

Determination of original mine of vermilion collected from ancient burial mounds in Japan using an improved sulfur isotope analytical method for small amounts of vermilion

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ABSTRACT

Vermilion was used in funerary ceremonies for decorating the physical remains and the inner surfaces of burial facilities in ancient Japan. As the sulfur isotope ratio of cinnabar ore samples taken from mines was dependent on the locality, it is thought that the original mine of vermilion can be determined from the ratio of sulfur isotope. However, although a comparatively large amount of vermilion was needed for measurement of the ratio of sulfur isotope, the amount of vermilion collected from ancient burial mounds is small in many cases. The assay method was subsequently improved, and a reliable value of sulfur isotope ratio can now be obtained when 10 mg or more of vermilion is available. The ratios of sulfur isotope from vermilion collected from three ancient tombs from the Japanese Kofun period were compared with cinnabar ore samples obtained from five mines where vermilion was probably collected at ancient times. The sulfur isotope ratio results indicated that the vermilions used in the three ancient tombs were collected from one cinnabar mine; Niu mine in Mie Prefecture in Japan.

In conclusion, a suitable method for the determination of an original cinnabar mine is to measure the sulfur isotope ratio of vermilion in burial mounds. In addition, a continuously flow system for analysis of sulfur isotope is an effective for measurement of small amounts of vermilion.

1. INTRODUCTION

In ancient times, the red-color pigments were used for decorating, painting, tattooing etc. all over the world. For these red pigments, three minerals - vermilion, red ocher, and red lead - were used [1, 2]. In addition, because a vivid red color was considered one of the most valuable symbols, vermilion was considered a precious substance among these three minerals. In Japan, it is thought that the custom of using vermilion for funerary ceremonies such as decorating the physical remains and the inner surfaces of burial facilities began from the graves of the middle of the Yayoi period. Yayoi period began about 500 B.C. in Japan, and the culture was based on wet-rice agriculture after the hunting-gathering lifestyle known as the Jomon period [3]. Numerous powerful families had fought, and it is known that some of them sent tribute to the Chinese emperor from the record of Chinese dynastic histories. The Kofun period started at the end of the 2nd century A.D. as the first unified polity called the ancient

Yamato dynasty emerged [4, 5]. Large burial mounds were constructed until the end of the Kofun period, at the end of the 6th century A.D. From the end of Yayoi to the middle of the Kofun period, several burial mounds used 10 kg or more of vermilion. Why would ancient people use such large amounts of vermilion in one burial mound? One possible explanation is to display their power to people. The custom using of vermilion for funerary ceremonies was probably transmitted from the ancient Chinese and vermilion itself was also originally imported from China to Japan with customs. However, people living in Japan had used vermilion from the Jomon period for decorating earthenware [6]. Therefore, it is suggested that people used Japanese vermilion for funerary ceremony from a certain time. We previously reported that the sulfur isotope ratio of cinnabar ore collected from Chinese mines showed positive values, while the ratio of cinnabar ore collected from Japanese mines showed negative values [7].

In addition, positive values of sulfur isotope ratio were obtained from vermilion collected from several burial mounds in northern Kyushu and the San-in area [7, 8].

If the locality of the burial goods found in graves can be clarified, more information on powerful people of the time and their movements may be known. However, it is difficult to presume the locality of the burial goods found from graves. For example, although copper mirrors are often found in Japanese grave, it is possible that the mirror was processed and/or underwent remachining. So, to determine the locality of copper is difficult from an analysis of copper. However, vermilion is a brilliant red pigment made from powdered cinnabar ore. Therefore, if the vermilion locality used in burial mounds can be clarified, more information on powerful people of the time and their movements may be known. To this end, we tried to improve the analytical method for determination of the sulfur isotope ratio using small amounts of vermilion, and attempted to discern the original mine of vermilion used for large graves in the Kofun period.

2. MATERIALS AND METHODS

We selected cinnabar mines where vermilion was collected at ancient times based on the following conditions: (i) It is known from ancient documents or ruins to have yielded vermilion. (ii) Cinnabar deposits are abundant. (iii) A cinnabar ore exists near an exposure. From these conditions, we selected two cinnabar mines in China, Wanshan of Guizhou Province and XunYang of Shaanxi Province, and three Japanese mines, Niu of Mie Prefecture, Yamato-Suigin of Nara Prefecture, and Sui of Tokushima Prefecture.

Most analyzed cinnabar ores were donated by the Geological Museum (Tsukuba, Japan) and same samples were collected on site. Archaeological samples of vermilion were donated by the Archives and Mausolea Department, Imperial Household Agency in Japan. In the present study, we collected vermilion from three ancient tombs: Tsudoshiroyama tomb in Fujiidera, Osaka, Niwa-torizuka tomb in Habikino, Osaka, and Tsukamawari tomb in Sakai, Osaka. Both Tsudoshiroyama and Niwa-torizuka tombs were built in the second half of the 4th century A.D. and Tsukamawari tomb was built in the first half of the 4th century. All three tombs were built in Osaka Prefecture of the neighboring Nara Prefecture which was the center of the ancient Yamato dynasty. It is thought that these tombs represent typical tombs from the middle of the Kofun period.

Reference materials such as S-2 as silver sulfide, S-3 as silver sulfide, and S-4 as sulfur were purchased from International Atomic Energy

Agency (IAEA) Reference Materials Group (Vienna, Austria). Both hydrochloric acid and nitric acid for ultratrace analysis and bromine were obtained from Wako Pure Chemicals (Osaka, Japan).

3. MEASUREMENT OF SULFUR ISOTOPE

After collecting vermilion from the burial mounds, sand, wood, and other materials were carefully removed from the samples under a stereomicroscope, and the samples were sonicated with concentrated HCl solution. After removing supernatants, 10 mg or more of sample was rinsed in ultrapure water. Then, the sample was added into 4 ml of reverse aqua regia and heated at 95 °C for 2 hours. After dissolving, one drop of bromine was added to the solution. The solution was then heated again at 95 °C for 2 hours, and 4 ml of ultrapure water was added into the solution after cooling. One milliliter of barium chloride (0.1 M) was added to the solution and the solution was heated at 65 °C for 2 hours to give a precipitation of barium sulfate. The precipitation was rinsed with ultrapure water several times and dried prior to analysis. About 40 µg of barium sulfate was put into a tin cup with one mg of vanadium pentoxide and sulfur dioxide gas was obtained using an elemental analyzer, vario PYRO cube (Elementar Analysensysteme GmbH, Hanau, Germany). The conditions were as follows; carrier He gas: 230 ml/min, O₂ gas: 90 sec for introduction and 38 ml/min, combustion tube: 1120 °C, reduction tube: 850 °C, sulfur dioxide column detachment temperature for sulfur dioxide gas: 280 °C. Furthermore, sulfur dioxide gas was directly induced in the isotope ratio mass spectrometer, IsoPrime100 (Isoprime Ltd. Cheadle Hulme, Cheadle, England). The peak height was set to about 1nA. The value was revised with reference materials such as S-2, S-3, and S-4. The isotope compositions are presented as conventional ratios of ³⁴S/³²S (δ³⁴S‰). The δ³⁴S value of the Canyon Diablo meteorite was employed as a standard for the ratio of primitive magma on the earth. Sulfur compounds with abundant ³⁴S have positive δ³⁴S values relative to the standard, while compounds with abundant ³²S have more negative values.

4. RESULTS AND DISCUSSION

There are many cinnabar mines in both Japan and China [9, 10]. However, we selected only five mines from historical records for the measurement of sulfur isotopes. Furthermore, we thought that people living in ancient times probably mined ore close to the surface, while we obtained ore samples from deeper locations. So, there is a question whether the value of the ore we collected reflects

the value of the ore collected in ancient times. When the sulfur isotope ratio of ore collected from different depths in one vein was measured, the ratio did not depend on the depth of the collection location [7]. In addition, Ishihara et al. [11] reported that the sulfur isotope ratio varied regionally rather than by sulfide species or type, or the commodity of the ore deposits. Therefore, we assume that the data for ore obtained from deep locations are representative of the ore that people living at ancient times would have collected from the same mine. We previously reported that the sulfur isotope ratio of cinnabar ore showed a significant difference between Japanese and Chinese mines [7]. The ratios of cinnabar ore in mines were repeatedly measured as follows: $+22.6 \pm 3.6 \text{ ‰}$ (n = 15) in Wanshan mine, $+10.5 \pm 0.1 \text{ ‰}$ (n = 4) in XunYang mine, $-7.3 \pm 1.9 \text{ ‰}$ (n = 34) in Niu mine, $-2.4 \pm 1.4 \text{ ‰}$ (n = 17) in Sui mine, and $-2.1 \pm 1.6 \text{ ‰}$ (n = 66) in Yamato-Suigin mine [8]. From these results, it is suggested that the sulfur isotope ratio of cinnabar ore of Niu mine differs significantly from the ratios of ores from both Yamato-Suigin and Sui mines, as of course the cinnabar ore from Japanese and Chinese mines can be distinguished.

In our previous reports [7], we measured the ratio of sulfur isotope using a dual inlet system. The merit of this system is that isotopic fractionation does not happen easily, but the demerit is that a large amount of sample is needed. In the burial mounds, vermilion is collected from only one point or a few points and in many cases vermilion is available in only small amounts, even if there is a large quantity of vermilion in the mound. So, the method for measurement was improved from our previous report [7] and a continuously flow system was used. The merit of the continuously flow system is that only a small amount of sample is required for analysis, while the demerit is that isotopic fractionation may occur. For the reference materials, both IAEA-S2 and IAEA-S3 showed disagreement with the value of the reference material when the starting amount of sample was less than 10 mg. However, even when the starting amounts of both IAEA-S4 and vermilion sample refined from cinnabar ore were less than 10 mg, the difference from the value of the reference material was not so large, as shown in Table 1. The standard deviation of each measured value was less than 0.2 ‰. It is thought that isotopic fractionation occurred in IAEA-S2 and IAEA-S3, while for IAEA-S4 and the vermilion sample we think that fractionation does not occur easily. The reason why isotopic fractionation occurs easily with certain materials is unknown. There are thought to be three opportunities for isotopic differentiation: when the chemical compound is dissolved, when some sulfur in the dissolved

solution vaporizes during heating, and when barium sulfate is produced.

Table 1. Relationship between the starting amount of sample and the ratio of sulfur isotope

	(mg)	(mg S)	$\delta^{34}\text{S}$ (‰)	Δ (‰)
IAEA-S2 (Ag ₂ S)	0.10	0.01	+10.31	-12.39
	3.75	0.49	+13.20	-9.50
	6.53	0.84	+16.16	-6.54
	10.00	1.29	+22.73	+0.03
	29.69	3.84	+23.02	+0.32
IAEA-S3 (Ag ₂ S)	43.25	5.60	+23.25	+0.55
	0.10	0.01	-25.66	+6.64
	3.58	0.46	-19.43	+12.87
	6.05	0.78	-24.02	+8.28
	10.00	1.29	-31.54	+0.76
IAEA-S4 (S)	34.39	4.45	-31.47	+0.83
	43.11	5.58	-31.50	+0.80
	0.10	0.10	+15.95	-0.95
	1.24	1.24	+16.77	-0.13
	3.46	3.46	+16.72	-0.13
Sample (HgS)	10.00	10.00	+16.79	-0.11
	24.61	24.61	+16.86	-0.04
	31.28	31.28	+16.83	-0.07
	3.43	0.47	-4.25	-0.79
	7.26	1.00	-4.41	-0.63
Sample (HgS)	8.00	1.10	-4.98	-0.06
	35.19	4.85	-4.79	-0.25
	42.57	5.87	-5.04	0.00

Reference value: IAEA-S2: +22.7 ‰; IAEA-S3: -32.3 ‰; and IAEA-S4: +16.9 ‰

Sample: vermilion refined from cinnabar ore

mgS: Sulfur content converted from the amount of sample

Δ : Difference from reference value

If isotopic differentiation occurs, a sample size of 10 mg or more should be used to obtain reliable data for the measurement of sulfur isotope ratio.

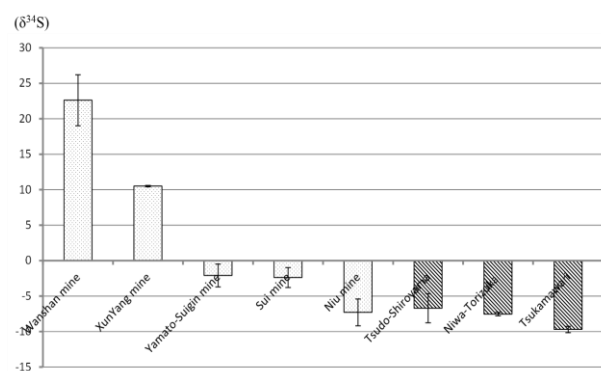


Figure 1 - Ratios of sulfur isotopes of vermilion collected from tombs of the Kofun period in Japan.

Figure 1 shows the ratios of sulfur isotopes of vermilion collected from tombs of the Kofun period in Japan. Both Tsudō-shiroyama and Niwatorizuka tombs were built in the second half of the 4th century A.D. and Tsukamawari tomb was built in the first half of the 4th century. The Kofun period was from the end of the 2nd century to end of the 6th century A.D. and the first unified polity called the ancient Yamato dynasty was established. Therefore, it is thought that these three tombs were built in the middle of the Kofun period. From these data, vermilion used in these three tombs was collected from Japanese mines, not Chinese mines. Furthermore, the value of vermilion was significantly different from the value of cinnabar ore obtained from Yamato-Suigin and Sui mines. It is suggested that vermilion using in all three tombs was obtained from the Niu mine, which is close to center of the ancient Yamato dynasty. We previously reported that vermilion obtained from burial mounds in the western regions of northern Kyushu and San'in at end of Yayoi period showed positive values [12]. The vermilion was probably imported from China. When the Kofun period began at the end of 2nd century, this negative value was observed in graves surrounding those which the positive value was observed. Japanese vermilion was probably used in those burial mounds. In addition, including the present results, it is suggested that to determine the original mine of vermilion may shed light on transitions of power in historical Japan.

In conclusion, it appears possible to determine the original mine of vermilion used for the burial mounds by using the ratio of sulfur isotope of vermilion. In addition, it is suggested that the assay method using a continuously flow system for sulfur isotope ratio is very useful when measuring small amounts of vermilion.

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