CHEMICAL STUDIES ON THE ANTARCTIC IRON METEORITES, YAMATO-790724, ALH-77263 AND ALH-77289

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Abstract: Three Antarctic iron meteorites, Yamato-790724, ALH-77263 and ALH-77289 have been studied from the viewpoint of analytical chemistry. Fourteen elements, Ni, Co, P, As, Au, Cr, Ga, Ge, Ir, Pt, Re, Ru, Sb and W were determined. From the results, Yamato-790724 was classified into Group IIIA. ALH-77236 and ALH-77289 were classified into Group I. The elemental distributions of Ni, Co, P and S in the three meteorites were examined. Phosphide, (Fe, Ni)₈P and sulphides, FeS and FeCr₂S₄, were detected. Morphology of the compounds was observed and the distribution of them was measured. Some discussions are given to the facet pits formed by the etching method and the orientations. Twinned structures found in ALH-77289 are considered to have been caused by strong mechanical shock.

1. Introduction

Three Antarctic iron meteorites, Yamato-790724, ALH (Allan Hills)-77263 and ALH-77289, have been studied from the chemical point of view. In this paper, we report the chemical composition of the iron meteorites in order to classify them. And we also report the elemental distributions of main elements and the morphologies of the chemical compounds found in the iron meteorites.

2. Experimental

2.1. Sample

The three samples, Yamato-790724,62 (weight 13.975 g), ALH-77263,51 (6.970 g) and ALH-77289,52 (6.861 g), were studied here.

2.2. Elemental analysis

Neutron activation analysis and ordinary chemical analysis were carried out in

order to determine the chemical composition of the iron meteorites. Twelve elements, Co, As, Au, Cr, Ga, Ge, Ir, Pt, Re, Ru, Sb and W were determined by neutron activation analysis. Ni was determined by the nickel glyoxime gravimetric method and P by the molybdenum blue spectrophotometric method, according to the Japan Industrial Standard, JIS G 1216–1981 and 1214–1980.

Neutron activation analysis was carried out as follows. A sample of 0.1g was irradiated for 1 min in F 24 irradiation pit $(1 \times 10^{12} n/cm^2 \cdot s)$ of the nuclear reactor, TRI-GA Mark II, of Atomic Research Laboratory, Rikkyo University, and cooled for 2 hr. Gamma rays from the activated Ge was measured by the Ge(Li) solid-state detector (Canberra Ind., 8100 type, measuring time: 5 min). The sample was irradiated again for 15 min, cooled for 24 hr and then γ -rays from the other 11 elements were measured by the same detector (measuring time: 15 min).

2.3. Distribution and compound analysis

Three new analytical methods were used for study of elemental distribution and compound analysis.

2.3.1. CMA

CMA is an abbreviation of Computer-aided Micro Analyzer (TAGUCHI *et al.*, 1981). The sample surface is irradiated by an electron beam in vaccum and the amount of characteristic X-ray emission is measured. By repeating this procedure and processing the analytical data for many points on the sample surface (maximum: 1 million points) by a computer, the CMA quantitatively displays the distribution of elements and compounds on the sample surface, and the results are shown by a color displayer.

The CMA has been developed by a high-grade combination of EPMA (Electron Probe X-ray Micro Analyzer) and a computer. A new large area scanning system and a data processing system have been applied to the CMA. It has been used for quantitative analysis of elemental segregation of steel slab samples.

2.3.2. SPEED

SPEED is an abbreviation of Selective Potentiostatic Etching by Electrolytic Dissolution (TAGUCHI, 1981). A sample is subjected to potentiostatic etching using a nonaqueous electrolyte, such as 10% acetylacetone -1% tetramethyl ammonium chloridemethanol.

Only 1 to $2 \mu m$ of the sample surface is selectively dissolved, leaving the compounds untouched. Analysis and observation are performed by a scanning electron microscope with an energy dispersive X-ray analyzer. The SPEED method has been applied to an *in situ* observation of a chemically unstable compound in steel samples, such as intermetallic compound.

2.3.3. PSPC

PSPC is an abbreviation of Position Sensitive Proportional Counter. Microfocussed PSPC manufactured by JEOL was used in this study. The operating conditions are as follows; generator: 40 kV, 1.2 mA, target: Cr, collimator: 30 μ m in diameter, measuring time: 20 min. In situ X-ray diffraction analysis was carried out on the compounds on surface of a sample.

3. Results and Discussion

3.1. Chemical composition

The results of investigations of the three iron meteorites by neutron activation analysis and chemical analysis are given in Table 1. From Table 1, Yamato-790724 was classified into Group IIIA according to the information summarized in Table 27 of BUCHWALD (1975), based mainly on the contents of Ni, P, Ga and Ir.

Element	Yamato-790724	ALH-77263	ALH-77289
Ni	74700 ppm	67800 ppm	67900 ppm
Со	4500	4700	5200
Р	1200	2000	1800
As	4.0	10.6	14.0
Au	0.5	1.5	1.7
Cr	9.7	2.8	5.1
Ga	15.6	99.4	97.5
Ge	48.9	409	360
Ir	10.0	3.1	3.5
Pt	9.1	5.5	6.7
Re	0.14	0.06	0.02
Ru	9.9	3.5	4.8
Sb	14.7	2.1	2.7
W	0.5	1.3	1.6

Table 1. The analytical results of Yamato-790724, ALH-77263 and ALH-77289.

The other two iron meteorites were classified into Group I according to the BUCH-WALD's criteria. CLARKE (1982) classified the two iron meteorites into Group IA and grouped them with three other meteorites under the name ALHA76002. The data presented by CLARKE (1982) for some elements such as Ni, Ga, Ge and Ir in ALHA77263 and ALHA77289 are approximately the same as ours. The chemical composition of ALH-77263 is very similar to that of ALH-77289. The similarity probably suggests that the two iron meteorites represent the same fall.

3.2. Elemental distribution and observation of compound

3.2.1. Yamato-790724

Elemental distributions of Ni, P and Co were measured by CMA and presented in Fig. 1. A full area of the sample surface was analyzed by CMA. The results of the distributions of Ni, P and Co are shown in green, red and blue, respectively. Figure 1a shows the results of Ni and P simultaneously. Originally P is shown in red, but green (color for Ni) and red make yellow. Thus, yellow area indicates the existence of the phosphide (schreibersite, (Fe, Ni)₃P). The phosphide was also identified by Xray analysis using PSPC. Figure 1b gives the results of distribution of Co. In Fig. 1 and the figures given later, each of three primary colors (red, green, blue) is shown in 16 shades according to the concentration of an element.

From Fig. 1, segregation of Ni is noticed and many granular phosphides are found. Comparison of Fig. 1a with Fig. 1b, shows that the segregation of Ni is opposite to that of Co.



Fig. 1. Elemental distributions of Ni(a), P(a) and Co(b) in Yamato-790724; Ni: green, P: originally red but apparently yellow due to color mixing, Co: blue. White frames show the areas for further CMA inspection (see Figs. 2 and 3).



Fig. 2. Elemental distributions of Ni, P and S in Yamato-790724; Ni: green, P: originally red but apparently yellow due to color mixing, S: blue. Photographs a and b refer to areas A and B in Fig. 1, respectively.



Fig. 3. Elemental distributions of Ni, P and S in Yamato-790724 (area C in Fig. I); Ni: green, P: originally red but apparently yellow due to color mixing, S: blue White circles and square show the sulfides subjected to X-ray analysis.

The further studies on the distributions of Ni, P and S using smaller analysis spot of 10 μ m, were carried out and the results are shown in Figs. 2 and 3. The areas for distribution measurements are shown by the white frames of Fig. 1a. Figures 2a, 2b and 3 are the analytical results for areas A, B and C, respectively, of Fig. 1a. Figures 2 and 3 show the segregation of Ni and the presence of phosphide (yellow) and sulphide (blue). Phosphide and sulphide are granular and much larger than those found commonly in iron and steel industrially produced.

The sulphides found in Fig. 3 (in white circles and square) were analyzed by Xray analysis using PSPC in order to examine the structures. The results show that the sulphides located at the white circles are troilite, FeS. The sulphide located at the white square was furthermore studied by CMA. Characteristic X-ray images of this sulphide are shown in Fig. 4. From Fig. 4 its main elements were Cr and S. It was quantitatively analyzed by CMA and the following results were obtained: Cr 27.1, Fe 16.0, S 56.9, in atomic %. Thus this sulphide was found to be daubreelite, FeCr₂S₄.

Fine phosphide particles were observed by the SPEED method. Figure 5 shows the results. Many specks of phosphide, (Fe, Ni)₃P were also found in this meteorite



Fig. 4. Characteristic X-ray images (Fe, Ni, Cr, S) of the sulfide found in Yamato-790724 (area C, white square, see Fig. 3).



Fig. 5. Fine phosphide, $(Fe, Ni)_3P$, observed in Yamato-790724 (area B of Fig. 1) by the SPEED method (scale bar 10 μ m).



Fig. 6. Elemental distributions of Ni, P and S in ALH-77263; Ni: green, P: originally red but apparently yellow due to color mixing, S: blue, analyzed area: 10×8 mm.

except larger ones shown in Figs. 1a, 2a, 2b and 3. The streaks in Fig. 5 are the crystal boundaries.

3.2.2. ALH-77263

Elemental distributions of Ni, P and S were measured as shown in Fig. 6. Almost full area of the sample surface $(10 \times 8 \text{ mm})$ was subjected to the CMA measurement. Segregation of the phosphide, (Fe, Ni)₈P, along the boundaries, is characteristic. Small phosphides are also found in this meteorite. Large sulphides are fewer in number. Small phosphide grains were recognized in this sample by the SPEED method as shown in Fig. 7. Many small phosphides under 0.1 μ m were shown around the large phosphide at the center of Fig. 7.

3.2.3. ALH-77289

Elemental distributions of Ni, P and S were measured and the results are shown



Fig. 7. Phosphide, (Fe, Ni)₃P. observed in ALH-77263 by the SPEED method (scale bar 1 µm).



Fig. 8. Elemental distribution of Ni, P and S in ALH-77289; Ni: green, P: originally red but apparently yellow due to color mixing, S: blue, analyzed area: 550×550 µm.

in Fig. 8. Taenite lamellae and small granular phosphides were found in this iron meteorite, and sulphides were fewer in number. A small phosphide was observed by the SPEED method, as shown in Fig. 9. The cubic pit seen at upper left is a facet pit.

Figure 10 shows a secondary electron image of a part of the area shown in Fig. 8 after etched by the SPEED method. Figure 11 is explanatory of Fig. 10. The whitish zones in Fig. 10 are taenite lamellae. Six points of the taenite lamellae and 3 points of the kamacite matrix were subjected to quantitative analysis by CMA. The analytical results of Fe and Ni of the taenite lamellae and the kamacite matrix are shown in Tables 2 and 3, respectively. Facet pits in Fig. 10 show the grain orientations as follows: area to upper right, {112}; the other area, {122}. As illustrated in Fig. 11, we can clearly recognize three twin boundaries. Further inspection of the {112} area of Fig. 10 reveals that there is slight difference in facet pit orientation as regards the subareas bordered by the twin boundaries. From Fig. 10, it is recognized that the twin



Fig. 9. Phosphide, (Fe, Ni)₃P, observed in ALH-77289 by the SPEED method (scale bar 2 μ m).



Fig. 10. Secondary electron image of ALH-77263 after etched by the SPEED method.



Fig. 11. Explanation of Fig. 10.

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No.	Fe (wt %)	Ni (wt %)
1	59.35	38.27
2	60.47	38.27
3	60.32	38.42
4	54.76	44.25
5	60.20	38.80
6	58.93	39.01
Average	59.01	39.50

Table 2. The analytical results of Fe and Ni at the circled positions of Fig. 11 (taenite lamellae).

 Table 3. The analytical results of Fe and Ni at the circled positions of Fig. 11 (kamacite matrix).

No.	Fe (wt %)	Ni (wt %)
7	92.71	6.83
8	92. 32	6.64
9	92.53	6.76
Average	92.52	6.74

boundaries formed in the kamacite matrix do not penetrate the taenite lamellae. The twinned structures as shown in Fig. 10 are understood to have been caused by strong mechanical shock at low temperatures.

4. Summary

(1) Three Antarctic iron meteorites, Yamato-790724, ALH-77263 and ALH-77289 were analyzed and classified according to the results.

(2) The elemental distributions of Ni, Co, P and S in the three meteorites were investigated. The segregation of the elements and the compounds was noticed.

(3) Phosphide, (Fe, Ni)₃P and sulphides, FeS and FeCr₂S₄, were detected and the shapes of the compounds were observed.

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