LETTER

Quantitative micro-PIXE analysis of heavy-metal-rich framboidal pyrite

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Framboidal pyrite in mudstone is known to be a reservoir of arsenic, yet few studies have conducted quantitative analyses of framboidal pyrite with ppm-level sensitivity. In this study, we used micro-PIXE to measure the concentrations of heavy metals in framboidal pyrite from drill-core samples of mudstone from the Late Cretaceous Hakobuchi Group, central Hokkaido, Japan. Pyrite framboids that occur in polyframboids can be divided into two types based on framboid diameter (D) and the average diameter of microcrystals within framboids (d): type 1, being relatively small grains; and type 2, being relatively large grains. Higher concentrations of As are observed in most type 2 framboids than in type 1 framboids. High concentrations of Pb generally occur as isolated islands within type 1 framboids, concentrated along the rims of polyframboids. It could be concluded that contrasting formation processes among different framboids led to the observed changes in heavy metal concentrations.

Keywords: Framboidal pyrite, Micro-PIXE, Heavy metals, Mudstone, Hakobuchi Group

INTRODUCTION

The formation process of framboidal pyrite is one of the most challenging problems in mineralogy, remaining unresolved despite having been debated since the late 1950s (e.g., Love, 1957; Rickard, 1970; Taylor, 1982; Wilkin and Barnes, 1997). Framboidal pyrite is also important to understand mobilization processes of As and other heavy metals. Because As can substitute for S (Smedley and Kinniburgh, 2002), framboidal pyrite is a potential reservoir of As. This is important because contamination of the environment by As has been documented in many regions of the world, including drinking water in Bangladesh and in West Bengal, India (Nickson et al., 1998; Acharyya et al., 1999; Ahmed et al., 2004). It is generally recognized that soluble As is involved in the formation of framboidal pyrite under reducing conditions, and that As is released from framboids under oxidizing conditions (e.g., Smedley and Kinniburgh, 2002). In the field of environmental sciences, knowledge of the concentrations of heavy metals in the context of the morphological characteristics of framboidal pyrite in sedimentary rock might contribute to our understanding of the mobilization of As. The quantitative analysis of framboidal pyrite with ppm-level sensitivity and high resolution could provide important data regarding its formation process and mechanisms of heavy-metal mobilization. Heavy metals in euhedral pyrite grains have been analyzed previously using micro-PIXE (particle-induced X-ray emission) (e.g., Meyer et al., 1994; Przybylowicz et al., 1995; Reimold et al., 1999, 2004; Belcher et al., 2004), revealing zoning and unique concentration patterns; however, few studies have used micro-PIXE to measure the concentrations of heavy metals in the context of the formation process of pyrite framboid.

Using micro-PIXE analyses, Graham and Robertson (1995) investigated whether a sulfur-rich precursor phase plays an important role in the formation process of framboidal pyrite in matrix with abundant carbonaceous materials. Although the authors focused on the S/Fe atomic ratio, they reported high concentrations of Fe, Ni, As, and Pb in the analyzed framboids. So far, however, little information has emerged in terms of the concentrations of...
heavy metals in framboids and their aggregations.

To address this shortcoming, in the present study we use micro-PIXE to analyze drill-core samples of mudstone from the Late Cretaceous Hakobuchi Group, central Hokkaido, Japan, with the aim of determining the concentrations of heavy metals and the formation process of framboidal pyrite.

**GEOLOGICAL SETTING AND PETROGRAPHY**

We obtained drill-core samples of mudstone from the Late Cretaceous Hakobuchi Group, central Hokkaido, Japan. The Hakobuchi Group in the study area (Ashibetsu-Yubari) is mainly composed of sandstone, with lesser siltstone, carbonaceous mudstone, and acidic tuff (Takahashi and Kito, 1990).

Thin sections and polished sections were prepared for analysis and detailed observations. Mudstone within the Hakobuchi Group consists of a matrix with dark spots and thin layers rich in carbonaceous materials as well as layers poor in carbonaceous materials. The matrix is dominated by clay minerals that are difficult to identify by reflected-light microscopy; however, framboidal pyrite is observed within or close to carbonaceous material, with most being aggregated with other framboids (we refer to such aggregations as ‘polyframboids’). Analyses by secondary electron microscope reveal that the framboids consist of numerous microcrystals of 0.4–1.9 µm in size.

The pyrite framboids within individual polyframboids range in size from less than 2 µm to more than 50 µm (Figs. 1a and 1b); in contrast, microcrystals within individual framboids are all of similar sizes (Fig. 1c). Figure 2 shows the average microcrystal diameters (d) plotted against the diameters of pyrite framboids (D). This figure enables us to identify 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 µm to 9 µm and from 0.4 µm to 0.9 µm, respectively, while the D and d values for type 2 framboids range from 8 µm to 50 µm and from 0.5 µm to 1.8 µm, respectively.

**ANALYTICAL PROCEDURE**

The concentrations of heavy metals in pyrite framboids were determined by micro-PIXE housed at CSIRO (Commonwealth Scientific and Industrial Research Organisation) Exploration and Mining, School of Physics, the University of Melbourne, Australia. Because the background noise of the characteristic X-ray employed by micro-PIXE is approximately two orders of magnitude lower than that used in EPMA (Reuter et al., 1975; Johansson and Johansson, 1976), PIXE is one of the most powerful tools in measuring geologically important elements at ppm-level sensitivity (Campbell et al., 1990; Ryan et al., 1990). Quantitative two-dimensional (2-D) elemental images were obtained via Dynamic Analysis (Ryan et
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al., 1995), which is an analytical method for projecting quantitative element images from PIXE. The Dynamic Analysis method removes artifacts caused by overlapping elements, detector effects, and background, and sorts the full spectral signatures of different elements to generate quantitative 2-D images (Ryan et al., 1995; Ryan, 2001).

Concentrations of heavy metals were measured quantitatively from polished sections and carbon-coated thin sections. Analyses were performed with an Al filter, a proton beam size of 2.54 µm, beam currents of 6–10 nA, and an acceleration voltage of 3 MeV.

RESULTS

The quantitative 2-D elemental images generated from micro-PIXE analyses reveal that the maximum concentrations of Ni, Cu, Zn, As, and Pb within the analyzed framboidal pyrites are 421, 2863, 2903, 1070, and 579 ppm, respectively whereas the maximum concentrations within the carbonaceous matrix are 51, 24, 120, 20, and 9 ppm, respectively (Fig. 3). High concentrations of Ni (approximately 200–420 ppm) are observed in some of analyzed framboids, and several framboids show high concentrations of Cu. Concentrations of Zn are very low, commonly below the detection limit. A correlation between Cu and Zn concentrations is observed in sample 16, but other samples do not show this correlation. Fe, Ni, As, and Pb concentrations are significantly enriched in framboidal pyrites relative to the matrix, as previously reported by Graham and Robertson (1995).

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

Figure 3. Quantitative two-dimensional (2-D) elemental images compiled from micro-PIXE analyses of framboidal pyrites in the Hakobuchi mudstone. These images clearly show the detailed concentrations and distributions of heavy metals within the analyzed polyframboids.
DISCUSSION

Our quantitative analyses of pyrite framboid by micro-PIXE produced valuable results in terms of clarifying the distributions of heavy metals, clearly revealing inhomogeneities in the concentrations of heavy metals within the analyzed polyframboids. Based on micro-PIXE analyses, previous studies have described various zoning patterns of Ni, Co, As, and Pb in euhedral pyrite grains, leading to the suggestion of temporal changes in the physicochemical conditions from which pyrite was precipitating (Belcher et al., 2004; Reimold 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 Ni, As, and Pb.

The present study revealed for the first time that the concentrations of heavy metals within framboids that make up a polyframboid in the Hakobuchi mudstone vary substantially even though their morphological characteristics are similar. Our results also demonstrate a variety of patterns of As concentrations within an individual thin section. This fact suggests that the pyrite framboids formed over multiple stages under a variety of environmental conditions, thereby explaining the observed heterogeneity in heavy metal concentrations.

REFERENCES