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Chemical Compositional Signatures of Constituent Minerals of Iron Slags and Ores from the Khmer Monuments

Etsuo Uchida *, Motoki Murasugi, Ayaka Kuroda and Yusu Lu

Department of Resources and Environmental Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku, Tokyo 169-8555, Japan; motoki.m@suou.waseda.jp (M.M); hati96a@gmail.com (A.K.); wilsonluyusu5133@gmail.com (Y.L.)

* Correspondence: weuchida@waseda.jp; Tel.: +81-3-5286-3318

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Abstract: Iron slags and ores were collected from 22 sites (A to V) in Preah Khan of Kompong Svay, the area surrounding Phnom Daek, and the Angkor monuments. Iron ores were taken from two outcrops in Phnom Daek. The chemical compositions of fayalite and wüstite in the iron slags and magnetite in the iron ores were determined using a scanning electron microscope equipped with an energy dispersive spectrometer. Cluster analysis and principal component analysis using averaged chemical compositional data for fayalite allowed for the investigated slag dumps to be classified into two main groups: Groups 1 and 2. The slag dumps in the area surrounding Phnom Daek and those in the Angkor monuments were classified as Group 1, and those in Preah Khan of Kompong Svay were classified as Group 2, except for sites C and U, which were classified as Group 1. Radiocarbon dating was carried out on 10 charcoal fragments from slag dumps outside the Angkor area. The dating results indicate that iron making in Preah Khan of Kompong Svay was conducted in and after the 13th century except for sites C and U, where iron ores may have been supplied from Phnom Daek before the 13th century.

Keywords: Khmer monuments; iron slag; iron ore; chemical composition; radiocarbon dating; Phnom Daek

1. Introduction

The Khmer monuments consist of Hindu and Buddhist temples built by the Khmer people between the 9th and 15th centuries. The monuments are distributed in Cambodia, Thailand, Laos, and Vietnam. The most famous and important Khmer monuments include the Angkor monuments, which are distributed mainly around Siem Reap City (Figure 1). Because the temples are built mostly of stone, iron tools, such as chisels, were required to quarry stone blocks. A scene in the bas-relief of the Inner Gallery of Bayon shows individuals quarrying stone blocks using long chisel-like sticks (Figure 2a). However, quarries in the Angkor period at the foothill of Mt. Kulen, which are located ~30 km northeast of the Angkor monuments [1], have oblique quarrying traces on their stone surface (Figure 2b). This may suggest that pickaxes, instead of long chisels, were used to quarry stone blocks (Sato and Yamaguchi, personal communication). However, incomplete bas-reliefs in some Khmer Temples, such as the Terrace of Leper King, indicate that chisels were used to carve the bas-relief. In the Khmer monuments, stone blocks were piled up without cement-like adhesives between blocks. To fasten stone blocks to each other, H-shaped crampons have been used in some places (Figure 2c) [2]. In the Ta Keo and Bakong temples, many holes remain from theft of these iron crampons (Figure 2d). Therefore, iron products were used to construct the Khmer monuments. This suggests that iron making was carried out in the Khmer period. In addition to iron tools for stone quarrying and processing, it is expected that iron was used for agricultural and military objectives [3]. Iron fragments that are considered to be part of armatures were found at the Royal Palace in the Angkor monuments [4]. As evidence of iron making, iron slags, which were generated and disposed of in the iron-making process, have been found at the Khmer monuments [5]. Many slag dumps exist in Preah Khan of Kompong Svay [6,7]. Iron ores have also been found in the slag dumps. In this study, iron slags and ores were collected from the slag dumps, and the chemical compositions of constituent minerals were analyzed to determine whether the compositions of the iron slags and ores were different, and to deduce the provenance of the iron ores. In this paper, the term "minerals" was used for convenience for the chemical phases constituting iron slags although they are not natural products [8].

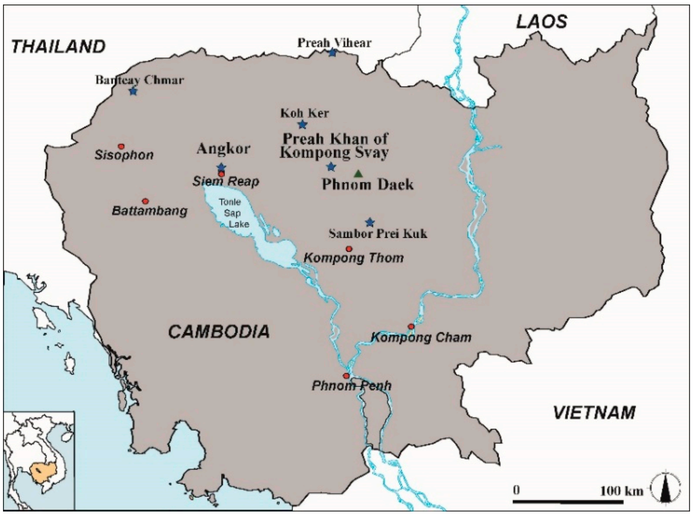

Figure 1. Map of Cambodia showing locations of the Angkor monuments, Preah Khan of Kompong Svay, and Phnom Daek.

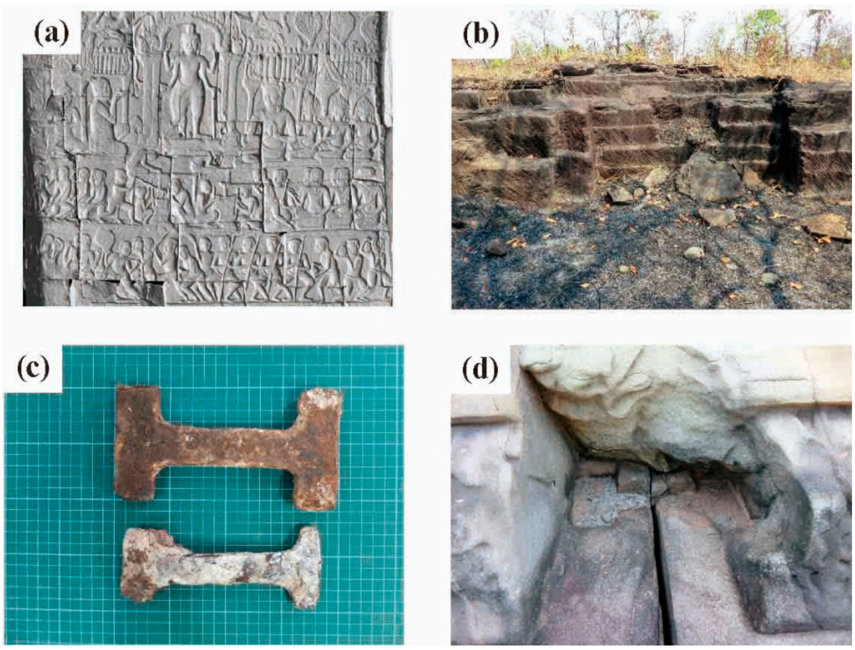

Figure 2. Evidence for iron making and iron products in the Khmer period. (**a**) Three-dimensional image of bas-relief in the Inner Gallery of Bayon, which shows individuals quarrying stone blocks using long chisel-like sticks, (**b**) traces on stone surface formed by iron tools during stone quarrying, (**c**) crampon from the Southeastern Corner Tower in the Outer Gallery of Bayon, and (**d**) a hole drilled to steal a crampon in Ta Keo.

2. Materials and Methods

2.1. Materials

The collection of iron slags and ores was carried out based on the information of Jacques and Lafond [6], Hendrickson et al. [7], Pryce et al. [9], Hendrickson and Evans [10], and local people. Iron slags and ores were collected from 22 sites (Table 1), including seven new sites (D to H, M, and V). Figure 3 shows sampling sites of the iron slags and ores in the area surrounding Phnom Daek, and Figure 4 shows those in Preah Khan of Kompong Svay.

Table 1. List of investigated iron slags and ores.

Sampling Site	Latitude	Longitude	Slag	Iron Ore
Ben Sre, PKKS (A)	13°25′05.5″ N	104°44′43.6″ E	A10	A8
Ben Sre, PKKS (B)	13°25′08.8″ N	104°44′48.9″ E	B12, 13	B11
East Gate of 4th Enclosure, PKKS (C)	13°24′38.3″ N	104°45′11.2″ E	C11, 12, 13, 15, 16	C14, 15, 16
South of causeway near East of 3rd Enclosure, PKKS (D)	13°24′38.6″ N	104°45′17.2″ E	D1, 4, 5, 7, 8	D10, 11, 12
North of causeway near East of 3rd Enclosure, PKKS (E)	13°24′42.7″ N	104°45′16.0″ E	E3, 5, 6	E1, 2, 3, 4, 5
Svay Damnak (F)	13°19′34.0″ N	104°55′08.9″ E	F1, 2, 3, 4, 5, 6	F1, 2
Prasat Suor Prat, Angkor monument (G)	13°26′47.6″ N	103°51′38.0″ E	G1, 2, 3, 4, 5, 6, 7	-
Bayon, Angkor monument (H)	13°26′27.5″ N	103°51′33.0″ E	H1, 2, 3, 4	-
Sre Tomnup, PKKS (I)	13°24′19.8″ N	104°45′31.1″ E	I3, 4, 5, 6	I1, 2
Sre Tomnup, PKKS (J)	13°24′20.8″ N	104°45′38.9″ E	J2, 4, 5	J1
Sre Tomnup, PKKS (K)	13°24′20.0″ N	104°45′39.1″ E	K2, 3, 4	K1
Trapeang Ach Daek Thom, PKKS (L)	13°24′08.5″ N	104°45′52.4″ E	L3, 4, 6	L1, 2
Trapeang Ach Daek Thom, PKKS (M)	13°24′10.5″ N	104°45′51.8″ E	M2, 3, 4	M1
Trapeang Ach Daek Toch, PKKS (N)	13°24′06.3″ N	104°46′12.3″ E	N2, 4, 5	N1
Trapeang Ach Daek Toch, PKKS (O)	13°24′06.7″ N	104°46′15.4″ E	O2, 3, 4	O1
Plau Kuk Daek, PKKS (P)	13°24′53.8″ N	104°45′12.5″ E	P2, 3	P1, 7, 8
Ben Sre, PKKS (Q)	13°25′12.0″ N	104°44′53.7″ E	Q2, 3, 4	Q1
Ben Sre, PKKS (R)	13°25′00.1″ N	104°44′31.9″ E	R2, 3, 5	R1
Sanlong Java (S)	13°16′49.2″ N	104°59′47.0″ E	S5, 6, 8	S1, 2, 3, 4
Sanlong Tonle Bak (T)	13°17′16.6–18.1″ N	105°00′43.3–48.3″ E	T1, 2, 3, 4	T1, 2, 4
Trapeang Sanlong, PKKS (U)	13°24′24.8″ N	104°45′44.9″ E	U1, 2, 3	U4, 5, 6
Angkor Thom, Angkor monument (V)	-	-	V1	-
Iron mine 1, Phnom Daek	13°19′13.7″ N	105°00′35.2″ E	-	MINE1-2, 1-3, 1-7
Iron mine 2, Phnom Daek	13°19′31.0″ N	105°00′45.0″ E	-	MINE2-2, 2-4, 2-5

Abbreviation: PKKS: Preah Khan of Kompong Svay.

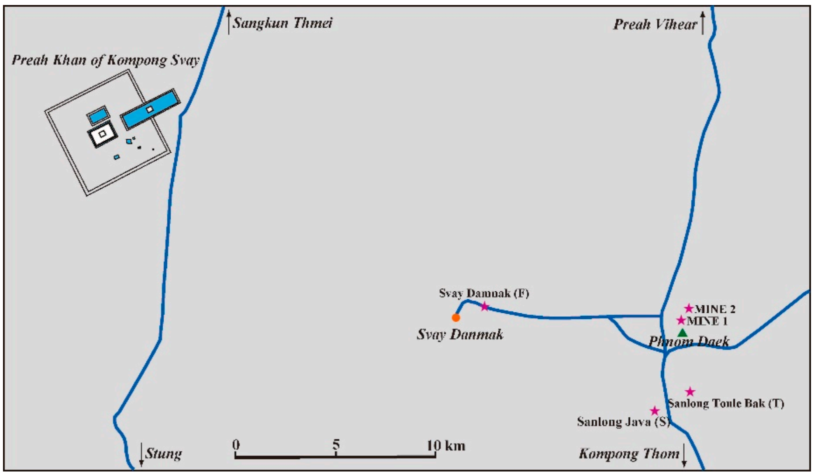

Figure 3. Map showing locations of Preah Khan of Kompong Svay and Phnom Daek.

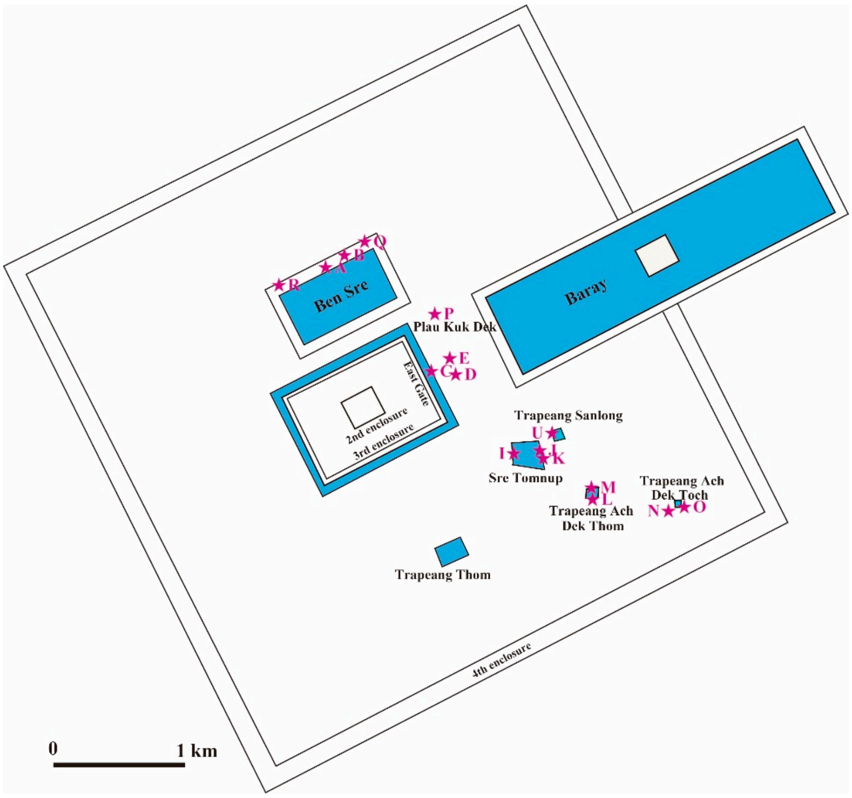

Figure 4. Plan of Preah Khan of Kompong Svay showing sampling sites of iron slags and ores.

Most iron slags and ores were collected from Preah Khan of Kompong Svay, where sampling was performed mainly on the bank of the Baray called Ben Sre, at banks of small ponds between the third and fourth Enclosures, and at three sites near the East Gopura of the third Enclosure.

We collected iron slags and ores from two sites (Sanlong Java (S) and Sanlong Tonle Bak (T)) in the south of Phnom Daek (meaning Iron Mountain), which is situated 30 km southeast of Preah Khan of Kompong Svay and has been considered as the source of iron ores in the Khmer period [4]. We also collected samples from one site (F) at the roadside near Svay Damnak between Preah Khan of Kompong Svay and Phnom Daek.

We analyzed iron slags from Bayon (G) and Prasat Suor Prat (H) in the Angkor monuments found during the excavation by the Japanese Government Team for Safeguarding Angkor (JSA). One iron slag was collected by a member of JSA in the forest southeast of the Bayon Temple of Angkor Thom (V), and was analyzed. To date, iron ore has not been found at the Angkor monuments.

We sampled iron ores from two outcrops (MINE 1 and MINE 2) in Phnom Daek. The iron deposit in Phnom Daek is of hydrothermal origin and is related to the magnetite-series granodiorite of the late Jurassic to early Cretaceous periods [11].

Fragments of charcoal that was used as fuel and reducing agent rarely remain in the iron slags. Ten charcoal fragments were collected from the iron slags for radiocarbon dating; six samples were from Preah Khan of Kompong Svay; two samples were from Svay Damnak; and two samples were from Sanlong Java.

2.2. Methods

After embedding 1–2 cm-diameter iron slag or ore fragments in an epoxy resin (EpoFix, Struers), the mounts were ground with waterproof silicon-carbide papers (#80, #180, #800, #1200, and #2400, Struers) and were polished with 3 μm and then $\frac{1}{4}$ μm diamond pastes (Struers Diamond Pastes M and P, respectively).

The polished slag and ore samples were studied under a reflected polarizing microscope, and mineral identification was carried out. The chemical composition analyses of minerals that constituted iron slags and ores were conducted on a polished cross section of each sample using a scanning electron microscope (JSM-6300, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (INCA Energy, Oxford Instruments, Abingdon, UK) (SEM-EDX). The samples were coated with carbon. The accelerating voltage was fixed at 15 kV, and the beam current was adjusted so that the X-ray count was 2000 count/s on the Co surface. The analysis time at each point was fixed at 60 s. For each sample, the analysis was carried out on three to 10 grains of fayalite and wüstite, respectively, and 3 to 6 grains of magnetite for each sample.

Radiorcarbon dating was carried out on the charcoal fragments that were collected from the iron slags. Measurements were carried out by Paleo Labo Co., Ltd. [12].

3. Results

3.1. Descriptions of Materials

3.1.1. Iron Ores

Iron ores from the slag dumps and outcrops in Phnom Daek consisted mainly of magnetite and hematite (Figure 5a). We observed a texture where hematite replaced the magnetite in part. Therefore, it is thought that the iron ores consisted mainly of magnetite initially, and that the magnetite changed partly to hematite by hydrothermal alteration. The iron ores are commonly accompanied with quartz, and grandite-series garnet was present in the iron ores that were collected near Svay Damnak. These facts suggest that iron ores were formed by a hydrothermal metasomatism of carbonate rocks, which is related to granitic rocks.

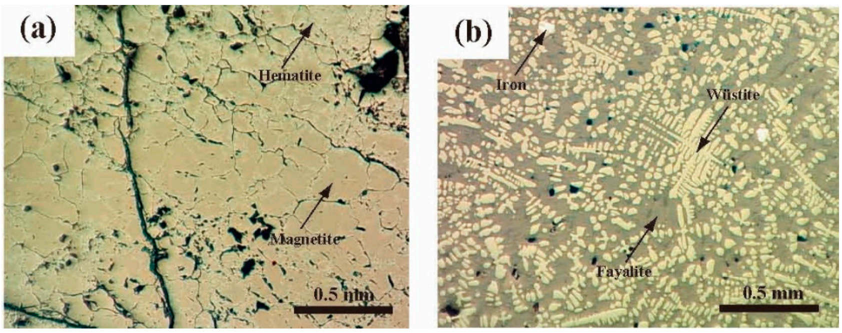

Figure 5. Photomicrographs of iron slags and ores under reflected polarizing microscope. (**a**) magnetite (grey) partly replaced by hematite (grey white) (sample no. C14-3), and (**b**) fayalite (dark grey) and wüstite (yellow) in iron slag with a small amount of iron (white) (sample no. D7).

3.1.2. Iron Slags

The iron slags consist mainly of fayalite and wüstite (Figure 5b). Wüstite shows a skeletal texture often. In addition to the two minerals, magnetite or metallic iron was observed under the microscope, but these never coexisted. A small amount of hercynite was commonly observed.

Fragments of charcoal that was used as a fuel and as a reducing agent were rarely included in the iron slags. Metallic iron is often seen around the charcoal fragments.

3.2. Chemical Compositions

3.2.1. Fayalite in the Iron Slags

The ideal chemical formula of fayalite is expressed as Fe_2SiO_4. Because fayalite in the iron slags contains some MnO and MgO, fayalite was treated as a solid–solution in the system fayalite

(Fa)–tephroite (Tep)–forsterite (Fo). The presence of CaO up to 18 wt.% indicates that fayalite (olivine) forms a solid–solution with kirschsteinite (Ca(Fe,Mg,Mn)SiO_4). The analytical results are shown in Figure 6 as Fa–Tep–Fo triangular diagrams (Table S1). It was shown experimentally that fayalite forms a continuous solid–solution with tephroite and forsterite under hydrothermal conditions [13].

A cluster analysis was performed using the averaged chemical compositional data for fayalite (Table 2) from each site. Excel Tokei for Windows (Social Survey Research Information Co., Ltd., Tokyo, Japan) was used for a cluster analysis. The result for a cluster analysis using Ward's method is shown in the dendrogram in Figure 7. The slag dumps were classified into two main groups: Groups 1 and 2. Fayalite in the iron slags of Group 1 is rich in FeO and depleted in MnO, MgO and CaO, but that of Group 2 is enriched in MnO, MgO, and/or CaO. Group 2 could be classified into five subgroups: Groups 2-A to 2-E. Fayalite of Group 2-A is rich in CaO > MnO = MgO; that of Group 2-B is rich in MnO = CaO > MgO; that of Group 2-C is rich in MgO > MnO, but is depleted in CaO; that of Group 2-D is rich in MnO > CaO, but is depleted in MgO; and that of Group 2-E is rich in MgO > MnO > CaO.

A principal component analysis (PCA) was also carried out using the data in Table 2 to clarify the factors controlling the classification in the cluster analysis. The results were shown in Figure 8. The slag dumps were classified into two groups the same as the cluster analysis. However, Group 2-D and Group 2-E obtained in the cluster analysis overlap each other on a PC1 vs. PC2 diagram. This is because positions of MnO and MgO are close to each other on the PC1 vs. PC2 diagram (Figure 8). On the other hand, they were well separated on a PC1 vs. PC3 diagram.

Slag dumps in the area surrounding Phnom Daek and those in the Angkor monuments were classified as Group 1, and those in Preah Khan of Kompong Svay were classified as Group 2 except for sites C and U.

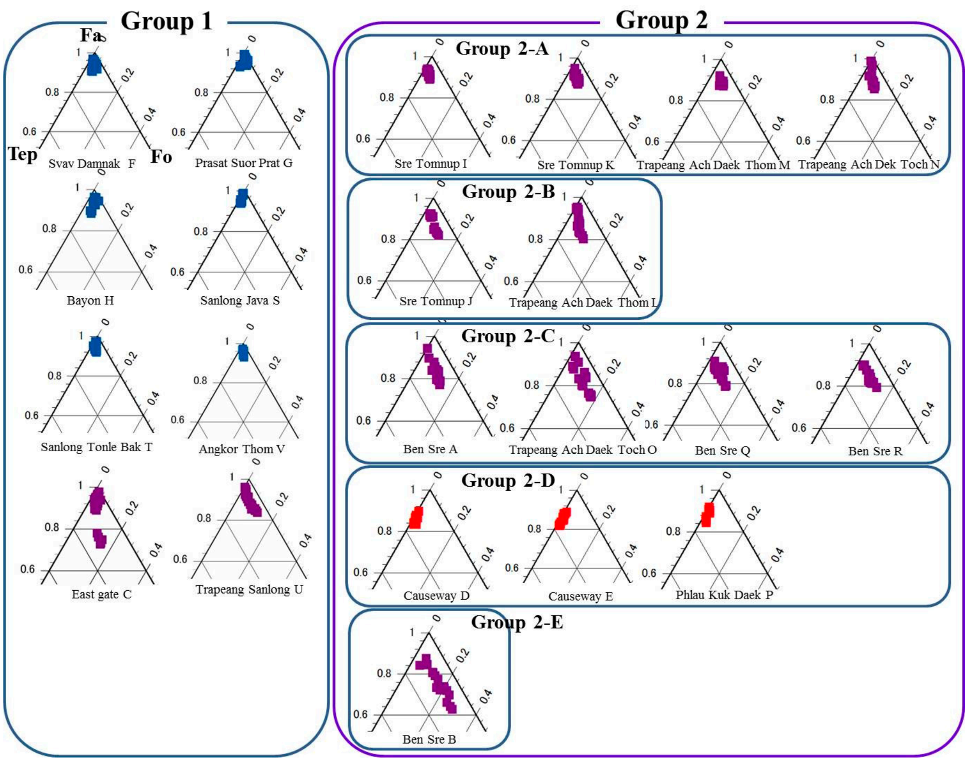

Figure 6. Fayalite (Fa)–Tephroite (Tep)–Forsterite (Fo) triangular diagrams showing chemical composition of fayalite in iron slags from the Khmer monuments. Grouping is based on a cluster analysis using the averaged chemical compositions of fayalite in the iron slags.

Table 2. Averaged chemical compositional data for fayalite in iron slags at each site (wt.%).

Group *	Site	SiO_2	Al_2O_3	FeO	MnO	MgO	CaO
2-C	Site A	29.95 ± 0.40 **	0.28 ± 0.08 **	60.27 ± 2.40 **	5.22 ± 0.79 **	3.51 ± 1.38 **	0.76 ± 0.34 **
2-E	Site B	31.62 ± 0.69	0.27 ± 0.36	53.61 ± 2.64	5.65 ± 1.01	6.49 ± 3.43	2.37 ± 2.26
1	Site C	27.98 ± 1.80	0.37 ± 0.21	67.55 ± 5.67	2.76 ± 2.79	0.97 ± 1.87	0.45 ± 0.36
2-D	Site D	29.86 ± 2.01	0.33 ± 0.19	57.88 ± 2.42	9.08 ± 1.51	0.40 ± 0.16	2.45 ± 1.68
2-D	Site E	30.12 ± 0.33	0.29 ± 0.24	58.63 ± 0.85	8.74 ± 1.00	0.47 ± 0.22	1.75 ± 1.17
1	Site F	31.49 ± 1.66	0.42 ± 0.37	64.32 ± 2.22	2.17 ± 0.92	1.01 ± 0.48	0.59 ± 0.23
1	Site G	30.57 ± 0.96	0.17 ± 0.13	66.80 ± 1.45	0.75 ± 1.05	0.82 ± 0.47	0.90 ± 0.54
1	Site H	31.16 ± 0.49	0.14 ± 0.11	62.93 ± 2.40	2.11 ± 1.53	1.27 ± 0.38	2.39 ± 1.10
2-A	Site I	30.18 ± 0.42	0.13 ± 0.12	57.33 ± 5.48	3.30 ± 0.65	0.90 ± 0.44	8.17 ± 5.73
2-B	Site J	29.44 ± 3.77	0.25 ± 0.38	57.97 ± 8.57	3.60 ± 0.92	2.00 ± 1.32	3.56 ± 1.94
2-A	Site K	32.41 ± 1.08	0.17 ± 0.11	53.91 ± 5.58	3.05 ± 0.48	1.50 ± 0.62	8.96 ± 5.71
2-B	Site L	29.54 ± 0.77	0.29 ± 0.20	59.85 ± 5.65	4.45 ± 1.50	1.76 ± 0.33	4.11 ± 5.32
2-A	Site M	30.98 ± 0.66	0.20 ± 0.30	49.97 ± 2.67	2.92 ± 0.43	1.76 ± 0.33	14.19 ± 2.20
2-A	Site N	30.46 ± 0.68	0.20 ± 0.14	58.21 ± 6.44	2.44 ± 1.19	1.48 ± 0.97	7.22 ± 4.50
2-C	Site O	30.23 ± 1.20	0.35 ± 0.26	59.88 ± 4.02	4.71 ± 1.13	4.52 ± 2.45	0.31 ± 0.12
2-D	Site P	29.09 ± 0.47	0.45 ± 0.32	61.11 ± 1.13	7.11 ± 1.51	0.49 ± 0.26	1.76 ± 1.12
2-C	Site Q	29.44 ± 0.52	0.62 ± 0.21	61.07 ± 1.31	5.02 ± 1.12	3.02 ± 1.02	0.84 ± 0.54
2-C	Site R	30.74 ± 0.42	0.20 ± 0.11	59.67 ± 1.20	5.46 ± 0.48	3.33 ± 1.10	0.61 ± 0.41
1	Site S	29.96 ± 0.49	0.58 ± 0.74	66.24 ± 1.19	2.17 ± 0.88	0.33 ± 0.21	0.72 ± 0.54
1	Site T	29.15 ± 0.78	0.46 ± 0.59	66.97 ± 1.65	2.26 ± 0.96	0.62 ± 0.41	0.54 ± 0.35
1	Site U	28.27 ± 2.26	1.04 ± 1.88	64.67 ± 2.54	3.50 ± 0.43	2.16 ± 1.38	0.34 ± 0.32
1	Site V	30.21 ± 2.12	0.13 ± 0.12	66.58 ± 2.75	1.54 ± 0.35	0.91 ± 0.32	0.63 ± 0.37

* Grouping is based on a cluster analysis using the averaged chemical compositional data for fayalite in iron slags.
** Standard deviation (2σ).

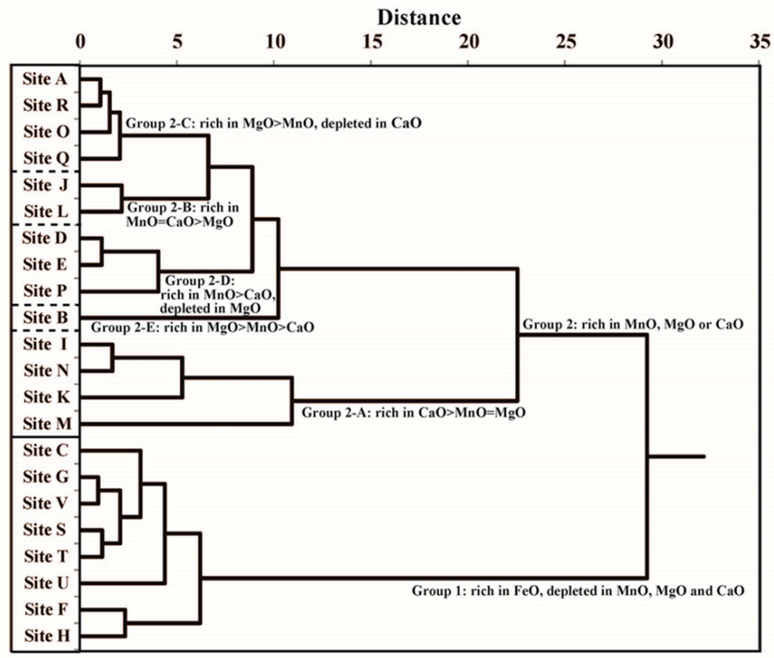

Figure 7. Dendrogram obtained from a cluster analysis (Ward's method), using averaged chemical compositional data for fayalite in iron slags from each site (Table 2). The iron slag sites were classified into two groups: Groups 1 and 2. Group 2 could be classified into five subgroups: Groups 2-A to 2-E.

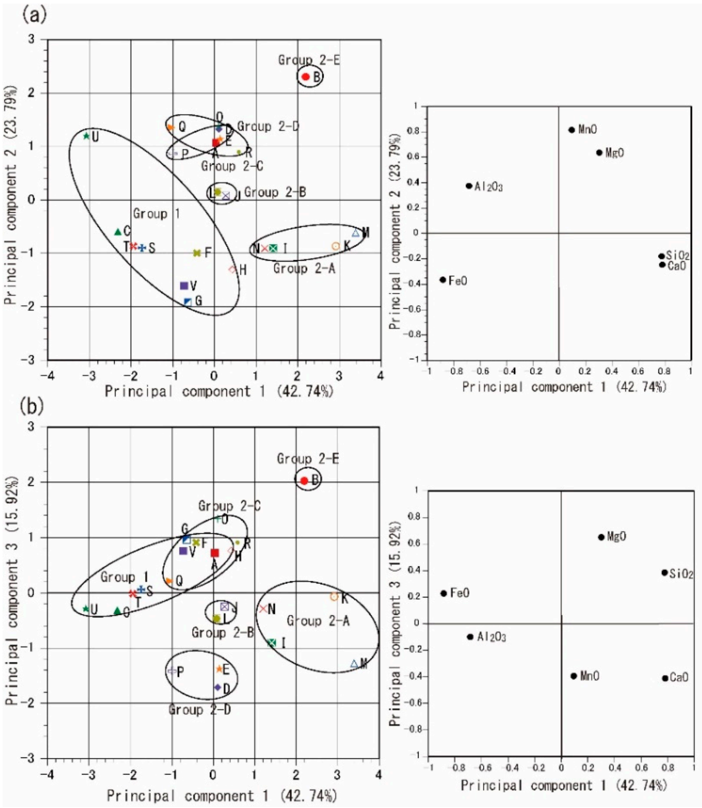

Figure 8. Results of a principal component analysis (PCA), using averaged chemical compositional data for fayalite in iron slags from each site (Table 2). The iron slag sites A to V were classified into two groups: Groups 1 and 2. Group 2 could be classified into five subgroups: Groups 2-A, 2-B, 2-C, 2-D, and 2-E. Group 2-C and Group 2-D separated in the cluster analysis overlap each other on a PC1 vs. PC2 diagram by a PCA (**a**), but they were well separated on a PC1 vs. PC3 diagram (**b**).

3.2.2. Wüstite in Iron Slags

The ideal chemical formula of wüstite is expressed as FeO, or more precisely as $Fe_{1\text{-}x}O$. Wüstite in the analyzed slags contains some MnO and also small amounts of SiO_2, Al_2O_3, TiO_2, and CaO (Table S2). We treated wüstite as a solid–solution between FeO and MnO. The analytical results are shown and compared in Figure 9 as FeO vs. MnO diagrams. The MnO content in wüstite is low compared with fayalite because the partitioning of MnO into wüstite against fayalite is very low. The MnO content in wüstite depends on the crystallization temperature and speed. Wüstite in the iron slags of Group 1 is depleted in MnO (less than 1.5 mol%), except for some iron slags in sites C and U. However, wüstite in Group 2 is relatively rich in MnO, except for that in Group 2-A, which is rather rich in CaO. The MnO content ranges from 0 to 4 mol% in Group 2. A large overlap was found in the chemical compositions of wüstite between Groups 1 and 2.

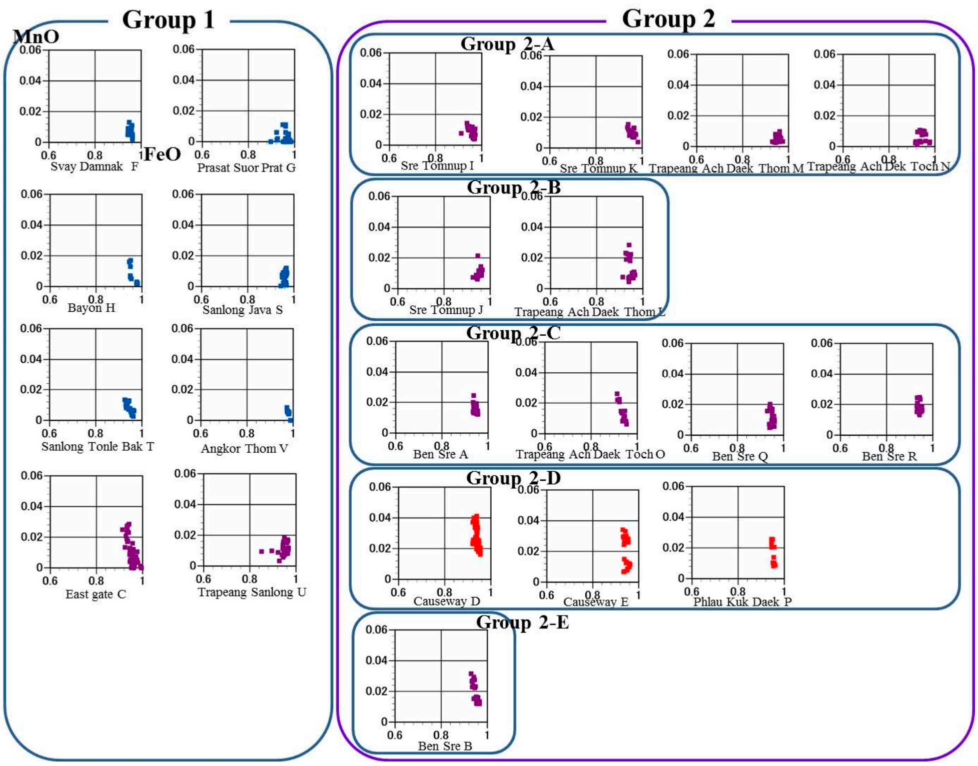

Figure 9. FeO–MnO diagrams showing mole fractions of FeO and MnO of wüstite in iron slags from the Khmer monuments. Grouping is based on the averaged chemical compositional data for fayalite in the iron slags.

3.2.3. Magnetite in Iron Ores

The analyzed magnetite in the iron ores is composed mainly of Fe_2O_3, FeO, MnO, and MgO with small amounts of SiO_2, Al_2O_3, and TiO_2 (Table S3). Magnetite (Mgt) forms a continuous solid solution with jacobsite (Ja) and magnesioferrite (Mgf) under hydrothermal conditions [14]. The Mgt, Ja, and Mgf contents were calculated as follows. The chemical composition of magnetite can be expressed as AB_2O_4. In the calculation of Mgt, Ja, and Mgf in magnetite, it was assumed that Fe^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+} enter the A site and that Fe^{3+}, Si^{4+}, T^{i4+}, and Al^{3+} enter the B site. The total analyzed iron was divided into FeO and Fe_2O_3 so that the ratio of A to B is 1:2.

The chemical compositions of magnetite in the iron ores were plotted in Mgt–Ja–Mgf triangular diagrams (Figure 10). According to the grouping based on the chemical compositions of fayalite in the iron slags, magnetite of Group 1 contains less than a few mol% of Ja + Mgt, except for some iron slags in C and U sites, and that of Group 2 contains a large amount of Ja + Mgt up to 40 mol%, except for Group 2-D. Although fayalite of Group 2-D is rich in Tep, the Ja content in the magnetite of Group 2-D is low, at less than several mol%. This result is comparable with the Ja content in the magnetite of Group 1. Although the magnetite of Groups 1 and 2-D is depleted in Ja and Mgf, the magnetite of Group 2-D appears to be slightly richer in Ja compared with that of Group 1.

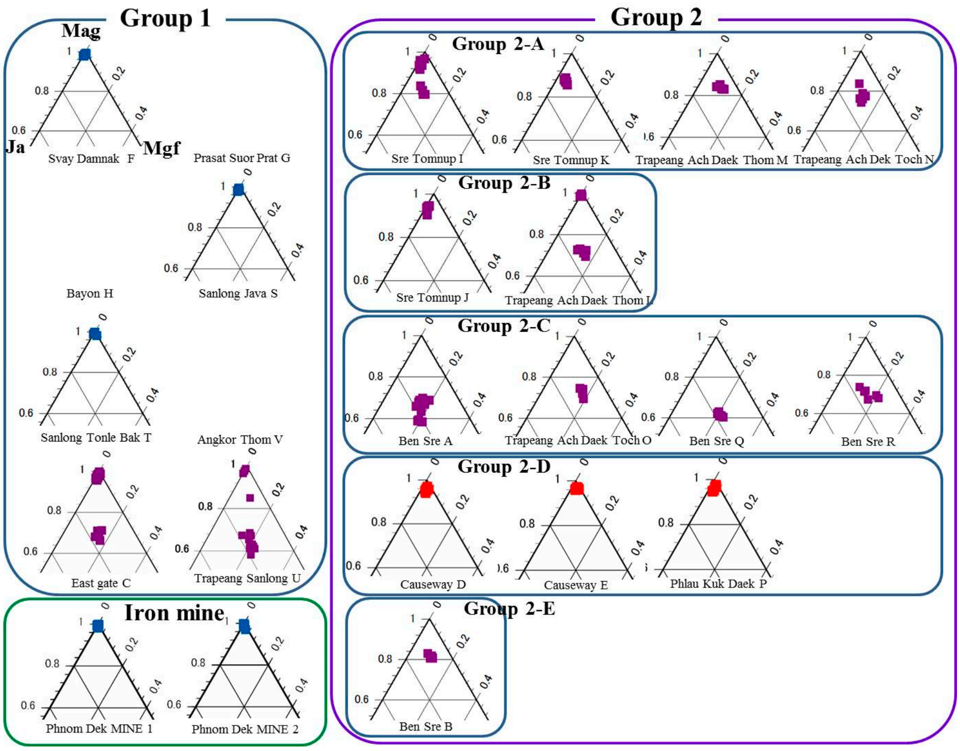

Figure 10. Magnetite (Mgt)–jacobsite (Ja)–magnesioferrite (Mgf) triangular diagrams showing chemical composition of magnetite in iron ores from the Khmer monuments and Phnom Daek. Grouping is based on the averaged chemical compositional data for fayalite in the iron slags.

The contents of Ja and Mgf in magnetite in the iron ores from the outcrops in Phnom Daek are low, at less than several mol% in total, and these contents are the same as those of the magnetite of Group 1, but are slightly different from those of the magnetite of Group 2-D.

3.3. Radiocarbon Dating

Radiocarbon dating was carried out on 10 charcoal fragments from iron slags at the following sites: two samples from Ben Sre (A) in Preah Khan of Kompong Svay, one sample near the Eastern Gopura (C) in Preah Khan of Kompong Svay, two samples from the south (D) and north sides (E) of the causeway near the Eastern Gopura in Preah Khan of Kompong Svay, one sample from Phlau Kuk Daek (P) in Preah Khan of Kompong Svay, two samples from Svay Damnak (F), and two samples from Sanlong Java (S) (Figure 3; Figure 4).

The radiocarbon-dating results are summarized in Table 3. The $\delta^{13}C$ values were used in the calculation of the radiocarbon age and error to correct for isotopic fractionation in nature. Only two charcoal samples from Svay Damnak (F) were older than the 13th century, that is, from the 11th to 12th centuries. Other samples were from the 13th century and later. The two samples from Sanlong Java (S) were youngest, from the 17th to 20th centuries.

Table 3. Radiocarbon ages for charcoal fragments from iron slags from the Khmer monuments.

Lab No. (PLD-)	Sample No.	Sampling Point	$\delta^{13}C$ (‰)	^{14}C Age (yrBP ± 1σ)	Calibrated ^{14}C Age (Probability)	
					1σ	2σ
PLD-19382	No. A-1	Ben Sre, Preah Khan of Kompong Svay	−28.65 ± 0.14	390 ± 20	1451–1486 cal AD (68.2%)	1445–1515 cal AD (82.8%) 1600–1618 cal AD (12.6%)
PLD-19383	No. A-2	Ben Sre, Preah Khan of Kompong Svay	−28.57 ± 0.15	390 ± 20	1450–1485 cal AD (68.2%)	1445–1513 cal AD (84.2%) 1601–1617 cal AD (11.2%)
PLD-30928	No. C-1	near East Gate of 3rd Enclosure, Preah Khan of Kompong Svay	−24.01 ± 0.29	535 ± 20	1400–1425 cal AD (68.2%)	1326–1344 cal AD (12.4%) 1394–1432 cal AD (83.0%)
PLD-30929	No. D-1	South of causeway near East Gate of 3rd Enclosure, Preah Khan of Kompong Svay	−24.51 ± 0.35	440 ± 20	1436–1453 cal AD (68.2%)	1426–1470 cal AD (95.4%)
PLD-30930	No. E-1	North of causeway near East Gate of 3rd Enclosure, Preah Khan of Kompong Svay	−28.54 ± 0.29	745 ± 20	1263–1278 cal AD (68.2%)	1248–1286 cal AD (95.4%)
PLD-32588	No. F-1-2	Svay Damnak	−26.72 ± 0.31	965 ± 20	1025–1045 cal AD (30.2%) 1095–1120 cal AD (32.1%) 1141–1147 cal AD (5.9%)	1020–1054 cal AD (35.6%) 1078–1154 cal AD (59.8%)
PLD-32589	No. F-4	Svay Damnak	−24.30 ± 0.19	940 ± 15	1036–1050 cal AD (12.5%) 1083–1126 cal AD (41.3%) 1136–1151 cal AD (14.3%)	1030–1059 cal AD (21.1%) 1064–1154 cal AD (74.3%)
PLD-30931	No. P-1	Phlau Kuk Daek, Preah Khan of Kompong Svay	−27.36 ± 0.30	635 ± 20	1297–1315 cal AD (25.1%) 1356–1388 cal AD (43.1%)	1289–1325 cal AD (38.1%) 1345–1394 cal AD (57.3%)
PLD-32476	No. S-1	Sanlong Java	−27.20 ± 0.15	205 ± 20	1661–1671 cal AD (15.3%) 1778–1799 cal AD (34.3%) 1942–1954 cal AD (18.6%)	1652–1681 cal AD (26.0%) 1738–1751 cal AD (3.4%) 1762–1802 cal AD (45.0%) 1937–1955 cal AD (21.0%)
PLD-32477	No. S-2	Sanlong Java	−26.15 ± 0.18	140 ± 20	1680–1695 cal AD (11.3%) 1726–1739 cal AD (9.6%) 1743–1763 cal AD (11.8%) 1801–1813 cal AD (8.7%) 1837–1842 cal AD (2.7%) 1853–1860 cal AD (3.6%) 1860–1867 cal AD (3.8%) 1874–1875 cal AD (0.6%) 1918–1938 cal AD (16.1%)	1670–1700 cal AD (15.2%) 1702–1707 cal AD (0.6%) 1719–1779 cal AD (29.5%) 1799–1819 cal AD (11.0%) 1823–1825 cal AD (0.3%) 1832–1881 cal AD (20.2%) 1914–1943 cal AD (18.2%) 1952–1953 cal AD (0.3%) 1954–1955 cal AD (0.1%)

4. Discussion

4.1. Sources of Iron Ores

The slag dumps could be classified into two main groups by a cluster analysis and a principal component analysis using the averaged chemical compositional data for fayalite in the iron slags. The slag dumps of Group 2 are located in Preah Khan of Kompong Svay. Except for Group 2-D, they are located at the waterside, such as reservoirs, ponds, and a moat. The slag dumps of Group 1 are located in places other than Preah Khan of Kompong Svay except for sites C and U, that is, in the area surrounding Phnom Daek (Sanlong Tonle Bak (T), Sanlong Java (S), and Svay Damnak (F)), and in the Angkor area (Bayon (H), Prasat Suor Prat (G), and Angkor Thom (V)).

Fayalite in the iron slags, and magnetite in the iron ores from the slag dumps of Group 1 are depleted in MnO, MgO, and CaO except for some iron slags from sites C and U. MnO, MgO, and/or CaO contents were relatively high in minerals in the slag dumps of Group 2, except for magnetite in the iron slags of Group 2-D. The chemical compositions of fayalite in Sre Tomnap (I and K) and Trapeang Ach Daek Thom (M) of Group 2-A are similar to those of the slag dumps of Group 1 in Figure 6, but fayalite in these slag dumps is rich in CaO, and the chemical compositions of magnetite in these slag dumps are considerably different from those of the slag dumps of Group 1.

In terms of the chemical compositions of wüstite, Groups 1 and 2 exhibit a similar tendency to that of fayalite with some exceptions: wüstite in Group 1 is depleted in MnO except for some iron slags from sites C and U, but that in Group 2 is relatively rich in MnO, except for Group 2-A. The MnO content of wüstite from sites C and U appears to lie between that of Groups 1 and 2. Wüstite in Group 2-A is rich in CaO compared with that of Group 1.

Fayalite in Group 2-D contains almost no MgO, but is rich in MnO (7–20 mol%), which is different from that of Groups 2-A to 2-C and 2-E. The MnO content of wüstite in Group 2-D is high, and is similar to that of Groups 2-B, 2-C, and 2-E. However, magnetite in Group 2-D is depleted in MnO and MgO but is slightly rich in MnO and MgO compared with the magnetite of Group 1, except for sites C and U.

The iron-ore samples were taken from two outcrops (MINE 1 and MINE 2) in Phnom Daek. These iron ores consist mainly of magnetite, and show a texture under a reflected polarizing microscope in which magnetite is replaced partially by hematite. This texture is similar to that of iron ores from the slag dumps. Magnetite in the iron ores from the outcrops in Phnom Daek contains almost no MgO or MnO and has a similar chemical signature to the iron ores from the slag dumps of Groups 1 and 2-D. This may suggest that the iron ores of Groups 1 and 2-D have been supplied from Phnom Daek. However, because magnetite of Group 2-D tends to be slightly rich in MgO and MnO compared with that of Group 1 and Phnom Daek, it is possible that the iron ores of Group 2-D have been supplied from an iron mine other than Phnom Daek.

Pryce et al. [9] conducted whole chemical analysis using SEM-EDX for iron slags and ores from Ben Sre (A and B), Sanlong Java (S), Sanlong Tonle Bak (T), and Trapeang Ach Daek Toch (O), and also for iron ores from Phnom Daek. They found that the iron slags from Sanlong Java (S) and Sanlong Tonle Bak (T), which belong to Group 1 of this study, contained lower MnO, MgO, and CaO contents, but the MnO, MgO, and CaO contents of the iron slags from Ben Sre (A and B), which were classified as Groups 2-C and 2-E, respectively, were higher. The MnO, MgO, and CaO contents of the iron slags from Trapeang Ach Daek Toch (O) range from high to low. The iron ores from Phnom Daek were depleted in MnO, MgO, and CaO. The chemical compositional results for fayalite in iron slags and magnetite in iron ores obtained in this study are consistent with the chemical compositional results for iron slags and ores by Pryce et al. [9].

Magnetite can contain MnO (Ja) and MgO (Mgf) at any ratio under high-temperature and high-pressure conditions. However, because natural hydrothermal magnetite is rarely enriched in MnO and MgO, it can be said that the iron ores of Group 2, except for Group 2-D have a characteristic chemical composition. The magnetite grain size in the iron ores is medium to large and the iron ores are accompanied frequently by quartz. Therefore, we deduce contact metasomatism of carbonate rocks that are rich in MnO and MgO through a hydrothermal fluid derived from granitic magma as the formation environment of the iron ores of Group 2, except for Group 2-D. No information exists on iron mines in Cambodia that produce magnetite that is rich in MnO and MgO.

4.2. Dating for Charcoal Fragments from Iron Slags

Radiocarbon dating was performed on 10 charcoal fragments from the slag dumps, on 15 charcoal fragments by Hendrickson et al. [7], and on 10 charcoal fragments by Pryce et al. [9]. No charcoal fragments were present in the iron slags from the Angkor monuments.

Except for the slag dump (C) near the Eastern Gopura, the charcoal fragments from Preah Khan of Kompong Svay showed radiocarbon ages from the 13th century and later (Table 3). The ages for the iron slags of the slag dump (C) range from the 10th to the 17th centuries.

Relatively old ages were obtained for the iron slags from Sanlong Tonle Bak (T) and Svay Damnak (F) from the 7th to the 12th centuries and the 11th to the 12th centuries, respectively. In contrast, the iron slags from Sanlong Java (S) showed younger ages from the 17th to 20th centuries. Many charcoal fragments originated after 1431 when the Angkor Empire had fallen. This suggests that iron making was practiced during the post-Angkor period.

Because Phnom Daek is located close to Preah Khan of Kompong Svay, it has been thought that iron ores were supplied from Phnom Daek to Preah Khan of Kompong Svay during the Angkor period. The chemical compositions of constituent minerals of the iron slags and ores indicate that the iron ores used in Preah Khan of Kompong Svay, except for part of the iron ores in sites C and U, were supplied from an iron mine that is different from Phnom Daek. The radiocarbon-dating results indicate that iron ores rich in MnO and MgO were supplied in and after the 13th century from iron mines other than Phnom Daek. It is highly likely that the iron ores were supplied from Phnom Daek to Sanlong Java, Sanlong Tonle Bak, and Svay Damnak, which are situated near Phnom Daek. Iron ores in sites C and U may have been supplied from Phnom Daek before the 13th century. Because the iron slags from the Angkor area are depleted in MnO and MgO, the iron ores may have been supplied from Phnom Daek to the Angkor area. However, because iron ores with such chemical compositions are common, it cannot be concluded that the iron ores used in the Angkor area were supplied from Phnom Daek. According to the geological map of Tbeng Meanchey published in 1972 by Bureau de Recherches Géologiques et Minières of France, iron mines which were not yet investigated, are located about 5 km east of Phnom Kulen.

5. Conclusions

Chemical composition analyses using SEM-EDX were carried out for fayalite and wüstite in the iron slags and magnetite in the iron ores from the slag dumps in Preah Khan of Kompong Svay, the area surrounding Phnom Daek, and the Angkor area. On the basis of a cluster analysis and a principal component analysis using the averaged chemical compositional data for fayalite, the slag dumps were largely classified into two groups: the slag dumps in Preah Khan of Kompong Svay, except for sites C and U, were classified as Groups 2, and the other slag dumps were classified as Group 1. Fayalite of Group 1 was depleted in MnO, MgO, and CaO, except for sites C and U, whereas that of Group 2 was enriched in MnO, MgO, and/or CaO. Group 2 could be classified into five subgroups: Groups 2-A to 2-E. Fayalite in the iron slags of Groups 1 and 2 has a similar chemical compositional trend to magnetite in the iron ores of Groups 1 and 2, respectively, except for Group 2-D. Because magnetite in the iron ores in Phnom Daek is depleted in MnO and MgO, Phnom Daek does not appear to have been a source of iron ores related to Group 2, except for Group 2-D of Preah Khan of Kompong Svay. The mineral chemical compositions indicate that the iron ores of Group 1 have been supplied from Phnom Daek, but as for sites C and U of Group 1, iron ores may have been supplied from Phnom Daek before the 13th century. The iron ores of Group 2-D may have been supplied from an iron mine other than Phnom Daek.

Radiocarbon dating was carried out on 10 charcoal fragments from slag dumps outside the Angkor area. A combination of dating results with those by Hendrickson et al. [7] and Pryce et al. [9], indicates that iron making in Preah Khan of Kompong Svay was conducted in and after the 13th century except for sites C and U, where iron ores may have been supplied from Phnom Daek before the 13th century. The iron slags of Sanlong Tonle Bak (T) and Svay Damnak (F) were relatively old, and are believed to be from the 7th to the 12th centuries, but the iron slags of Sanlong Java (S) were considered younger and from the 17th to 20th centuries.

Supplementary Materials: The following are available online at http://www.mdpi.com/2571-9408/2/2/105/s1: Table S1: Chemical compositions of fayalite in iron slags by SEM-EDX., Table S2: Chemical compositions of wüstite in iron slags by SEM-EDX., and Table S3: Chemical compositions of magnetite in iron ores by SEM-EDX.

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