Journal of Osaka Kawasaki
Rehabilitation University Vol.*13.2019*
pp.*66-72*

Report

Experimental Dyeing with Tree Chip of Kurogaki (Black Persimmon; *Diospyros kaki* Thunb.)

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Abstract : Silk changed in color to black purple (Hue5Y3/2) and cotton did in color to yellow brown (Hue10YR4/6 - 6/6) after dyeing with the tree chip of Kurogaki (black persimmon; *Diospyros kaki* Thunb.) and blackish fine soil from a field in Kanazawa, Ishikawa, Japan. We studied the chemical composition of both of silk and cotton by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). We investigated the distribution, components, structure, and differentiation of silk and cotton. The data were generated an elemental content map. Specific elements in both materials indicated high Al (10–16%), Si (30–43%), and Fe (13–20%) associated with P (6–15%), S (4–10%), and Sr (5–6%) after dyeing. This method is simple and results in no chemical environmental pollution.

Keywords : Kurogaki (black persimmon; *Diospyros kaki* Thunb.), silk, cotton, SEM-EDS, elemental content maps

Introduction

Kurogaki (black persimmon; *Diospyros kaki* Thunb.) grows very slowly, has very hard wood, and is known for its striking black and beige coloration, referred to as a "peacock pattern". Patterned Kurogaki occurs very rarely, as only one of every 1,000–10,000 trees found in Japan and China. This tree was previously planted in Kanazawa city, Japan and is very important from a historical and artistic perspective in Kanazawa, Ishikawa, Japan, particularly in the Edo period (1603–1868). The "peacock pattern" of Kurogaki wood is used to manufacture various artifacts, such as small tables, tea canisters, pens, key holders, earrings, and origami-crafts in Japan (**Fig. 1A, B, D**).

"Dorozome" is a traditional dyeing method that uses muddy clays and is conducted on Amami-Oshima Island, Kagoshima, Japan. The brilliant black color of dyed "Oshima Tsumugi" is derived from the muddy clay in Dorota (small ponds with muddy clays). The muddy clays consist of Fe-rich chlorite, vermiculite, mica minerals, kaolin minerals, and iron hydroxides associated with high P_2O_5, N, C, and S contents in the muddy field [1)]. The black color of "Ohshima Tsumugi" is conferred by high concentrations of S, Ca, and Fe, whereas

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Received 20 September 2018 ; Accepted 1 November 2018

the white parts without dye contain small amounts of such elements. This creates a specific condition in which iron hydroxides are important factors in forming the brilliant black dye under reducing conditions.

Furthermore, the deep purple color of dyed silk is derived from lake sediments in Shibayama-gata lagoon, Ishikawa, Japan. A quick and easy dyeing method for the color purple was developed by using blackish gray fine clay sediments in the lagoon, which contains hot spring water. The lake sediments reside under reducing conditions, with an oxidation-reduction potential of -150 mV, dissolved oxygen content of 0.31 mg/L, pH 6.7, and electrical conductivity of 1.12 mS/cm. The sediments contain large amounts of Fe associated with K, Ca, Ti, and Mn. The wet silk was dyed as deep purple with the lake sediments for few minutes; the color deepened with increasing soaking time.

Anaerobic iron bacteria contribute to reducing Fe conditions and dyeing of the purple color [2].

In this study, we found that natural Kurogaki tree chip could be used to dye both silk and cotton, as shown by electron microscopic observations. We characterized the chemical compositions and structures of Kurogaki tree chip and black soils used for dyeing by scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS).

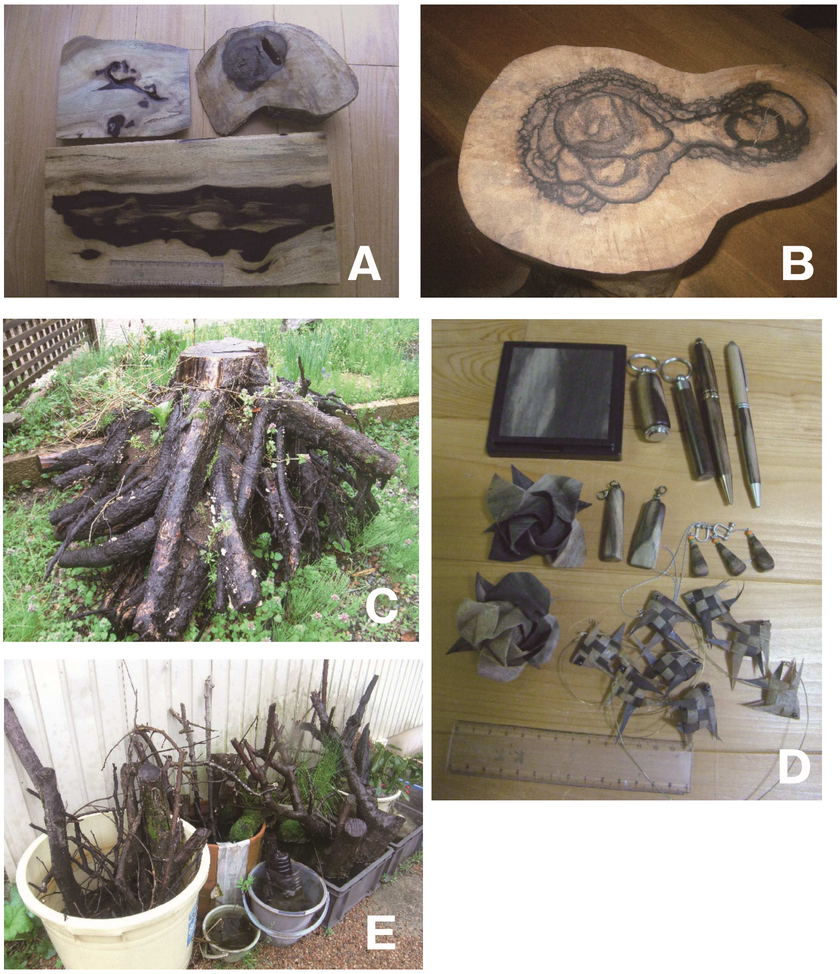

Fig 1. Kurogaki (Black persimmon; *Diospyros kaki* Thunb.) with "peacock pattern" (A) (B). A table (B), small articles and belonging pieces, such as pen, key rings, earrings, and origami-crafts (D) are made of Kurogaki. Experimental dyeing materials of Kurogaki roots and twigs before forming chips (C) (E).

Experimental

Materials

1. Kurogaki tree chip

Samples of Kurogaki tree chip and black soils were obtained from Tawara and Makiyama, Kanazawa city, Japan, respectively (**Fig. 2**). The trees were cut down in December 2016 and had grown for more than 100 years in a mixture of relatively fresh andesite rocks and weathered rocks (Tomuro andesite) associated with dark brown soils.

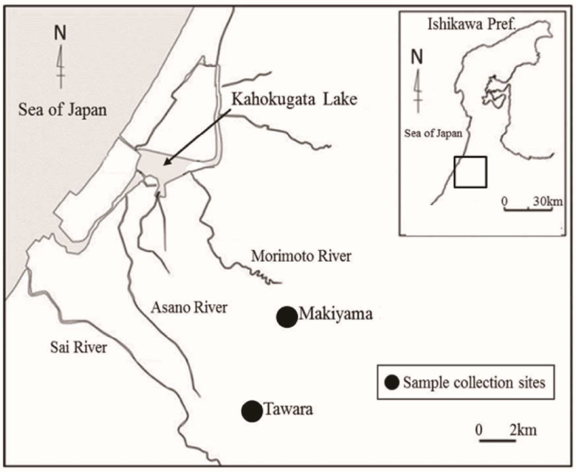

Fig 2. Locality map of the samples of Kurogaki tree chips in Tawara and black soils samples collected from Makiyama.

The Kurogaki chips were made by chopping the roots and branches (**Fig. 1C, E**). Many roots, 5–10 m in length, 30–50 cm in diameter, developed in all directions. We collected several trees with a black color on the branches, trunk, and roots and their associated andesitic soils. We characterized their structures and properties for making small artistic ornaments, such as stands, table, pens, key holder, and origami crafts (**Fig. 1 A, B, and D**).

2. Black soils

The black soils were collected from Makiyama, Kanazawa city, where abundant Kurogaki trees grow on black soils. X-Ray fluorescence analyses revealed that the black soils are rich in O (48.6 mass%), Si (24.3 mass%), Al (8.69 mass%), Ca (4.13 mass%), C (3.20 mass%), K (3.11 mass%), Fe (2.71 mass%), Mg (2.17 mass%), and Na (1.09 mass%)[3]. Views of cut-down Kurogaki trees in the hilly Makiyama field and black soils are shown in **Fig. 3A** (arrow). The black soils were used for dyeing both white silk and cotton as a mordant (**Fig. 3B**).

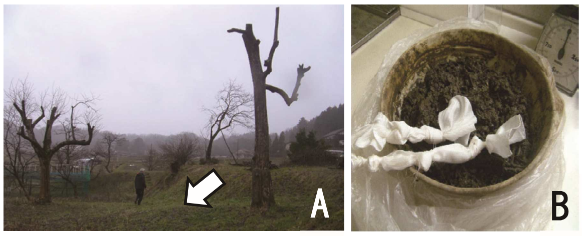

Fig 3. Black soil samples were from Makiyama, Kanazawa, Ishikawa, Japan (A) (B).

3. Methods

[a] Dyeing process is procedures with the next. Cloths made from silk and cotton (30 × 50cm) were tied with rubber bands to form a pattern design. The clothes were originally designed.

[b] Next, 400 g of Kurogaki tree chips were added to 1.5 Litter of tap water and boiled. The pH was pH6.7 after boiled. When the water began boiling, the cloth was soaked in the water for 20 min. The clothes remained in the solution for 1 day.

[c] The cloth was soaked in 1–2 kg of Makiyama black soil as a mordant, which was softened with a small amount of water, and incubated for 1 h.

[d] After [c], the soil was washed out and steps [c] and [d] were repeated for 4 times.

Analytical methods

SEM-EDS

Specific elements concentrated in the silk and cotton were detected by SEM-EDS (Horiba EMAX, Kyoto, Japan). The data were used to generate elemental content maps of the dyed silk and cotton cloth. The conditions used were as follows: 15 kV accelerating voltage, 70–80 μA current, analytical time of 1,000 s, and area of 10 mm × 10 mm on a carbon double tape with Pt coating.

Results

1. Kurogaki tree chip dyeing

The silk changed to a color of black purple (Hue5Y3/2) (**Fig. 4**) and the cotton did to a color of yellow brown (Hue10YR4/6-6/6) as observed by SEM image and determined from the elemental content map of silk and cotton 4 times after one day dyeing (**Figs. 5, 6**).

Fig 4. Silk and cotton changed color to black purple (Hue5Y3/2) and yellow brown (Hue10YR4/6-6/6) after one day of dyeing 4 times.

2. SEM-EDS elemental content maps

SEM-EDS elemental content maps of black purple parts of silk, which contained various elements (**Fig. 5**). A fine and regular texture of silk was observed in the SEM images, showing abundant distributions of Na, Mg, Al, Si, P, S, Cl, K, Fe, Rb, Sr, and Pb as indicated by the elemental content maps (**Fig. 5**). Particularly, the content map of P clearly showed sharp grains. Al, Si, Rb, and Sr spots were scattered across cloth surface based on SEM-EDS images.

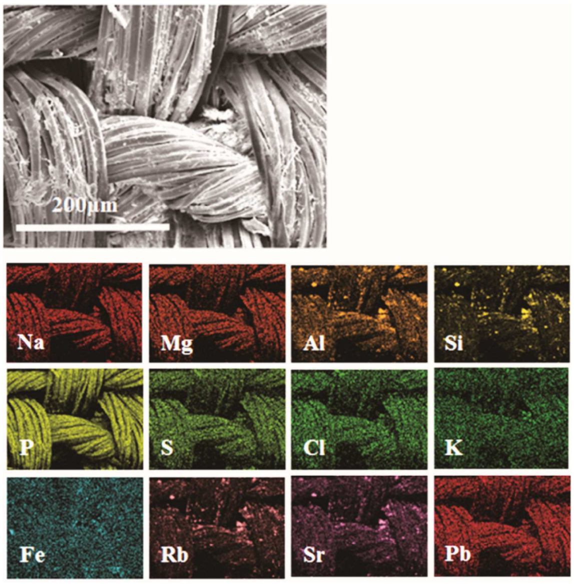

Fig 5. Scanning electron microscopy equipped with energy dispersive analysis (SEM-EDS) of black purple part on silk, showing the spectra and elemental content maps of dyed silk with various elements.

The dyed cotton containing various elements, showing a regular distribution of P and S, whereas the distributions of Al, Si, Rb, and Sr were markedly scattered in the yellow brown parts of the cotton (**Fig. 6**).

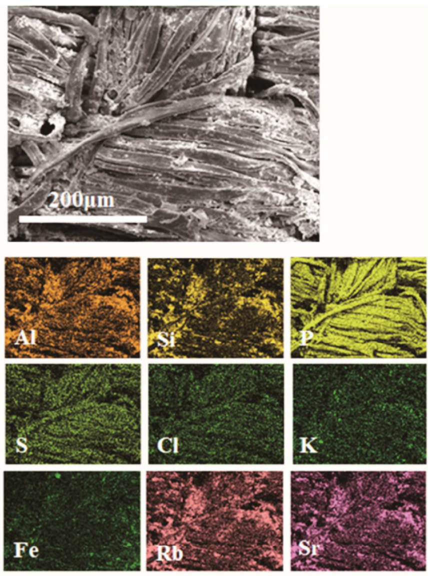

Fig 6. Scanning electron microscopy equipped with energy dispersive analysis (SEM-EDS) of yellow brown part of cotton, showing the spectra and elemental content maps of dyed cotton with various elements. The small grain spots are scattered markedly at Al, Si, Rb, and Sr.

3. SEM-EDS elemental analyses

Energy dispersive elemental analyses of black purple silk and yellow brown cotton indicated that the concentrations of Al, Si, P, S, Fe, and Sr were higher after dyeing than before dyeing (**Table 1**). The Al, Si, and Fe concentrations increased after dyeing in both of silk and cotton. Point 3 in silk and point 4 in cotton shown in “white” are without color, indicating low Al, Si, and Fe and high P, S, and Sr (**Table 1**).

Discussion

The deeply dyed parts of silk and cotton contained high concentrations of Al, Si, Fe, P, S, and Sr and small amounts of K, Ca, Cu, Zn, and Rb. The original cloths without dyeing showed high levels of P, S, and Sr before. The silk and cotton can absorb easily and reacted with Al, Si, Fe, P, S, and Sr. These elements at deeply dyed parts comprise approximately 60–70%. Therefore Al, Si, and Fe derived from black soils were used as a mordant, whereas P, S, and Sr were derived from Kurogaki tree chips (**Table 1**).

Both materials contained high levels of Al (10–16%), Si (30–43%), and Fe (13–20%) associated with P (6–15%), S (4–10%), and Sr (5–6%) after dyeing. This method is simple and causes no chemical environmental pollution.

Physical and chemical analytical data for

Table 1. Scanning electron microscopy equipped with energy dispersive analyses (SEM-EDS) of black purple parts of silk and yellow brown parts of cotton after Kurogaki chip dyeing experiments. The Al, Si, and Fe concentrations were increased after dyeing.

Hitachi ; Pt corting, acc.vol. 15KV, 1000sec.

	Silk - black purple			Cotton - yellow brown				
Elements	Point1	Point2	Point3	Point1	Point2	Point3	Point4	Point5
Na Kα1	1.38	1.59	1.86	0.67	0.64	1.30	1.66	0.79
Mg Kα1	1.11	0.80	1.22	0.83	1.18	0.81	0.75	1.01
Al Kα1	**16.52**	**16.30**	**3.65**	**13.79**	**16.51**	**7.76**	**7.08**	**10.18**
Si Kα1	**40.77**	**41.74**	**15.48**	**35.85**	**43.10**	**24.97**	**27.42**	**29.85**
P Kα1	**6.17**	**5.58**	**25.99**	**9.92**	**5.61**	**14.93**	**21.28**	**12.76**
S Kα1	**4.98**	**4.46**	**19.78**	**6.71**	**4.19**	**9.93**	**14.51**	**8.35**
Cl Kα1	0.46	0.43	2.13	1.05	0.62	1.03	1.75	1.09
K Kα1	1.84	4.51	0.50	2.14	2.62	1.43	1.68	1.66
Ca Kα1	1.73	1.46	3.66	1.28	1.27	1.35	1.13	1.42
Cr Kα1	0.10	0.04	0.02	0.07	0.00	0.04	0.00	0.00
Mn Kα1	0.26	0.17	0.70	0.19	0.20	0.00	0.06	0.15
Fe Kα1	**13.75**	**12.83**	**6.61**	**13.18**	**13.99**	**19.76**	**4.57**	**16.74**
Cu Lα1	2.40	1.75	5.14	3.38	1.73	4.79	5.07	4.18
Zn Lα1	1.80	1.24	4.05	2.67	1.31	3.88	3.78	3.38
Rb Lα1	1.25	1.29	2.02	1.76	1.33	1.82	1.84	1.84
Sr Lα1	**5.42**	**5.49**	**6.91**	**6.31**	**5.53**	**6.23**	**7.28**	**6.42**
Cd Lα1	0.00	0.01	0.00	0.00	0.00	0.00	0.06	0.00
Ba Lα1	0.26	0.19	0.30	0.21	0.16	0.08	0.08	0.19
Hg Mα1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb Mα1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pd L	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
Total %	100.20	99.98	100.02	100.01	99.99	100.11	100.00	100.01
Content			white				white	

Atomic content (%) : ±3σ　　White : not dyed parts

Makiyama black soil and Kurogaki tree trunk and roots from Tawara obtained by XRD, XRF, and inductively coupled plasma-mass spectrometry were reported previously [3, 4].

Botanical dyeing using natural materials can be performed for environmental learning in school education or life-studies lectures [5-9]. Botanical dyeing and the soil dyeing apply to many fields such as science, art, chemistry, and home economics in school education.

Our dyeing process is inexpensive, safe, simple, and easy. The tie-dyed technique can be used to make different designs on cloth based on individual creativity. Recently, the advantages of botanical materials have been revaluated not only for dyeing cloth but also for use as a hair-dye and wall paper color without using chemicals.

Dyeing cloth using botanical materials can be conducted as an alternative to traditional dyeing techniques used in Japan.

Conclusion

This study confirmed that silk cloth was dyed to a black-purple color, whereas cotton cloth was dyed to a yellow brown color using the roots and stem chips of Kurogaki tree associated with black soil without using harsh chemicals. The elements in black soil such as Al, Si, P, S, Fe, Cu, Rb, and Sr conferred 2 colors to the cloths (black-purple and yellow brown). However, the yellow brown color of cotton was richer in P, S, Cl, Cu, Zn, and Sr compared to the black-purple color of silk.

Both materials contained high levels of Al (10–16%), Si (30–43%), and Fe (13–20%) associated with P (6–15%), S (4–10%), and Sr (5–6%) after dyeing. This method is simple and does not cause chemical environmental pollution.

Acknowledgments, Author Contributions

We are grateful for the support of sampling Kurogaki tree and black soil to Teruaki Takehara, Kazunori Kobayashi, Hirono Tazaki, and Mr. and Ms. Hashida in this research.

Conceived and designed the fieldwork, sampling, operated the SEM-EDS: K.T., Interpreted the data and wrote the manuscript: K.T., A.F., F.T., Designed the Figures and Table: K.T., A.F., F.T. Authors have no competing financial interests.

References

1) Wakimoto R, Tazaki K, Nawatani N, et al, Characterization of muddy clays for “Oshima Tsumugi” using traditional dye method. Earth Science. 2004;58(4):199-214.

2) Tazaki K Characterization of lake sediments for quick and easy dyeing method in purple. Clay Science. 2004;44(2):68-80.

3) Tazaki K, Takehara T, Hashida Y, et al, Physical and chemical characteristics and biomineralization of “Scarcity Black Persimmon Tree”. Earth Science. 2017;71(3): 97-113.

4) Tazaki K, Fukuyama A, Tazaki F, et al, Electron microscopy observation of biomineralization white in wood tissues of Kurogaki. Minerals. 2017;7(7):123-145.DOI:10.3390/min7070123

5) Kimura M, Kimizuka K Study of Teaching Material in Environmental Education using Natural Dye. University Bulletin of Ibaraki-University. 2010;29:91-99.

6) Kimura M, Motogoe A Application of Natural Dyes Found in Regional Environments as Teaching Materials in Elementary Schools. University Bulletin of Ibaraki-University. 2011;30:103-112.

7) Touda Y Instruction of Natural Dyeing for Primary Schoolchild. Text of Teacher Training programs for elementary, junior high and high school science teachers, Osaka Education University Center of Science Education, 2011;17.
8) Sato H, Aragaki S, Yoshioka Y, et al, Workshop of natural dyes found in regional environments:A lifelong learning program for adults. University bulletin of Faculty of Education University of Ryukyu. 2013;83:49-54.
9) Fujiyoshi M, Hirano N, Uenishi M, et al, Utilization of Natural Dyeing to Environmental Education – Selection of Suitable Plants for Natural Dyeing in Regional Environments. Environmental Education. 2015;25(2):107-114.