1400, giving maximum around 1770, then decreased afterwards; the (Sr$^{2+}$/Mg$^{2+}$) ratio was not constant, and therefore the source of Sr may not be the same as that of Mg. The mineral quantities weathered in the soil might increase due to acidification of the soil. Afterwards, the low SO$_4^{2-}$ concentrations suggested that the acidification of the soil was suppressed. Figure 3(B) shows the sulfate concentration in the O-2 stalagmite for about the past 2000 years; from 100 to 1400 A.D., the fluctuation in the sulfate concentration was low and the concentration was almost the same as the lowest value of the O-1 stalagmite. The sulfate concentration has significantly increased from the 15th century, suggesting the extensive smelting of copper ores in the sulfide zone. The sulfate concentration was then reduced after reaching a peak in the early 1700s, but increased again from 1900. As shown in Fig. 3(B), the Mg$^{2+}$ concentrations varied in the 12th century parallel to those of SO$_4^{2-}$, and then started to increase in the 15th century. Recent drastic increases in the SO$_4^{2-}$ and Mg$^{2+}$ are greater than those for the O-1 stalagmite, probably due to the differences in the catchment areas of the two stalagmites. Although the $\delta^{34}$C values were almost constant, such high concentrations of SO$_4^{2-}$ and Mg$^{2+}$ should show the vegetation change from the forest to grassland and therefore the vegetation may have been changed from forest to grassland predominant with the C3 plant Pleioblastus chino var. viridis. The recent decreases in the SO$_4^{2-}$ and Mg$^{2+}$ concentrations reflect the present forest vegetation.

5. Reconstruction of Acid Deposition and Vegetation Records Extracted from the Stalagmites, Ancient Documents, Old Picture Maps and Others

According to pollen analysis,\cite{39} the Ogiri-dani valley was surrounded by warm-temperate forest mainly composed of Quercus subgenus Cyclobalanopsis, before the start of the Naganobori Mine development in the 8th century. After the operation of Naganobori Mine, Pinus started to increase and Q. subgenus Cyclobalanopsis decreased. However, Quercus subgenus Cyclobalanopsis was continuously used as a fuel-wood forest, because its pollen fraction remained high (>50%). Pinus pollen fraction increased to an extremely high extent since the Edo Period. Gramineae, Artemisia and Stellaria fractions also increased at the same time. These increases of light-demanding species indicate clear-cut of Q. subgenus Cyclobalanopsis and significant opening up of the landscape in the surrounding area. The uppermost sediment layers are characterized by a rapid increase in Cryptomeria.
Table 2. Summary of environmental change records extracted from the stalagmites, ancient documents, old picture maps, and topographical maps.

| Time Period | Historical Record | Description |
|-------------|-------------------|-------------|
| 1605        | province map of Nagato | Grassland was drawn around Naganobori Mine. |
| 1649        | province map and cadastral record of Nagato | Grassland was drawn around Naganobori village in pictorial map. Naganobori-dozan (Naganobori Copper Mine) was described as kusayama (grass mountains) in cadastral record. |
| 1729        | map and report of Naganobori village | Three feudal forests composed of pine trees were established in Naganobori village. Precinct forests were established around shrines and temples. Grasslands were distributed around Ogiri copper-mine. |
| 1755        | feudal forests cadastre | Kudarihayama replaced Kameyama as feudal forest. |
| 1802        | village map of Naganobori | Lots of tress in Kanbayama feudal forest were cut to make charcoal and construction material for mining at Kitabira, Hakusan, and Hamanomiyu mines. |
| 1862        | village map of Naganobori | Three feudal forests were established in Naganobori village. Private forests were distributed in the eastern part of Naganobori village and on the steep slopes developed surrounding the Akiyoshi-dai plateau. Grasslands were distributed around Ogiri Copper Mine. |
| 1860s-1880s | Mine county map | Feudal and private forests were distributed in the eastern part of Naganobori village. Grasslands were distributed on the Akiyoshi-dai plateau. |
| 1902        | 1:20 000 topographic map of Ohda | Forests including bamboo were distributed on the slopes along lowland. Grasslands were distributed around Ogiri Copper Mine and the gentle slopes on mountain ridge. |

![Fig. 4](Image). Relationship between the change in SO$_4^{2-}$ contents in the O-1 and O-2 stalagmites and the history of the Naganobori Copper Mine. Change in the SO$_4^{2-}$ contents: +, <10 mg/kg; ++, 10–103 mg/kg; ++++, >30 mg/kg. History of the Naganobori Copper Mine: [1] 11–12C, temporarily closed; [2] late 14C–early 15C, restarted; [3] 16C, under the management by the Ouchi and Mori Families; [4] late 16C, decline due to the development of the Iwami Silver Mine; [5] early 17C, under the direct management by the Choshu clan; [6] 1637, eruption of veins of water; [7] late 17C, restarted under private management; [8] early 18C, temporarily closed; [9] middle to late 18C, lead smelting at Kitabira 2 km northwest; [10] 19C, continued to be temporarily closed; [11] 1905, opening of the Hananoyama smelting site; [12] 1960, closed.

pollen, showing that Cryptomeria has been planted to the abandoned grasslands and the clear cutting sites since the Meiji Period.

Landscape patterns since the Edo period were reconstructed around Naganobori Village using historical maps and documents (Table 2). In the province map prepared in 1605, Naganobori-yama (Naganobori Mine) was drawn as grassland-like. In the province map and its accompanying cadastral record submitted to the Bakufu at Edo in 1649, the Akiyoshi-dai Plateau and the area around Naganobori was described as kusayama (grass mountains). The first maps where grasslands on the Akiyoshi-dai Plateau could be precisely identified in spatial terms were the village pictorial maps in 1729. Grasslands were widely distributed on the plateau including the area around the Ogiri-dani valley, while wooded areas for feudal, common and private forests were located on the steep slopes developed on surrounding the plateau and the side of the mountain in the eastern and southern parts of Naganobori Village. The feudal forests were logged for mining purposes during the 18th century.

Grassland on the plateau had become a key source of grass as an organic fertilizer for cultivated lands during the Edo period. The increased use in fossil fuels and chemical fertilizers since the 19th century caused gradual changes in vegetation patterns from grassland to forest.

Figure 4 shows the relationship between the change in the SO$_4^{2-}$ contents in the O-1 and O-2 stalagmites and the history of the Naganobori Copper Mine. Except for the increase in the late 13th century, almost all changes were in fairly good agreement with the information from the historical sources. At present, the reason for the increase in the late 13th century is unclear. The O-1 stalagmite recorded only C3 vegetation at this time, while C4 vegetation might have been severe. Unfortunately, we could not extract information about the vegetation older than the 14th century, because the O-2 stalagmite recorded only C3
plants throughout the 2000 years. The vegetation should have been changed from forest to grassland. The increase in \( \text{SO}_4^{2-} \) and \( \text{Mg}^{2+} \) concentrations of the stalagmites started in the 14th century, suggesting that the vegetation may have been changed from forest to grassland at that time. The recent decreases in \( \text{SO}_4^{2-} \) and \( \text{Mg}^{2+} \) concentrations reflect the present forest vegetation.

6. Conclusion

The surface around the Ogiri No. 4 pit is a forest now, but it has been determined that the forest might have disappeared due to acid rain in the past. Information from historical sources, such as historical records and ancient documents, was in good agreement with that extracted from the stalagmites. According to the picture map drawn in 1605, Naganobori was depicted as a grassland in the early Edo period. Different from other areas of the Akiyoshi-dai Plateau, the deforestation might be due to local acid rain caused by sulfide-ore smelting rather than set aside for grassland by burning. The older information about vegetation is unavailable from historical materials, but we can conclude that the copper used for the Great Buddha of Nara casting has the oxidizing zone in the 8th century.

Acknowledgments

We thank Ms. Mai Tomita, Mr. Kouki Sonoyama, Ms. Masami Aoki of Kyushu University and Ms. Miho Masaki of Kumamoto University for using these data in their MS or BS theses. We are also grateful to Professor Eiji Izawa of Kyushu University for his valuable suggestions and critical reading of the manuscript. This study was partially supported by Grants-in-Aid for Scientific Research (B), no. 19310011 for K. Y. (2007–2009) and no. 22310011 for K. Y. (2010–2012), from the Japan Society for the Promotion of Science.

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