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2 **Formation process of pyrite polyframboid based on heavy-metal analysis by micro-PIXE**
3 HISANARI SUGAWARA^{1,*}, MASAYUKI SAKAKIBARA¹, DAVID BELTON² and TETSUYA
4 SUZUKI³
5

6 ¹Graduate School of Science and Engineering, Ehime University, 2-5 Bunkyo-cho, Matsuyama,
7 Ehime 790-8577, Japan

8 Corresponding author, e-mail: sugawara@sci.ehime-u.ac.jp

9 ²CSIRO Exploration and Mining, School of Physics, University of Melbourne, Victoria 3010,
10 Australia

11 ³Chi-ken Sogo Consultants Co., Ltd., 2-3 kita 6 jyo nishi 22 chome, Chuo-ku, Sapporo, Hokkaido,
12 Japan
13
14

Abstract: Pyrite framboid in sedimentary rocks could be concerned with arsenic contamination in groundwater of acidic environment and has been studied for the formation process of its unique morphology. However, little has been discussed about the formation process based on heavy-metal distribution in pyrite framboids and their aggregates. To reveal the formation process of pyrite framboids and their aggregates, mudstone from the Late Cretaceous Hakobuchi Group, central Hokkaido, Japan, are investigated for mode, petrographical, mineralogical, and micro-PIXE (**particle-induced x-ray emission**) analysis in this study. Spherical and sub-spherical pyrite framboids observed in polyframboids can be divided into two types based on diameter of framboids (**D**) and the average diameter of microcrystals (**d**) within framboids: type 1, **ranging from 2 to 9 μm and from 0.4 to 0.9 μm , respectively, and type 2, ranging from 8 to 50 μm and from 0.5 to 1.8 μm , respectively.** Based on the quantitative traverse analyses and 2-D elemental mapping results by micro-PIXE, heterogeneities in the concentrations of heavy metals within the analyzed aggregations of pyrite are exhibited. On the basis of the As and Pb zoning patterns, the time range and chronological stages of pyrite-aggregation growth are revealed.

Keywords: framboidal pyrite, polyframboid, mudstone, arsenic, Cretaceous, Hakobuchi Group, micro-PIXE

1. Introduction

Pyrite, forming framboidal morphology called **pyrite framboid**, is one of the most notable minerals in environmental science and mineralogy. Arsenic contamination of groundwater has been reported from many areas in the world (Acharyya et al. 1999; Ahmed et al. 2004; Nickson et al. 1998; Krishna and Govil 2008; Petrini et al. 2011; Stamatis et al. 2011), and As dissolution from **pyrite framboids** within natural sediment or sedimentary rock is suspected as the cause of the contamination (Smedley and Kinniburgh 2002). Although a part of sulfur in pyrite is known to be substituted for As, little is known about As concentration and distribution within framboidal pyrite.

In mineralogy, the formation process of framboidal pyrite has been actively argued since the late 1950s but not yet completely understood. It has been hypothesized to be formed by particulation of primary gel droplets or agglomeration (Farrand 1970; Sunagawa et al. 1971; Kribek 1975). On the basis of the above hypotheses, simple framboids may be formed by agglomeration; however, particulation of the original form is required for the formation of several sizes of framboidal pyrite, such as microframboids, framboids, and polyframboids.

Although there have been a number of reports, very few quantitative analyses of framboidal pyrite have been done in previous studies (Przybylowicz et al. 1995; Reimold et al. 1999 and 2004); hence, the formation process of pyrite **framboid** and polyframboid has been rarely discussed with heavy metal distributions and concentrations. In the present study, quantitative analyses are performed to elucidate the elemental concentrations and distributions of framboidal pyrites and polyframboids within mudstone, and then formation process of polyframboid is revealed by petrography and the results of quantitative analyses.

2. Materials and methods

2.1. Material

The studied mudstone samples were collected from a borehole at 10.6 -10.7 m in depth drilled from the Late Cretaceous Hakobuchi Group in Yubari city, central Hokkaido, Japan (Fig. 1). The Hakobuchi Group in the Yubari area is composed mainly of sandstone, and intercalated with siltstone, carbonaceous material-rich mudstone, and acidic tuff (Takahashi and Kito 1990).

2.2. Petrographical and mineralogical observations

The polished slab section and carbon-spattered polished thin sections of the Hakobuchi mudstone were observed with reflected-light microscope and scanning electron microscope (SEM) for petrographic analyses. BSE images are taken using a JEOL JSM-5400 (JEOL) SEM housed in the Department of Earth Sciences, Ehime University, Japan. Operating conditions were an accelerating voltage of 15 kV, beam current of 5×10^{-9} A, a beam size of $\sim 1 \mu\text{m}$, and 20 mm working distance in order to observe the morphological characteristics and to measure the sizes of microcrystal, pyrite framboïd, and polyframboïd.

2.3. Micro-PIXE (particle-induced x-ray emission) analysis

Quantitative analyses of the Hakobuchi mudstone including framboïdal pyrites were performed by micro-PIXE at CSIRO Exploration and Mining, School of Physics, University of Melbourne, Australia. Micro-PIXE is a powerful tool in measuring heavy metals at mg kg^{-1} -level sensitivity because the background noise of the characteristic X-ray employed by PIXE is approximately two orders of magnitude lower than that used in EMP (Electron Microprobe) (Reuter et al. 1975; Johansson and Johansson 1976; Campbell et al. 1990; Ryan et al. 1990a). Elemental concentrations were measured quantitatively from carbon-coated thin sections with a proton beam of $2.54 \mu\text{m}$. Samples were probed with a beam current of 6–10 nA and acceleration voltage of 3 MeV, and analyses were performed with an Al filter and a large Ge (Li) detector. Elemental maps based on

1 elemental concentrations were generated using the GeoPIXE software suite (Ryan et al. 1990a).

2 Quantitative analysis was standardless and has been described in detail (Ryan et al. 1990a,b).

3 Little has been reported about concentrations and distributions of heavy metals in sedimentary
4 rocks because of the difficulty of quantitative measurement of heavy metals at mg kg^{-1} level by EMP
5 which has been one of the most popular micro-analytical equipment for quantitative analysis of
6 geological materials. Micro-PIXE is one of such developed means for quantitative analysis of
7 geological materials. Micro-PIXE analysis catches the attention of geologists for its outstanding
8 advantages as follows: (1) lower background, (2) quantitative measurement capability in mg kg^{-1}
9 level, (3) readily quantified (standardless), (4) in-situ multi-element analytical capability, (5) deeper
10 penetration depth up to 30-50 μm , (6) non-destructive, and (7) micron spatial resolution (Reuter et al.
11 1975; Johansson and Johansson 1976; Campbell et al. 1990; Ryan et al. 1990a). The penetration
12 depth of the proton beam is more than 30 μm from the surface of a sample so that the obtained
13 signals have the quantitative information of not only surface area (Sie 1997). Quantitative
14 two-dimensional (2-D) elemental images are obtained via Dynamic Analysis, which is an analytical
15 method for projecting quantitative element images from PIXE. The Dynamic Analysis method
16 removes artifacts caused by overlapping elements, detector effects, and background, and sorts the
17 full spectral signatures of different elements to generate quantitative 2-D maps (Ryan et al. 1995;
18 Ryan 2000).

20 3. Results

21 3.1. Petrography

22 The matrix of the Hakobuchi mudstone is divided into two types; carbon-rich matrix and clay
23 mineral-rich matrix. Carbon-rich matrix appears to be dark spots and thin layers rich in
24 carbonaceous materials. Clay mineral-rich matrix is in lighter gray color and poor in carbonaceous

materials. Silt-sized quartz grains are present within clay matrix. Pyrites are observed within or close to carbonaceous-rich matrix.

3.2. Morphology of pyrites

Pyrites in the Hakobuchi mudstone are present as disseminated euhedral microcrystal, microcrystal aggregation, or massive forms. Disseminated euhedral microcrystals are either octahedral (Fig. 2a) or cubic while cubic microcrystals form clusters within carbonaceous materials but are hardly observed. Most microcrystal aggregates are divided into spherical, sub-spherical, and united framboids (Fig. 2a-c). ‘United’ pyrite framboids refer to the morphological types that multiple spherical or sub-spherical pyrite framboids are united (Fig. 2c). Disseminated euhedral microcrystals are often present between pyrite framboids (Fig. 2d). Most pyrite framboids are aggregated with other pyrite framboids forming ‘polyframboids’ (Love 1971).

Targeted polyframboids are labeled as #1, 2, 10, 16, and 17. Polyframboids #1, 10, and 17 are observed within the rim of carbon-rich matrix whereas #2 and 16 are located close to carbon-rich materials but in clay mineral-rich matrix. Observations by reflected-light microscope and SEM show that pyrite framboids in polyframboid range from 2 μm to 50 μm in diameter; in contrast, SEM observation reveals that framboid-forming microcrystals range from 0.4 μm to 1.9 μm in their average diameters. Framboid-forming microcrystals in a framboid are very similar in their sizes. Figure 3 shows the average diameters of framboid-forming microcrystals (d) plotted against the diameters of pyrite framboids (D). The figure enables the identification of two types of pyrite framboids in polyframboids based on values of D and d : type 1 framboids have D and d values that range from 2 to 9 μm and from 0.4 to 0.9 μm , respectively, while the D and d values for type 2 framboids range from 8 to 50 μm and from 0.5 to 1.8 μm , respectively. Massive pyrites with homogeneous surfaces are divided into spherules and irregulars (Fig. 2d). SEM observation also

exposed the presence of pyrite framboid with loose packing of microcrystals embedded in some parts of the massive irregular pyrite.

3.3. In-situ quantitative analysis by micro-PIXE

The quantitative 2-D elemental analyses by micro-PIXE revealed the average concentrations of Cu, Zn, As, and Pb in polyframboids, carbon-rich matrix, and clay mineral-rich matrix (Table 1(a)). The maximum concentrations of Cu, Zn, As, and Pb within pyrite framboid (Sugawara *et al.* 2008), pyrite massive, carbon-rich matrix, and clay mineral-rich matrix were obtained as well (Table 1(b)).

Several framboids show concentrations of Cu (up to 2893 mg kg⁻¹) whereas the concentrations of Zn are very low, commonly below the detection limit (below 10-35 mg kg⁻¹). A positive correlation between Cu and Zn concentrations is not observed in sample #1, 2, 10, 17 but in sample #16. The concentrations of Fe, As, and Pb are significantly enriched in pyrite framboids, as previously reported by Graham and Robertson (1995), and pyrite massives relative to the matrix.

The 2-D images of As and Pb concentrations reveal a number of significant features. High Pb concentrations are generally not observed in type 2 framboids in whole, however, are observed as small islands within both pyrite massives and framboids. High As concentrations are observed as (1) small islands within massives and framboids, (2) small islands within those framboids on the rims of polyframboids, and (3) large islands within type 2 pyrite framboids, especially those greater than 23 µm in diameter (Fig. 4).

Traverse quantitative analyses performed on the sample #1, 2, 10 and 16 exhibit the elemental variation among Fe, As, and Pb of pyrite and mudstone matrix in the analyzed areas (Fig. 5). All traverse profiles were extracted from the areas (shown in Fig. 4) scanned from A to A'. A data plot represents the quantitative chemical profile from surface to volume down to ~30 µm by nature of micro-PIXE analysis. The maximum concentrations of Fe, As, and Pb in each profile are listed

(Table 1(c)). Concentrations of Fe in matrix are approximately 5 wt. %. In the elemental correlation diagram of As versus Pb, data plots display the positive correlation ($R^2=0.9001$), and a large number of plots are present either in the areas of As- and Pb-poor (approximately 0-70 mg kg⁻¹ of As and 0-80 mg kg⁻¹ of Pb) or As- and Pb-rich (approximately scattered 200-500 mg kg⁻¹ of As and 220-620 mg kg⁻¹ of Pb). There are no plots confirmed in the As-rich and Pb-poor area and As-poor and Pb-rich area. The plots with poor As and Pb concentrations appeared to have an average Fe-concentration of about 5 wt. % in other two correlation diagrams. On the other hand, most of As- and Pb-rich data plots have the Fe concentration of larger than 30 wt. %. These higher concentrations of Fe with respect to the lower Fe-concentrations in matrix represent the data of pyrite. It suggests that As- and Pb-poor plots shown in the diagram of As versus Pb are the values for matrix in the Hakobuchi mudstone. Higher concentrations of Pb as spikes ranged 610-640 mg kg⁻¹ are reflected on the elemental correlation graphs (Fig. 5). Their concentrations of Fe are about 47 mg kg⁻¹. These higher concentrations of Pb are also rich in As and have a proportional trend to the concentrations of As.

Data plots generated by the traverse analysis for the area in #2 resulted as the mixture of three end members: Pb-rich type 1 framboid, As- and Pb-poor framboids, and mudstone matrix (Fig. 5). Concentrations of Fe in matrix are approximately 5 wt. %. There are also two trends of plots confirmed in the correlation diagram of As versus Pb; As- and Pb-poor area (approximately 0-25 mg kg⁻¹ of As and 0-50 mg kg⁻¹ of Pb), and the other is a scatter from 0-240 mg kg⁻¹ of Pb and 25-150 mg kg⁻¹ of As. The former trend in the correlation diagram of Fe versus As shows the plots with an approximate average value of 5 wt. % of Fe-concentrations. The latter trend of the scattered plot distribution could be subdivided into two sub-trends. The first trend is clearly confirmed in the correlation diagrams of both Fe versus As and Fe versus Pb. In the diagram of Fe versus As plots with As-rich concentrations (95-140 mg kg⁻¹) are gathered between 30 and 45 wt. % of

Fe-concentrations, and it corresponds to the plot distribution within 30-40 wt. % of Fe-concentrations and 50-150 mg kg^{-1} of As-concentrations. Again, higher Fe-concentration leads to the plot of data measured on framboidal pyrite. The second trend is the plots scattered larger than 150 mg kg^{-1} of Pb-concentration in the correlation diagram of As against Pb.

The traversed area in #10 including pyrite massives are composed of As- and Pb-poor (both less than 200 mg kg^{-1}) pyrite, As-rich and Pb-poor pyrite, As-poor and Pb-rich pyrite, and mudstone matrix (Fig. 5). Concentrations of Fe in matrix are approximately 5 wt. %. In the elemental correlation diagram of As versus Pb, data plots show the positive correlation. Concentrations of Fe within most framboids in sample #10 range from 30 to 43 wt. %; and their ranges of As and Pb concentrations are 90-140 mg kg^{-1} and 60-150 mg kg^{-1} , respectively.

The end members of the traversed area in #16 are composed of As-poor framboids, Pb-poor framboids, and mudstone matrix. The average concentrations of Fe in the mudstone matrix is approximately 2 wt. %. In the correlation diagram of As versus Pb, three trends are confirmed. The first trend is the Pb-poor plots with approximately 0 mg kg^{-1} of Pb-concentration. The second trend is the As-poor plots with about 0 mg kg^{-1} of As-concentration. The third trend consists of scattered plots in the area of moderate As- and Pb-concentrations. The first trend of Pb-poor plots shows a bimodal distribution in the correlation diagram of Fe against Pb, which are plotted around 2 wt. % and the range of 17-30 wt. % of Fe-concentrations. The former mode represents the plots of mudstone matrix, and the latter represents Pb-poor framboidal pyrite. In the correlation diagram of Fe against As, most As-poor plots of the second trend range between 2-10 wt. % of Fe concentrations. These plots range in wider Pb-concentrations (0-65 mg kg^{-1}) in the correlation diagram of Fe against Pb. This result suggests that the second trend is mixed of matrix to Pb-rich framboids with smaller diameters.

It is summarized that the aggregations of pyrite in the Hakobuchi mudstone can be divided

into two groups according to distributions of As and Pb concentrations; one shows higher concentrations of As and Pb on the rims of aggregations, such as sample #10 and #17 (namely as ‘zoning type’); and the other aggregations (sample #1, 2, and 16) do not show the zoning-like concentrations and exhibit small islands of higher As and Pb concentrations in polyframboids in whole (namely as ‘whole type’). Further, ‘whole type’ could be divided into two subgroups whether As and Pb have a positive correlation or not.

4. Discussion

4.1. Growth path of pyrite

The morphological investigations suggest a growth path of pyrite framboids and polyframboids. Pyrites in the Hakobuchi mudstone are divided into three morphological types by the packing degree of pyrite microcrystals having two morphological end members; dispersed pyrite microcrystal and massive pyrite. Mineralogy showed pyrites of various intermediate morphologies between two morphological end members. Especially the intermediates from pyrite framboids with their loose packing within cluster of disseminated pyrite microcrystals to pyrite massive with its solid surface suggest a continuous growth, which is consistent with the hypothesis of continuous pyrite growth from clusters of microcrystals to massive pyrite proposed in the past studies (i.e. Sawlowicz 1993). The Fe and As mapping images of #17 polyframboid are the best showing example for type 1 framboids forming a type 2 framboid. Most type 1 framboids are spherical to united based on Fe image, while As concentrations in some type 2 framboids are composed of some type 1 sized heterogeneous accumulations.

The variation of pyrite packing state was observed based on the BSE images and Fe mapping image by micro-PIXE. The concentrations of Fe display the amount of pyrite in depth (note that the x-rays are excited from a volume down to ~30 μm). Hence, the morphology of aggregates can be

discussed with not only BSE images but also the 2-D mapping images of Fe concentrations. Spherical and sub-spherical pyrite framboids in relatively smaller diameters are densely aggregated in the sample #1. Likewise, spherical and sub-spherical pyrite framboids are aggregated in the sample #2, 16, and 17; however, these three polyframboids are scarcer than #1.

4.2. Chronological stages of aggregate formation

The quantitative analyses revealed the relative time range of aggregation growth of pyrite polyframboids. The results of quantitative analyses showed two types of distributions of As and Pb in aggregations. The ‘zoning type’ represents the single change in chemical conditions from As- and Pb-poor conditions to As- and Pb-rich conditions in the Hakobuchi mudstone. On the other hand, the ‘whole type’ exhibits higher As- and Pb-concentrations in framboids than in the mudstone matrix distributed in a whole aggregate. The ‘zoning type’ could have been given a longer time range of growth, meaning preserving a longer history of chemical condition in the mudstone, whereas ‘whole type’ had grown in a relatively shorter time (Fig. 6).

Taking into account the relative time range of aggregation growth and elemental concentrations, the chronological order of aggregation growth for ‘whole type’ is determined. To normalize the amount of pyrite, the maximum concentrations of Fe are adjusted to 50 wt. %. The normalized maximum As and Pb concentrations are calculated for all samples: 486 mg kg⁻¹ and 614 mg kg⁻¹ for the sample #1, 171 mg kg⁻¹ and 274 mg kg⁻¹ for the sample #2, 547 mg kg⁻¹ and 799 mg kg⁻¹ for the sample #10, 159 mg kg⁻¹ and 119 mg kg⁻¹ for the sample #16, and 1124 mg kg⁻¹ and 543 mg kg⁻¹ for the sample #17, respectively. Given the chemical condition for As and Pb had been homogeneous within the examined areas of the Hakobuchi mudstone, the aggregates could have been grown in the order of #16, #2, #17, and #1 chronologically, while the ‘zoning type’ aggregate #10 covers a longer time range, preserving the gradual elevation of As and Pb concentrations.

The end members of chemical properties exhibited by traverse analyses correspond to the formation timing of pyrite in the context of the gradual change in As and Pb concentrations.

4.3. Change in As and Pb concentration of the fluid in the Hakobuchi mudstone

The variation of As- and Pb-concentration patterns within mudstone of the single drill-core is well-exhibited in 2-D elemental images, and it suggests the change in chemical condition in the Hakobuchi mudstone. Based on micro-PIXE analyses, previous studies have described various zoning patterns of As and Pb in euhedral pyrite grains, leading to the suggestion of temporal changes in the physicochemical conditions of the fluid from which pyrite was precipitating (Reimold et al. 2004; Belcher et al. 2004). In addition, Graham and Robertson (1995) analyzed framboidal pyrite and neighboring macerals by micro-PIXE, reporting both gradual and abrupt changes in the concentrations of As and Pb within pyrite framboids.

5. Conclusion

The quantitative analyses of pyrite aggregations by micro-PIXE produced the valuable results in terms of clarifying the concentrations and distributions of heavy metals, clearly revealing inhomogeneities in the concentrations of heavy metals within the analyzed aggregations of pyrite. The time range and chronological stages of pyrite-aggregation growth are revealed for the first time from the concentrations of As and Pb. This study suggests that pyrite framboids and pyrite polyframboids formed under a continuous change in chemical conditions, thereby explaining the observed heterogeneity in heavy metal concentrations.

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Figure captions

Fig. 1 The geological map showing the sampling location of Late Cretaceous Hakobuchi mudstone.

Fig. 2 BSE images of pyrite framboids with various microcrystal packing states a) and b) spherical to sub-spherical pyrite framboids, c) United pyrite framboids. d) Massive irregular pyrite.

Fig. 3 D-d diagram of pyrite framboids in the Hakobuchi mudstone. 'D' and 'd' represent a diameter of a pyrite framboid and a diameter of a microcrystal, respectively.

Fig. 4 BSE images by SEM and two-dimensional (2-D) elemental images obtained by micro-PIXE. In 2-D mapping images, a brighter color corresponds to a higher concentration. Maximum concentrations are shown in the lower left corner of each 2-D mapping image. Lines for performed traverse analyses are shown in the Fe images.

Fig. 5 Elemental correlation diagrams among Fe, As, and Pb for the areas #1, 2, 10, and 16 obtained by travers analyses using micro-PIXE.

Fig. 6 The formation model of the pyrite polyframboid in the analyzed area #10. The model shows the formation stages of zoning pattern with respect to time.

Table 1 (a) Mean concentrations of Cu, Zn, As, and Pb in polyframboids, carbon-rich matrix, and clay mineral-rich matrix. (b) Maximum concentrations of Cu, Zn, As, and Pb within pyrite framboid, pyrite massive, carbon-rich matrix, and clay mineral-rich matrix. (c) The maximum concentrations of Fe, As, and Pb in traverse profiles from sample #1, 2, 10, and 16.

(a)

Occurrence	Mean Cu (mg kg ⁻¹)	Mean Zn (mg kg ⁻¹)	Mean As (mg kg ⁻¹)	Mean Pb (mg kg ⁻¹)
Polyframboid	309 ± 11	17 ± 4	309 ± 5	84 ± 8
Carbon-rich matrix	33 ± 7	39 ± 4	16 ± 2	15 ± 5
Clay-mineral rich matrix	15 ± 5	54 ± 3	13 ± 1	9 ± 3

(b)

Occurrence	Max. Cu (mg kg ⁻¹)	Max. Zn (mg kg ⁻¹)	Max. As (mg kg ⁻¹)	Max. Pb (mg kg ⁻¹)
Pyrite framboid	2893 ± 82	86 ± 28	1070 ± 22	579 ± 37
Pyrite massive	218 ± 24	486 ± 15	454 ± 23	2563 ± 46
Carbon-rich matrix	35 ± 6	53 ± 4	18 ± 2	16 ± 5
Clay-mineral rich matrix	24 ± 6	120 ± 3	20 ± 2	9 ± 5

(c)

Sample	Max. Fe (wt. %)	Max. As (mg kg ⁻¹)	Max. Pb (mg kg ⁻¹)
#1	51.8 ± 0.9	504 ± 52	637 ± 86
#2	42.3 ± 0.6	148 ± 22	237 ± 44
#10	47.1 ± 0.9	515 ± 47	752 ± 101
#16	29 ± 0.5	92 ± 20	69 ± 20

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	BSE	Fe	Cu	Zn	As	Pb
#1		37.4 wt. %	164 mg/kg	<20 mg/kg	243 mg/kg	313 mg/kg
#2		47.0 wt. %	2893 mg/kg	<35 mg/kg	119 mg/kg	57 mg/kg
#10		43.3 wt. %	218 mg/kg	486 mg/kg	454 mg/kg	2563 mg/kg
#16		43.2 wt. %	526 mg/kg	73 mg/kg	196 mg/kg	160 mg/kg
#17		47.6 wt. %	163 mg/kg	86 mg/kg	1070 mg/kg	517 mg/kg

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Author/s:

Sugawara, H;Sakakibara, M;Belton, D;Suzuki, T

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