



Anthropogenic impact records of nature for past hundred years extracted from stalagmites in caves found in the Nanatsugama Sandstone Formation, Saikai, Southwestern Japan

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ABSTRACT

In the Nanatsugama area, Saikai City, Nagasaki Prefecture, Japan, covered by Paleogene calcareous sandstone, the environmental change information for the past hundred years was extracted from growing stalagmites in two limestone caves. Their annual microbanding information was used for dating. From the Shimizu-do Cave stalagmites, the vegetation change from forest to grassland during 1500 to 1700 could be read using the carbon isotope and Mg/Ca ratios of the stalagmites. Before 1500, the stable carbon isotope ratios ranged from -9 to -10‰ , which are characteristic of forest vegetation. From 1600 to 1700, the stable carbon isotope ratio increased ($\delta^{13}\text{C} = -2\text{‰}$), suggesting a drastic change to grassland vegetation probably for the purpose of collecting grasses for agricultural use. The increase in Mg/Ca due to the reduction in the biomass from 1500 to 1700 also showed the vegetation change from forest to grassland. A Ryuo-do Cave stalagmite recorded the change in the SO_4^{2-} concentration several times during the period from 1600 to 1900. In addition to the sulfate of sea salt origin, the higher concentration and smaller $\delta^{34}\text{S}$ of sulfate in the Ryuo-do Cave drip water compared to those in the Shimizu-do Cave drip water may be due to the oxidation of biogenic pyrite in the marine Kamashikiyama Tuff Formation, which covers the calcareous sandstone of the Nanatsugama Sandstone Formation. The oxidation of pyrite is promoted by the biological activity of sulfur-oxidizing bacteria under oxic conditions, indicating that the surface cover was repeatedly changed into non-paddy fields. The change in the SO_4^{2-} concentration could then be related to the changes in the amount of the Nagasaki Prefecture coal production in the early 20th century and the China fossil fuel consumption in the late 20th century transported a long-distance by a monsoon from the China continent. Thus, the combination of annual microbanding information and the Mg^{2+} and SO_4^{2-} concentrations and C and S stable isotope ratios of the stalagmites made it possible to extract local and/or global anthropogenic environmental changes in nature. The records extracted in this way were in good agreement with those partially extracted from ancient documents, ancient picture maps and topographical maps.

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1. Introduction

Humans have built a symbiotic relationship with nature since early times. However, when the population explosively increased with the development of food production, the impact sometimes exceeded the environmental self-reproduction ability of nature. The relationship

between past human populations and their natural environments is one of the major concerns in environmental science, being central to issues such as the spread of agriculture. The paleoenvironmental information from ancient times to the present can help us to understand the relationship between the natural environment and human impact.

One of the features characteristic of the karst areas is secondary deposits, such as speleothems in limestone caves. 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 far back into prehistory. The mechanism of deposition provides an intimate link to the surrounding

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environment and climate as the drip-water also carries chemical signals derived from the overlying soil (Fairchild et al., 2006; Ford and Williams, 2007).

Studies carried out during the past decade showed that $\delta^{18}\text{O}$ in the stalagmites grown in monsoonal areas chiefly reflected the monsoonal variability; $\delta^{18}\text{O}$ becomes lighter as the summer monsoon strengthens. In China, Wang et al. (2001) found a correspondence with Heinrich events (massive iceberg discharges in the North Atlantic). The $\delta^{13}\text{C}$ of the organics-derived soil CO_2 is affected by the relative abundance of the local C3 and C4 plants. The C3 plants (e.g., trees and most shrubs) that flourished under a wet/cool climate generally have $\delta^{13}\text{C}$ values of -32 to -22% , whereas the more heat- and drought-resistant C4 plants (e.g., maize, sorghum and prairie grass) have $\delta^{13}\text{C}$ values of -16 to -10% (Deines, 1980; Cerling, 1984). Therefore, the variations in $\delta^{13}\text{C}$ of the speleothems can be used to reflect changes in the nature and extent of the vegetation cover (Dorale et al., 1998; Hellstrom et al., 1998; Genty et al., 2003; Denniston et al., 2007). The vegetation change in the Akiyoshi-dai karst plateau, southwestern Japan, could be clarified using the carbon isotope ratios of a stalagmite developed in the grassland area that the yearly burning of the dead grass on the Akiyoshi-dai Plateau started about 400 years ago for agricultural use (Kurisaki et al., 2006).

Paleoenvironmental information can also be extracted using the trace components in the speleothems. When growth banding can be seen either optically or in the luminescence spectra or both, there is usually a correlative periodicity in some of the trace-element distributions (Huang et al., 2001). It was found that the changes in the Mg/Ca and Sr/Ca ratios were related to those in precipitation (Roberts et al., 1998; Fairchild et al., 2000; McDonald et al., 2004). On the other hand, speleothems also provide a local archive of atmospheric deposition and frequently contain appreciable concentrations of sulfur as sulfate which may reflect sulfur loading in the atmosphere (Frisia et al., 2005; Wynn et al., 2010).

In this study, we focused on the calcareous sandstone area, Saikai City, Nagasaki Prefecture, southwestern Japan. According to a picture map drawn in the 1700s during the Edo period, the predominant vegetation was pine forests around one of the caves. However, it is now covered with broad-leaf trees, and the pine forests have disappeared. We now present a chemical approach to interpreting past vegetation changes based upon the plant-derived Mg together with C isotope ratios and land use changes based upon the biogenic pyrite-derived sulfate preserved in the stalagmites, and discuss the relation with human activities and the land use in this area.

2. Study area and sampling

2.1. Study area

The calcareous sandstone of the Paleogene Nanatsugama Sandstone Formation, Nishisonogi Group, is distributed in Saikai City, Nagasaki Prefecture. The calcareous sandstone is shallow marine sandstones bearing frequent limestone beds dominated by Rodolith (non-geniculate coralline algae) (Fig. 1), and has near-horizontal bedding. The average carbonate content is about 50% (51.3% CaCO_3 and 0.6% MgCO_3), ranging from 30 to 80% (unpublished data). Most of the distributional area has been designated as one of the natural treasures of Japan in 1936 (Agency for Cultural Affairs, Japan, 2012). The natural entrance of the Shimizu-do Cave is located on the left bank of a valley carved by the Egouchi River, and near the small alluvial plain in the valley at a meeting point of the Shimizu River. The total length of the Shimizu-do Cave is about 1670 m, and a part of this cave is open for sightseeing. The Ryuo-do Cave is located on the hill slope where the calcareous sandstone is unconformably overlain by Kamashikiyama Tuff and Kamashikiyama Alternation Formations (Inoue, 1963). The total length of the Ryuo-do Cave is about 2020 m. The Kamashikiyama Tuff is a geological formation name and does not contain tuff beds in

this area (but the type locality of the formation has some acidic tuff beds). The formation is composed of shallow marine deposits bearing tuffaceous sandstones with trough-cross bedding and fossils of bivalves, and probably with biogenic pyrite. These formations are distributed around the top of the hills. Above the stalagmite collection site in the Ryuo-do Cave, the tourist park called Saikai Rakuen was constructed in 1989, but is now closed.

2.2. Collection of precipitation samples

We placed two automatic rain gauges (RG3-M, Onset, Bourne, USA) and the equipment for total fallout collection at the open site near the exit of the Shimizu-do Cave (Fig. 1, SR) and at a site in the rice fields located in the upper Shimizu River basin (Fig. 1, NR). The total fallout was collected in a 20 dm³ polyethylene tank at least once every season. At the sites, the water temperature and pH were measured using a pH/conductivity meter (WM-22EP, TOA, Kobe). The water samples were filtered through 0.45 μm membrane filters (Advantec, Tokyo, 25 mm in diameter), and stored in 30 cm³ polypropylene bottles. Sulfate ions in the water were concentrated using an anion-exchange column (Econo-Pac disposable chromatography column, 1.5 cm i.d., 12 cm long, Bio-Rad, Hercules, CA, USA) packed with 10 cm³ of Muromac AG 1-X4-Cl⁻ (50–100 mesh; Muromachi Technos, Tokyo). About 5 dm³ of water sample was flowed through the column and then the adsorbed sulfate was desorbed with 10 cm³ of 1 mol dm⁻³ NaNO_3 . The sulfate was recovered as barium sulfate by adding barium chloride, and the precipitate was provided for analysis of the ³⁴S/³²S isotope ratio.

2.3. Collection of drip water samples

In the Shimizu-do Cave and Ryuo-do Cave, the drip waters were collected using 20 dm³ polyethylene tanks. The field measurements and water treatments were done in similar ways as already mentioned. In order to collect the dissolved inorganic carbon in water at the sites, the filtered sample was mixed with a 10 cm³ saturated barium hydroxide solution in a 100 cm³ polyethylene bottle. The barium carbonate precipitates were filtered, washed with water and dried at 80 °C in the shortest possible time, and then stored in a vial with a screw cap. Sulfate ions in the water were collected as barium sulfate in the same way as mention in 2.2 for sulfur isotope analysis.

2.4. Collection of stalagmite samples

From the Shimizu-do Cave, three growing stalagmite samples were collected (Fig. 1). The sampling site **a** of stalagmite A was 400 m from the entrance and not open for sightseeing. The 34-cm tall stalagmite sample was collected from the floor of the passage. The sampling site **b** of stalagmite B was 150 m from the entrance and 4 m high from the passage. The 7-cm tall B-1 and 2.3-cm tall B-2 stalagmite samples were collected on a fallen block of calcareous sandstone of the host rock. Stalagmite B may reflect information of the surface more closely than stalagmite A because the residence time of the drip water at stalagmite B is much shorter than that of stalagmite A. The stalagmite sampling site in the Ryuo-do Cave was 90 m from the entrance and 20 m from the surface. The 20-cm tall sample (R-1) and 15-cm sample (R-2) were collected.

2.5. Collection of samples from the Kamashikiyama Tuff Formation

Tuffaceous sandstone samples were collected from the outcrop of the Kamashikiyama Tuff Formation located at about 150 m north from the ground surface just above the Ryuo-do Cave. After the powdered sample was treated with 30% H_2O_2 , the mixture was filtered through a 0.8 μm membrane filter (Advantec, Tokyo, 25 mm in

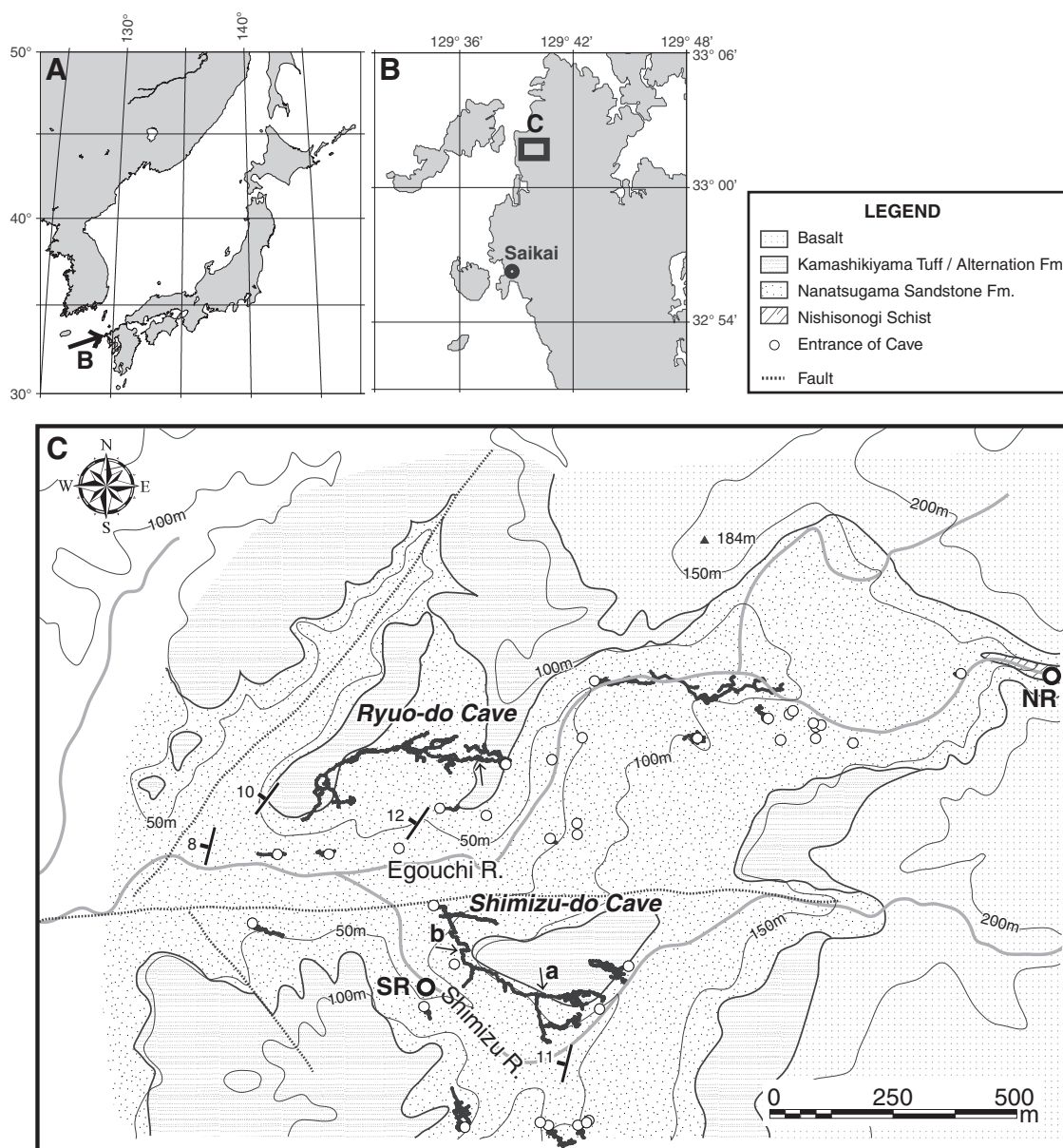


Fig. 1. Geological map of the studied area showing the locations of the stalagmite samples. The schematic vertical profile around Shimizu-do Cave and Ryuo-do Cave is shown in Fig. 7.

diameter) and then the sulfate was recovered as barium sulfate after adding barium chloride to the filtrate.

3. Analytical procedures

3.1. Chemical analysis of water

The Na^+ , K^+ , Mg^{2+} and Ca^{2+} concentrations in the water were determined by atomic absorption spectrophotometry (AA-7000, Shimadzu, Kyoto). The ionization and chemical interferences were suppressed by adding cesium chloride and lanthanum chloride to the sample solution at 0.01 and 0.001 mol dm⁻³, respectively (Yoshimura et al., 2001). The Cl^- , NO_3^- and SO_4^{2-} concentrations were determined by ion chromatography (ICS-90, Dionex, Sunnyvale, USA), consisting of a DS5 conductivity detector and an AMMS micromembrane suppressor. The separation was achieved on an anion-exchange column (Dionex IonPac AS12A) using a Na_2CO_3 – NaHCO_3 eluent. The alkalinity was determined by titration and the equivalent points were detected by the Gran method (Gran, 1952).

The reproducibility of the measurements for the respective major components had a relative standard deviation within 2%. The charge balance of cations and anions for all samples was fairly good, thus exhibiting a high data reliability (Table 1).

All chemicals were of analytical grade. Deionized water prepared with a Milli-Q SP system (Millipore) was used throughout. The chemical equilibrium calculations for the CaCO_3 – H_2O – CO_2 system were performed using the computer program PHREEQC (Parkhurst et al., 1980).

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 (Ichikuni and Tsurumi, 1990). A carbonate sample (0.01 g), Milli-Q water (1.5 g) and H^+ type cation-exchange resin (0.2 g, Muromac MAC-3, Muromachi Technos, Tokyo) were continuously mixed for 24 h in a PTFE container. After the dissolution of the carbonate fraction, the solution was filtered using a 0.45 μm

Table 1
Chemical and isotope compositions of drip water forming the stalagmites (concentrations in mg dm⁻³ except for alkalinity).

Collection period	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Alkalinity/ mmol dm ⁻³	pH	Tw (°C)	a _{CO₂} /10 ⁻⁶	δ ³⁴ S-SO ₄ (‰)
<i>Shimizu-do Cave A</i>												
111230	7.8	0.7	1.7	42.3	14.5	1.7	4.0	2.12	8.08	15.9	8.9	
111230-120314	7.9	0.7	1.7	41.5	14.5	1.6	4.0	2.11	8.18	15.9	11.0	
<i>Shimizu-do Cave B-1</i>												
090909-091208	15.8	0.3	5.5	52.4	22.3	0.5	9.1	3.08	8.15	14.1	14.2	8.2
091208-100219	15.9	0.2	6.1	73.1	23.7	0.8	9.3	4.24	7.76	10.8	7.3	6.9
100219-100521	16.5	0.3	6.2	80.0	23.6	0.4	9.2	4.24	7.60	14.1	5.5	7.4
100521-100810	16.3	0.3	6.1	66.8	23.4	0.6	9.2	3.68	7.62	15.7	5.2	8.2
100810-101031	15.7	0.1	6.3	70.3	26.4	0.0	9.9	3.79	7.61	15.5	5.2	8.5
101031-101203	15.1	0.0	6.2	62.5	24.8	0.0	9.0	3.37	7.88	13.9	8.5	8.2
101203-110124	15.0	0.0	6.2	62.4	24.4	0.0	9.5	3.43	7.86		8.1	8.3
110124-110609	15.5	0.1	6.0	93.6	23.9	0.0	10.0	5.01	7.57	14.4	6.1	8.1
Av.	15.7	0.2	6.1	70.1	24.1	0.3	9.4	3.86	7.76	14.1	7.5	8.0
SD	0.5	0.1	0.3	12.5	1.2	0.3	0.4	0.62	0.20	1.6	3.0	0.5
<i>Ryuo-do Cave R-1</i>												
090723-090909	11.9	0.2	4.7	57.7	24.5	1.9	13.9	2.62	8.09	19.9	12.0	-3.8
090909-091208	11.4	0.2	4.6	50.2	25.6	0.7	14.2	2.44	8.02	15.9	8.8	-3.5
091208-100219	11.4	0.2	5.0	47.5	26.5	1.8	14.5	2.17	8.11	16.8	9.8	-3.3
100219-100521	11.1	0.2	4.8	46.2	26.5	1.3	14.7	2.05	8.00	15.2	7.0	-2.8
100521-100810	11.3	0.2	4.7	42.8	25.6	1.4	14.5	1.95	8.18		11.4	-2.7
100810-101031	10.8	0.0	4.7	40.3	24.6	0.0	15.3	1.83	7.82	15.9	4.2	-3.8
101031-101203	10.6	0.0	4.7	41.7	24.1	0.0	14.8	1.93	8.03	15.3	7.1	-2.8
101203-110124	10.4	0.0	4.7	40.7	25.6	0.0	15.6	1.88	8.20	17.6	10.6	-2.8
110124-110609	10.2	0.0	4.7	41.4	24.5	0.0	16.1	1.87	8.29	16.5	12.6	-3.2
Av.	11.0	0.1	4.7	45.4	25.3	0.8	14.8	2.08	8.08	16.6	9.3	-2.2
SD	0.6	0.1	0.1	5.7	0.9	0.8	0.7	0.28	0.14	1.5	2.8	0.4

membrane filter. The sulfate ion concentration was determined by ion chromatography using the ICS-90 instrument from Dionex in a similar way as mentioned above. The reproducibility of the measurements had a relative standard deviation within 5%.

A carbonate sample (0.01 g) and 10% acetic acid (5 cm³) were continuously mixed for 12 h in a glass container. After dissolution of the carbonate fraction, the solution was filtered through 0.45 μm membrane filters (25-mm diameter, Advantec, Tokyo). The calcium and magnesium concentrations were determined by atomic absorption spectrophotometry in a similar way as mentioned above. The reproducibility of the measurements had a relative standard deviation within 2%.

3.3. Stable isotope composition analysis

The carbon isotope measurements were done by an IsoPrime mass spectrometer (IsoPrime, Cheadle, UK) at the Kyuden Sangyo Co. The carbon isotope compositions are given as permil deviations from the PDB reference material in the delta notation. The sulfur isotope measurements were completed by an IsoPrime EA (GV Instruments, Manchester) at the Graduate School of Natural Science and Technology, Okayama University. The sulfur isotope compositions are given as permil deviations from the CDT reference material in the delta notation. The analytical precisions for δ¹³C and δ³⁴S were ±0.1 and ±0.3‰, respectively.

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 (Shopov et al., 1994; Perrette et al., 2005). The fluorescence intensities of the stalagmite sample were observed using a microscope spectrofluorometer (ECLIPSE 80i, Nikon, Tokyo) equipped with an Hg-lamp (C-HGFI Intensilight, Nikon) and a monochromator (SPG120-UV, Shimadzu). The excitation wavelength was 365 nm, and the emission wavelength was 444 nm (Kurisaki and Yoshimura, 2008). The fluorescence intensity of the bandings was measured at

2 μm intervals along the growth axis using a microscopic spectrofluorometer with an XY-stage, then the annual average growth rate of the stalagmite was determined.

4. Results and discussion

4.1. Average growth rates of the stalagmites

The annual banding in the stalagmites is caused by the seasonal differences in the fulvic acid concentrations in the dripping water which forms speleothems (Shopov et al., 1994; Kurisaki and Yoshimura, 2008). Our dating method is especially effective for young, growing samples whose absolute age is very difficult to determine by other methods. The number of annual bandings was objectively counted using a personal computer.

The annual banding could be clearly observed in stalagmites from the studied caves, as shown in Fig. 2. The distribution of the annual banding widths was almost constant everywhere for the stalagmites of Shimizu-do Cave B-1 and B-2, and Ryuo-do Cave R-1. The average annual growth rates were determined to be 35 ± 9 (1σ) μm y⁻¹ for the B-1 stalagmite, 120 μm y⁻¹ for the B-2 stalagmite and 73 ± 13 μm y⁻¹ for the R-1 stalagmite. For the Shimizu-do stalagmite A, the width change in the annual bandings was observed 400 years ago. The drip water flow rate at the site was probably changed due to a change in the land utilization, which will be discussed later. It has been reported that the effective precipitation mainly controlling the drip rate affects the thickness of the stalagmite laminae (Genty and Deflandre, 1998). The drastic vegetation change may have resulted in the variation of the evapotranspiration. The average annual growth rate was 49 ± 3 μm y⁻¹ for the past 400 years and 27 ± 3 μm y⁻¹ for the period older than the past 400 years (Fig. 3).

4.2. Sulfate concentration of the stalagmites

Ichikuni (1980) reported the relationship between the trace constituent contents of the terrestrial carbonate and those of the corresponding mother liquid. When carbonate precipitates, the ions

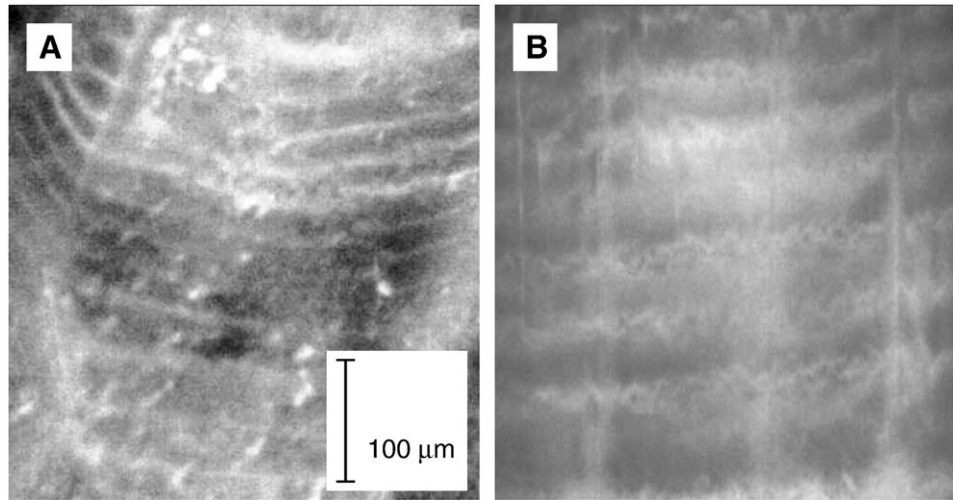
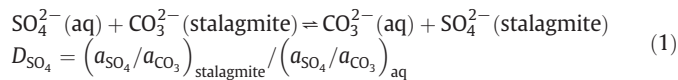


Fig. 2. Fluorescent microbandings of the Shimizu-do Cave A stalagmite. A: for the period older than the past 400 years; B: for the past 400 years.

contained in the solution coprecipitate. The SO_4^{2-} concentration can become an index of the local environmental pollution caused by acid deposition (Frisia et al., 2005; Wynn et al., 2010). A SO_4^{2-} ion is substituted for a CO_3^{2-} ion during the precipitation process of calcite according to the ion-exchange equilibrium (Takano et al., 1980; Ichikuni, 1995). The ion-exchange equilibrium is represented by:



where D_{SO_4} 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 waters of the Shimizu-do Cave A and B-1 and Ryuo-do Cave R-1 stalagmites, shown in Table 1, were relatively small and therefore D_{SO_4} was calculated to be 3.4×10^{-5} , 7.3×10^{-5} and 4.9×10^{-5} for the respective stalagmites using PHREEQC (Parkhurst et al., 1980) and the average analytical values in Table 1. The value of $(a_{\text{SO}_4} / a_{\text{CO}_3})_{\text{stalagmite}}$ was evaluated as the mole fraction of SO_4^{2-} using its concentration on the surface of the stalagmites. The D_{SO_4} values were almost constant, which were in fairly good agreement with those reported by Takano et al. (1980) ($D_{\text{SO}_4} = 1.6 \times 10^{-5}$ to 4.1×10^{-4}) for travertines precipitated from 40.5 to 99.0 °C hot spring waters. In

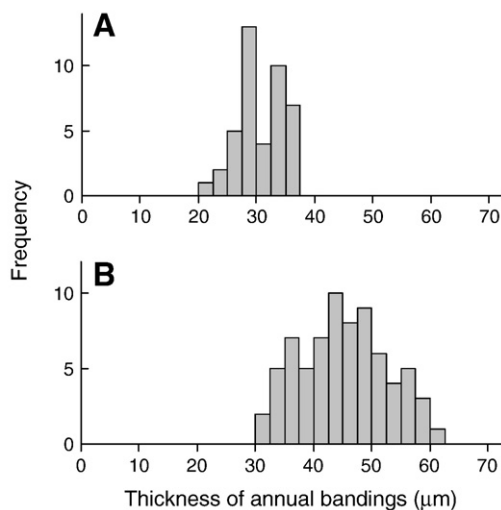


Fig. 3. Distribution of the thickness of annual bandings of the Shimizu-do A stalagmite. A: for the period older than the past 400 years; B: for the past 400 years.

this study, we introduced $D^*_{\text{SO}_4}$, proposed by Takano et al. (1980), as follows:

$$D^*_{\text{SO}_4} = \left(\text{SO}_4^{2-} \text{ mole fraction} \right)_{\text{stalagmite}} / \left(\left[\text{SO}_4^{2-} \right] / [\text{alkalinity}] \right)_{\text{aq}} \quad (2)$$

If the pH and temperature of the drip waters are constant, the $D^*_{\text{SO}_4}$ values can be more easily used as a measure of the past sulfate concentrations in the drip waters. The pH of the drip waters is mainly controlled by the degassing degree of CO_2 , depending on the cave air circulation and therefore on individual sites in the cave. The $D^*_{\text{SO}_4}$ was determined to be 0.0045, 0.023 and 0.0074 for the Shimizu-do Cave A and B-1 and the Ryuo-do Cave R-1 stalagmites, respectively.

For the Shimizu-do Cave A stalagmite, all the results are shown in Table S1 in the Supplementary file and only the variation in the past SO_4^{2-} concentrations of the drip water is shown in Fig. 4(A). The

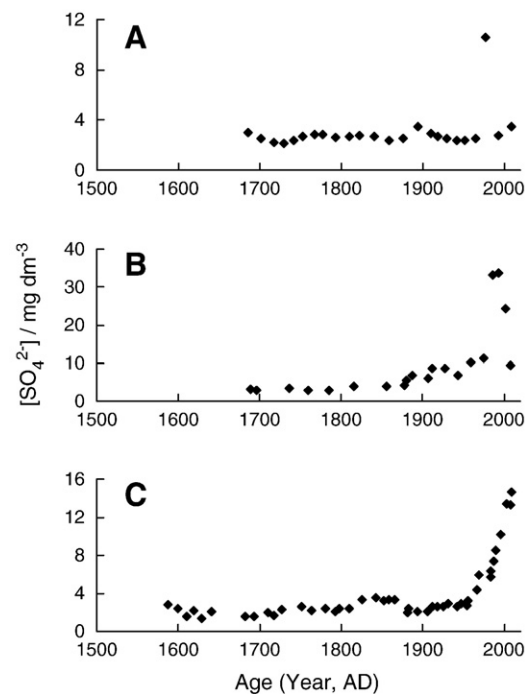


Fig. 4. Past SO_4^{2-} concentration of drip water recorded in the stalagmites. A: Shimizu-do Cave A stalagmite; B: Shimizu-do Cave B-1 stalagmite; C: Ryuo-do Cave R-1 stalagmite.

Shimizu-do Cave A stalagmite was located far from the surface, and the residence time of the drip water was long. Therefore, it took a long time until the precipitation becomes drip water, and the surface information became mixed to some extent. Nevertheless, a change in the SO_4^{2-} concentration was observed. The SO_4^{2-} concentration derived from sea salt [ss- SO_4^{2-}] was calculated to be 2.0 mg dm^{-3} based on the Cl^- concentration shown in Table 1 (Eq. (3)), which corresponded to the lowest values in Table S1.

$$[\text{ss-}\text{SO}_4^{2-}] = [\text{Cl}^-] \times \left(\frac{[\text{SO}_4^{2-}]}{[\text{Cl}^-]} \right)_{\text{sea}} \quad (3)$$

where $[\text{Cl}^-]_{\text{sea}} = 19.4 \text{ g kg}^{-1}$ and $[\text{SO}_4^{2-}]_{\text{sea}} = 2.7 \text{ g kg}^{-1}$. It was found that the calculated SO_4^{2-} concentration of the past drip water had increased in 1900 and 2000. An unusually high SO_4^{2-} concentration was recorded around 1990 probably due to the dust that adhered to the stalagmite surface such as cement supplied by the tunnel construction of the Shimizu-do Cave in 1987.

For the Shimizu-do Cave B-1 stalagmite, the SO_4^{2-} concentration of the drip water derived from sea salt was calculated by the Cl^- concentration to be 3.4 mg dm^{-3} . In the past, it was revealed that almost all of the SO_4^{2-} was of sea salt origin. The SO_4^{2-} concentration began to slightly increase in the late 19th century, and clearly from around 1980 (Fig. 4(B)). The SO_4^{2-} concentration greater than 30 mg dm^{-3} was recorded from 1985 to 2000. This may be due to the influence of the tunnel construction mentioned above.

For the Ryo-do Cave, the SO_4^{2-} concentration of the drip water derived from sea salt was calculated to be 3.5 mg dm^{-3} , which was somewhat higher than the lowest concentration in the past estimated by the sulfate concentration of the stalagmite. In the case of the Ryo-do Cave area, the contribution of Cl^- by human activities cannot be ignored if the Cl^- concentration of the present drip water is used for the ss- SO_4^{2-} concentration estimation (Fig. 4(C) and Table S1 in the Supplementary file). The lowest value of about 2 mg dm^{-3} in Table S1 may be the one derived from sea salt. From 1700, the values started to increase to give 3.5 mg dm^{-3} in the middle of 1800s. It is possible that the pyrite origin SO_4^{2-} was supplied by human activities, as described below. After 1900, the SO_4^{2-} concentration drastically increased to the present. It is compared to the amount of coal production in the Nagasaki Prefecture, because the atmospheric environmental change has been accompanied by the development of heavy industry in Sasebo City and Nagasaki City, and is regarded as an index of the air pollution due to human activities. The change in the SO_4^{2-} concentration after 1900 and that of the amount of coal production indicated a similar tendency. After the 1960s, the main domestic energies changed from coal to oil. On the other hand, the coal consumption by China has been exponentially increasing. Therefore, after the 1960s, it is thought that the long-distance transport from the China continent became the main air pollution factor in this area. However, an unexpected increase in the sulfate concentration was observed before 1900.

The SO_4^{2-} concentration and $\delta^{34}\text{S}$ of the total fallout collected at SR and NR, and the non-sea salt origin SO_4^{2-} (nss- SO_4^{2-}) concentration and $\delta^{34}\text{S}$ (nss- $\delta^{34}\text{S}$) that was calculated by the Na^+ concentration as an index of the sea salt origin are shown in Table 2. The mean of the precipitation $\delta^{34}\text{S}$ at SR was $+7.5\%$, and that at NR was $+7.3\%$, therefore, there is no regional difference in the same basin. The $\delta^{34}\text{S}$ of Chinese coal is distributed over the very wide range of -27.3% to $+28.9\%$, but almost all coal shows a positive value and its average value is $+7.8\%$ (Maruyama et al., 2000). The nss- $\delta^{34}\text{S}$ values can be related to the long-distance transport from the China Continent, which will be discussed elsewhere. The $\delta^{34}\text{S}$ values of the drip water are shown in Table 1. The average $\delta^{34}\text{S}$ value of the Shimizu-do Cave drip water was $+8.0\%$, close to the precipitation value. On the other hand, the value of the Ryo-do Cave drip water was -3.2% , much lower than that of the nss- SO_4^{2-} . The average SO_4^{2-} concentration of

Table 2
Relationship between the SO_4^{2-} concentration and $\delta^{34}\text{S}$ of the total fallout.

Period	$\text{SO}_4^{2-}/$ mg kg^{-1}	$\text{Na}^+ /$ mg kg^{-1}	$\delta^{34}\text{S}$ (‰)	nss- $\text{SO}_4^{2-}/$ mg kg^{-1}	nss- $\delta^{34}\text{S}$ (‰)
SR^a					
090909–091208	1.8	0.8	8.6	1.6	7.2
091208–100219	4.1	3.3	7.6	3.3	4.3
100219–100521	1.9	1.0	6.3	1.6	4.1
100521–100810	1.4	0.4	5.9	1.3	4.7
100810–101031	1.2	0.6	7.5	1.1	5.8
101031–101203	4.1	2.4	7.0	3.5	4.6
101203–110124	7.4	8.6	11.4	5.3	7.7
110124–110609	2.9	1.2	6.3	2.6	4.7
NR^a					
090909–091208	1.5	0.7	8.1	1.3	6.5
091208–100219	4.7	3.7	7.8	3.8	4.8
100219–100521	2.1	1.1	6.4	1.8	4.4
100521–100810	1.5	0.5	5.6	1.4	4.1
100810–101031	1.1	0.6	7.7	1.0	5.7
101031–101203	4.9	2.5	7.2	4.2	5.2
101203–110124	6.8	6.8	10.5	5.1	7.2
110124–110609	2.5	1.0	6.6	2.2	5.0

^a The sites are shown in Fig. 1.

the Shimizu-do Cave drip water was 9.4 mg dm^{-3} , and that of the Ryo-do Cave drip water was 14.8 mg dm^{-3} . Therefore, SO_4^{2-} with a small $\delta^{34}\text{S}$ may be added to the Ryo-do Cave drip water.

Near the entrance of the Ryo-do Cave, shallow-marine deposits called the Kamashikiyama Tuff Formation cover the calcareous sandstone, Nanatsugama Sandstone Formation. The samples were collected from the outcrop, located at about 150 m north from the ground surface just above the Ryo-do Cave. As shown in Table 3, the $\delta^{34}\text{S}$ value of the sulfate extracted from the fine-grained sample by H_2O_2 treatment was -32.2% , suggesting that the SO_4^{2-} is derived from the biogenic pyrite (Krouse and Grinenko, 1991; Darling et al., 2006). It was fairly difficult to collect the sulfate from the low SO_4^{2-} concentration stalagmite samples for the $\delta^{34}\text{S}$ measurements, and therefore, the restricted data for both of the caves stalagmites are presented (Table 3). The $\delta^{34}\text{S}$ value of the surface sample of the Ryo-do Cave stalagmite was lower than that of the Shimizu-do Cave A stalagmite. Above a stalagmite collection site of the Ryo-do Cave, the tourist park called Saikai Rakuen was constructed in 1989. The underground oxygen partial pressure began to increase when the surface cover was removed and/or disturbed. It is possible that the dissolution of pyrite promoted by the biological action of sulfur-oxidizing bacteria supplied additional SO_4^{2-} to the groundwater (Yoshimura et al., 2001). This is the reason why the SO_4^{2-} concentration of the Ryo-do Cave drip water was 5.6 mg dm^{-3} higher than that of the Shimizu-do Cave drip water (Table 1).

4.3. Variation in Mg/Ca ratios of the stalagmites

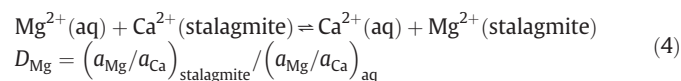
It can be expected that, under a climax condition, the amount of Mg supplied by the fallout and chemical weathering is equal to that removed by the runoff, i.e., the Mg budget is balanced, as in the similar

Table 3
 $\delta^{34}\text{S}$ of sulfate in stalagmites and sulfide in tuffaceous sandstone.

Sample	S content/ mg kg^{-1}	$\delta^{34}\text{S}$ (‰)	Note
Shimizu-do Cave stalagmite A	28	5.0	Distance from the top: 0–1.0 cm
Ryo-do Cave stalagmite R-1	170	1.7	Distance from the top: 7.7–13.8 cm
Ryo-do Cave stalagmite R-2	–	1.1	Distance from the top: 0–0.5 cm
Kamashikiyama Tuff Formation	2.7 ± 0.0 373 ± 3	3.8 –32.2	Coarse-grained Fine-grained

case for phosphate (Koga and Yoshimura, 2012). Because the chlorophyll of plants is a Mg complex, the Mg^{2+} concentration of the drip water will change with the biomass variation.

When calcium carbonate precipitates, Mg^{2+} in the drip water is taken into the calcite lattice by ion-exchange. The ion-exchange equilibrium of Ca^{2+} and Mg^{2+} is expressed as follows (Ichikuni, 1995):



where D_{Mg} is the distribution coefficient expressed by the activity ratios in the solid and solution phases. The values of 0.058, 0.073 and 0.034 were obtained from the results of the Shimizu-do Cave A and B-1 and Ryuo-do Cave R-1 stalagmites, respectively. The 0.057 value at 25 °C has been reported (Ichikuni, 1980), and they are in fairly good agreement. For a more practical scale, the change in Mg/Ca molar ratio of the stalagmite, can be a measure of that in the biomass. The other possibility of the change in Mg/Ca is related to prior calcite precipitation (PCP), exclusion of Mg from calcite precipitated upstream of the dripwater/speleothem site resulting in enrichment in the Mg/Ca ratios of residual effluent (Fairchild et al., 2000; Sinclair, 2011). At the sites of the Shimizu-do Cave A and Ryuo-do Cave R-1 stalagmites, the surface is covered by the Kamashikiyama Tuff Formation. During recent 500 years, there are no records on climate in detail in the surveyed area, but the drastic change affecting the extent of PCP may be excluded. In addition, the lower concentration of Ca^{2+} of the drip waters of these two sites (Table 1) may be due to the carbonate dissolution by soil CO_2 under the closed system condition (Yoshimura et al., 2001). In this case, the equilibrium partial pressure of CO_2 is relatively low ($10^{-3.18}$ and $10^{-3.04}$ atm for the Shimizu-do Cave and Ryuo-do Cave sites, respectively), and the degassing of CO_2 from the drip waters into cave air is not so extensive, suggesting that PCP does not largely concern the variation in Mg/Ca.

The results of the Shimizu-do Cave A stalagmite are shown in Fig. 5(A) and in greater detail in Table S2 in the Supplementary file. Because the drip water forming the Shimizu-do Cave A stalagmite

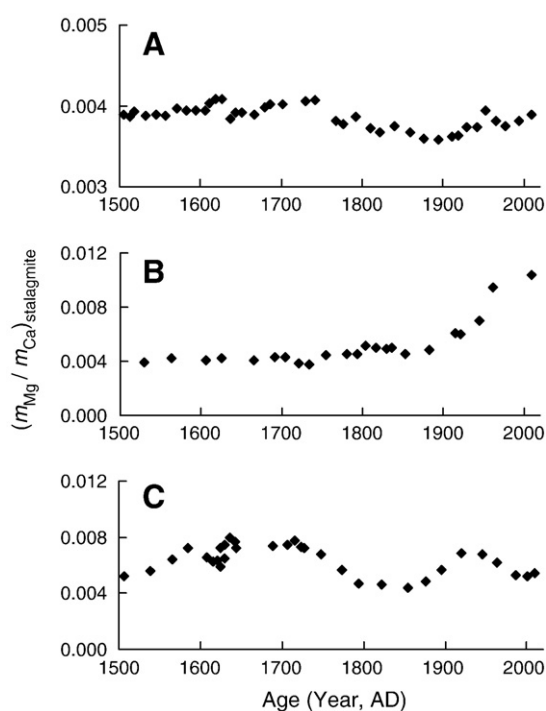


Fig. 5. Variation in the Mg mole fraction of the stalagmites. A: Shimizu-do Cave A stalagmite; B: Shimizu-do Cave B-1 stalagmite; C: Ryuo-do Cave R-1 stalagmite.

has a long residence time, its concentration variation was lower. The gradual increase in Mg/Ca after 1500 and then its decrease after 1750 were observed, followed by the slight increase in the late 19th century, and a peak in the middle of the 20th century. In the case of the Shimizu-do Cave B1 stalagmite site covered by the calcareous sandstone, the higher concentration of Ca^{2+} of the drip water (Table 1) may be due to the carbonate dissolution by soil CO_2 under the open system condition. Irrespective of almost constant Mg^{2+} concentration, the Ca^{2+} concentration varied with 18% RSD: the effect of PCP cannot be ignored (Table 1). However, the large increase in the Mg/Ca values after 1900 (Fig. 5(B)) should be due to the decrease in biomass.

For the Ryuo-do Cave stalagmite (Fig. 5(C)), detailed information has been recorded about events at the surface, since the stalagmite was growing 20 m from the surface. In the 1600s, the increase in Mg/Ca in the 17th century and 18th century may be due to the drastic decrease in biomass, i.e., the drastic change in vegetation. As mentioned later, the surface just above the stalagmite sampling site was a field in the late 1800s. The decrease and then constant magnesium concentration may be due to the removal of the crop. The increase in Mg/Ca from 1900 suggested that the biomass was further reduced.

4.4. Relationship between Mg/Ca and stable carbon isotope ratios

The stable carbon isotope ratios of the Shimizu-do Cave A stalagmite for the past 1000 years are shown in Fig. 6(A) and in greater detail in Table S3 in the Supplementary file. As shown in Fig. 1, the drip water forming the stalagmite was fed from an area near the top of the hill. It has been reported that the stable carbon isotope ratio of C3 plants that grow in a forest is -32 to -22‰ , and that of the C4 plants that grow in grasslands is -16 to -10‰ (Deines, 1980; Cerling, 1984). The average value of the carbon isotope ratio of plants and that of carbonate ($\delta^{13}C = -1.3$ to -0.1‰ (Oda, 1997)) were recorded in the stalagmites (Yoshimura et al., 2001; 2004). The isotopic fractionation when a stalagmite precipitates is about $+3\text{‰}$ (Hendy, 1971; Kurisaki et al., 2006), and therefore, the forest vegetation shows -14 to -8‰ , while the grassland vegetation is -6 to -2‰ in the stalagmite. Before 1500, the stable carbon isotope ratio of -9 to -10‰ revealed forest vegetation. In 1600–1700, the stable carbon isotope ratio increased ($\delta^{13}C = -2\text{‰}$), suggesting a drastic change in the grassland vegetation. Such the large change in $\delta^{13}C$ of

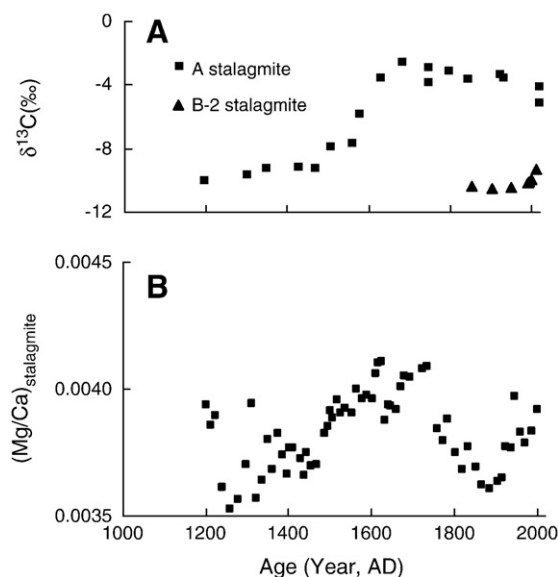


Fig. 6. Variation in $\delta^{13}C$ and the Mg mole fraction of the stalagmites. A: $\delta^{13}C$ of Shimizu-do Cave A and B-2 stalagmites; B: Mg mole fraction of the Shimizu-do Cave A stalagmite.

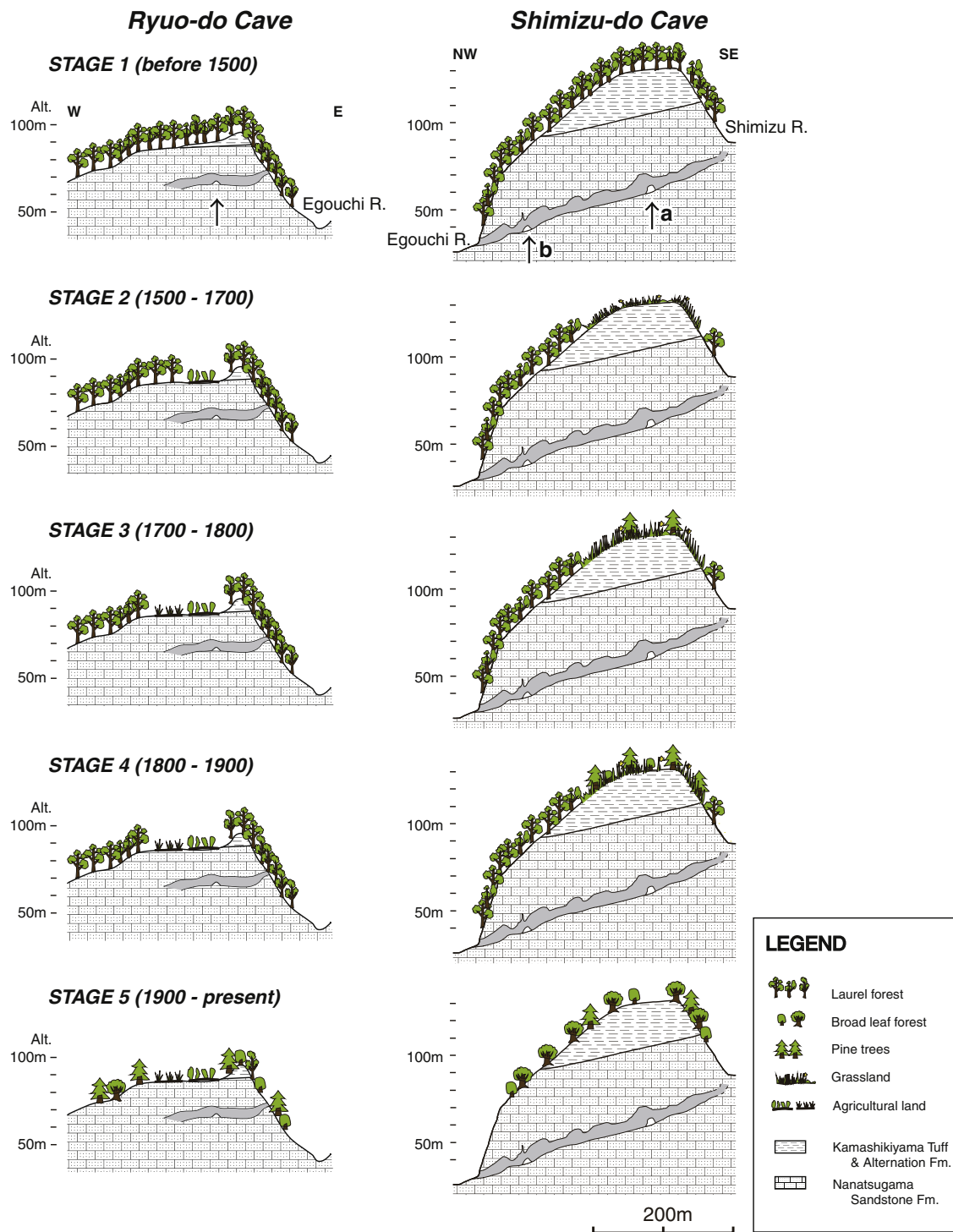


Fig. 7. Schematic diagram of the relationship between the vegetation change and human activities. The arrows show the sites of stalagmite collection.

a stalagmite from -8 to -7 to -5 to -4% was observed in Akiyoshi-dai karst Plateau, Yamaguchi, southwestern Japan (Kurisaki et al., 2006). In the temperate, humid climate in Japan, the climax vegetation is forest, but Akiyoshi-dai Plateau is covered by grass now owing to yearly burning of the dead grass on the plateau, which had started about 400 years ago.

In order to compare the change in the stable carbon isotope ratio to that of Mg/Ca, Fig. 6(B) was expanded regarding the ordinate of Fig. 5(A). The increase in the ratios expressed a reduction in the biomass from 1500 to 1700, and the possibility that the vegetation change from forest to grassland occurred due to human activities

was suggested. On the other hand, the Shimizu-do Cave B-2 stalagmite, which was collected around the foothills, showed $\delta^{13}\text{C}$ values characteristic of forest vegetation, as shown in Fig. 6(A).

4.5. Reconstruction of land use records extracted from the stalagmites, ancient documents, and old picture maps

For Japan, agricultural productivity started to increase because the political conditions stabilized in the early Edo period of the 1600s. According to the Omura Clan archive "Gosonki Nakaura-mura", belonging to the Nagasaki Museum of History and Culture, the annual

productivity in the Nakaura village was about 16 m³ in terms of a rice crop in the early Edo period of the 1600s, but increased to 55 m³ in 1862, the late Edo period. With the progress in cultivation, the demand of grass and young leaves as fertilizer for fields increased, and this situation stimulated the development of forests, which may have produced the following local environmental changes.

Using stalagmites, ancient documents, old picture maps, and topographical maps, the relationship between humans and nature in this area could be summarized as shown in Fig. 7 and Table S4 in the Supplementary file. Under the temperate humid climate condition, forest vegetation is predominant, and therefore, the surveyed area might be covered by forest before 1500. There has been, then, a very close relationship between the vegetation change and human activities.

Around Shimizu-do Cave from 1500 to 1700, the increase in the magnesium concentration and the carbon isotope ratio in the stalagmites suggested the reduction of biomass and a vegetation change from C3 to C4 plants, i.e., from forest to grassland around the top of the hill probably because of the demand of grasses as fertilizer. From 1700 to 1900, the biomass increased with the transition from the grassland to forest because the magnesium concentration decreased. According to the old drawing of the Ohmura Clan “Ohmura Kannai Ezu Shimakata”, drawn sometime between 1732 and 1814, now belonging to the Nagasaki Museum of History and Culture, Nagasaki, the hill above the Shimizu-do Cave was a pine forest. The following low, constant magnesium ion concentration suggested that there was a constant removal of biomass, such as pine needles and timbers, for kindling and building materials. Also in the case of the hillside, the increase in the magnesium concentration indicated the decline in pine forest changing into a broad-leaved forest from 1900 to the present. In the topographic maps published in 1901, 1924, 1954 and 1976, vegetation was mixed with broad-leaved and conifer trees; probably tall pine trees and young vertebral and oak trees which were used for fuelwood and charcoal. In the 2000 topographic map, the forest was broad-leaved trees, indicating that the pine trees had disappeared. Acid deposition by the domestic use of coal and by long-distance transport from East Asia was recorded as an increase in the sulfate concentration.

Around Ryuo-do Cave, the magnesium ion concentration increased, repeated an increase and decrease, and then finally decreased from 1600 to 1800. The sulfate concentration decreased after a small increase. The forest biomass was changed depending on the change in the forest use. Some field crops had begun on a small scale. The old drawing showed there to be forest without pine trees. In the late 19th century, the sulfate concentration increased, indicating a disturbance in the topsoil due to human activities to reclaim a field. According to the figure “Nakaurakitago Aza Sonogouchi Azagirizu”, drawn between 1873 and 1881, the surface just above the stalagmite sampling site was a field. The decrease and then constant magnesium concentration may be due to the removal of the crop. The increase in the magnesium concentration indicated a decline in the biomass. According to the topographic maps published in 1901, 1924 and 1954, there was a broad-leaved forest. In the maps published in 1976 and 2000, the vegetation was mixed with broad-leaved and conifer trees; the conifer trees were planted. Acid deposition by the domestic use of coal and by long-distance transport from East Asia was recorded as an increase in the sulfate concentration. In addition, the construction for the Saikai Rakuen Park was recorded as an increase in the sulfate concentration due to biogenic pyrite oxidation.

5. Conclusion

The combination of annual microbanding information and the Mg²⁺ and SO₄²⁻ concentrations and C and S stable isotope ratios of the stalagmites made it possible to extract local and/or global anthropogenic environmental changes in nature. The records extracted from ancient documents, ancient picture maps and topographical maps

were found to be also useful to cross-check the data. It is expected that the research technique reported in this paper will help in the understanding of the natural environment not only in this area, but also in all karst areas.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2013.04.006>.

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