Geochemical characteristics of ores and surface waters for environmental risk assessment in the Pinpet iron deposit, southern Shan State, Myanmar

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Abstract
Mining operations in the Pinpet Fe deposit, which is the second-largest Fe deposit in Myanmar, are currently suspended, in part because of possible contamination of heavy metals and hazardous elements (e.g., Fe, As, Cu, Zn, and U) into the surrounding aquatic environment and associated public concern. However, a scientific investigation of the source and degree of contamination in streams near the deposit has not yet been conducted. Therefore, we quantified heavy-metal and hazardous-element concentrations of stream waters and sediments in stream beds, and measured the speciation and concentration of these metals in deposit Fe ores using the sequential extraction method, to better understand the influence of mining activities on the surrounding environment. Geochemical results for Nan-tank-pauk stream and its tributaries indicate that the chemical compositions of their waters are controlled by carbonate bedrock and that no detectable contamination has occurred as a result of mining activity or hematite and limonite ore beneficiation processes in either the wet or dry seasons. All measured heavy-metal and hazardous-element concentrations were below the World Health Organization standards for drinking water and the proposed national drinking water quality standards in Myanmar. Bulk chemical compositions of stream-bed and tailings dam sediments show that As, Zn, and Cu concentrations are similar to those in uncontaminated sediments. Results of bulk mineralogical and chemical analyses of ore samples reveal that some limonite ore samples contain substantial amounts of As (up to 2 wt%). However, sequential extraction results indicate that most (>90%) of the As in these As-rich ores is hosted in insoluble fractions (e.g., crystalline Fe hydroxides and clays). Therefore, arsenic is unlikely to be...
The Pinpet deposit is the second-largest iron (Fe) deposit in Myanmar, in which pilot-scale open-cut mining and beneficiation processes for low-grade ores started in 2003. However, mine operations have been suspended since 2017, in part because of possible contamination of heavy metals and hazardous elements, such as Fe, arsenic (As), copper (Cu), zinc (Zn), and uranium (U), into the surrounding aquatic environments, and public concern about the effects of mining activities. Although minerals and ores are generally chemically stable under in situ geological conditions, they may become unstable when excavated and exposed to the atmosphere by mining activity (Younger and Wolkersdorfer, 2004). Heavy metals and hazardous elements can be leached to wastewaters generated during ore beneficiation. High levels of hazardous elements (e.g., As) can occur not only from mining activity but also through geogenic sources (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Ahoué et al., 2015). Anthropogenic influences on aquatic environments can also result from agricultural activities (e.g., excessive use of organic and chemical fertilizers) and domestic wastewater (e.g., detergents and human waste; Khan et al., 2013). Therefore, an appropriate scientific study needs to be conducted to investigate the presence, level, and source of contamination in streams near the Pinpet deposit.

Ore genesis in the Pinpet Fe deposit is not well understood. Previous reports (e.g., ESCAP, 1996) have classified the ore deposit variously as a limestone replacement, lateritic, or Fe-oxide–Cu–Au (IOCG) deposit. The ore bodies are composed solely of oxide ores: limonite ore (mainly goethite) and hematite ore. Limonite ores are particularly likely to be affected by laterization. The deposit size is 4.02 km × 0.80 km × 90 m, in which probable ore reserve is estimated to be 10 million tons of hematite ore with 56.4% of average grade (as Fe₂O₃) and 70 million tons of limonite ore with 42.6% of average grade (Krupp-Rohstoffe, 1962). Arsenic contents in some ores are high, up to 0.25% (Krupp-Rohstoffe, 1962). However, host minerals for As in such ores are varied and commonly uncertain. Although As can be incorporated into the crystal structure of some minerals (e.g., pyrite; Abraitis et al., 2004), it can also be adsorbed onto clay minerals and Fe hydroxides, or associated with organic matter (Mandal and Suzuki, 2002), with the mode of occurrence dictating the fate of As during mining and mineral processing.

Previous geochemical studies have investigated the chemical mobility of heavy metals such as Cu, Zn, and Pb (Galloway et al., 1982; Hudson-Edwards, 2003). Regarding As, laboratory studies have identified Fe (oxyhydr)oxides as key sorbents for this element (Raven et al., 1998; Goldberg and Johnston, 2001), although it can also be adsorbed by the surfaces of a variety of materials, including ferric oxides and aluminum oxides (Brannon and Patrick, 1987; Dzombak and Wiley, 1990), clays (e.g., montmorillonite and kaolinite), and carbonate minerals (Goldberg and Glaubig, 1988). The presence of primary As-bearing minerals in rocks and ores can be a long-term source of As pollution, but secondary minerals (e.g., Fe hydroxides and clays) formed by chemical weathering can also retain As in soils or laterites (Davis et al., 1996; Sadiq, 1997). Minerals can release As to the environment, particularly when they are amorphous or have only weakly bound As on their surfaces (Yan Chu, 1994; Sadiq, 1997). Although XRD is a common method for characterizing ore mineralogy, it provides information only on the major crystalline minerals, and quantitative estimation of the labile phases is difficult. As an alternative, sequential extraction can be used to determine the speciation and concentration of trace elements in labile and amorphous phases in various solid matrices (e.g., soils and sediments). Labile fractions are more toxic and display greater levels of As bioavailability while more stable fractions can be evaluated as As with less mobility.

Therefore, in this study, we aimed to (a) investigate the influence of mining activities on the environment near the Pinpet deposit, including heavy-metal and hazardous-element concentrations of stream waters and of sediments in stream beds; and (b) understand the speciation and concentration of these metals in the Fe ores of the deposit using the sequential extraction method.

2 | STUDY AREA

2.1 | Location, climate, and land use

The Pinpet Fe deposit is located 11 km east of Taunggyi city, the capital of southern Shan State in Myanmar (Figure 1a).
The deposit occupies the upper part of a ridge trending approximately NE–SW, with the maximum elevation of 1,385 m above sea level and 200 m above the surrounding plain (Figure 1b). The study area has a humid subtropical climate with an annual rainfall of 1,540 mm/year and in which the monsoon extends from June to mid-November and the dry season from March to the beginning of June. Nan-tank-pauk stream flows through the eastern part of the mining area. The stream water has been used not only for mineral processing (beneficiation), including washing and magnetic separation, but also for agricultural activities and human needs (e.g., laundry). Farmlands have been developed beside Nan-tank-pauk stream and have been cultivated for rice, corn, tea, peanuts, and vegetables using traditional methods that utilize available natural resources (such as animal waste) combined with synthetic chemicals such as

**FIGURE 1** (a) Regional geologic map around Taunggyi city in the Shan Plateau (after DGSE, 2015a; 2015b) and (b) map showing sample locations and bedrock geology in the study area (after DGSE, 2015a; 2015b)
fertilizers and pesticides (Myint, 1989). Small villages, with a total population of ~7,000, are also located along Nan-tank-pauk stream.

2.2 | Geology

The study area is located in the Shan Plateau, which constitutes part of the Shan-Thai Block in eastern Myanmar and comprises Cambrian–Ordovician sedimentary sequences with localized Ordovician volcanics and volcaniclastics, unconformably overlain by thick middle–upper Permian limestone sequences (Aung, 2012; Figure 1a). Thick Ordovician limestones and siltstones deposited under littoral and shelf conditions are found in northern and southern Shan State together with strata-bound carbonate-hosted Pb–Zn deposits (e.g., at Bawzaing), barite deposits (e.g., at Anisakan and Kyaukup), and Fe deposits (e.g., at Kyatwinye). Silurian phacoidal (lenticularly deformed) limestones and clastics, as well as local tuff and ash beds in southern Shan State, are associated with antimony deposits (e.g., at Loi-Har-Myar), manganese deposits (e.g., at Hwe-tak), and Fe deposits (e.g., at Pinpet).

The Pinpet deposit is hosted by lower Silurian limestone of the LInwe Formation (Figure 1b). The Linwe Formation is composed mainly of purple to pink phacoidal limestones with calcareous mudstones and shales and locally with tuffs, and was likely deposited under shallow-marine conditions. The study area is located between the regional-scale Kyaukkyan and Htam Sang faults. These two faults trend NE–SW, and fault scarps occur sporadically along the fault valley (Hopone valley). This elevated fault-block structure appears to control mineralization of the Pinpet deposit, as the mineralized zone occurs between the two faults. WNW–ESE-trending diagonal minor faults are also found in the mineralized shear zone associated with hematite ore zones. To the north of Pinpet deposit, where the origin and upstream reaches of Nan-tank-pauk stream are located, the dolomitic Nwabangyi Formation (Lower Triassic–upper Permian) is exposed. Although Ordovician limestones (e.g., the Lokepyin, Wunbye, and Nan-on formations) are distributed to the east of Pinpet deposit, they are covered by alluvial sediments in the area along Nan-tank-pauk stream.

3 | SAMPLING AND ANALYTICAL METHODS

3.1 | Sampling and field measurements

Water and sediment samples, as well as ore samples, were collected during November (wet season) 2017 and April–May (dry season) 2019. Eight water samples (S1–S8) were collected from upstream to downstream in Nan-tank-pauk stream, and two water samples from two tributaries: one flowing in the residential area of the mining town (TS1) and another flowing in the main ore zone (TS2; Figure 1b). Tributary samples were obtained only during the wet season because tributaries contained no water during the dry season. Sediment samples were taken from sites S5 and S8. They were obtained by shoveling sediments at 0–10 cm depth in the stream beds and stored in polyethylene bags. A water sample and a sediment sample were also collected from a tailings dam (DM) in the mine area, which stores rainwater that is used for beneficiation. Representative ore samples in the Pinpet Fe deposit were taken from hematite ore zones (H1–H2) and limonite ore zones (L1–L9).

Electrical conductivity (EC), dissolved oxygen (DO), pH, turbidity, temperature, redox potential (Eh), and alkalinity of water samples were measured at sample sites in the field. Alkalinity was measured by titrating HNO3 into a 50 ml water sample that had been filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane filter. The Gran function plot method was applied to obtain bicarbonate ion (HCO₃⁻) concentration from the alkalinity value (Rounds, 2015). Water was sampled using a plastic bucket and disposable cups, and then filtered using 0.20 μm PTFE membranes in the field. They were completely filled in two 50 ml polypropylene bottles sealed with Teflon tape: one (non-acidified) for anion concentration analysis and the other one (acidified with 1 vol% HNO₃; ultrapure grade, Kanto Chemical) for cation concentration analysis. After the samples were transported to Environmental Geology Laboratory, Hokkaido University, Japan, they were stored in a refrigerator kept at ~4°C until they were analyzed.

3.2 | Analytical methods

All the pretreatments and analyses for water, ore, and sediment samples were conducted in Hokkaido University. Water samples of non-acidified samples were diluted 10 times and analyzed for major dissolved anion (SO₄, Cl, and NO₃) concentrations using ion chromatography (861 Advance Compact IC, Metrohm). Acidified water samples were diluted by a factor of 5 and analyzed for major- and trace-metal concentrations measured using inductively coupled plasma–atomic emission spectroscopy (ICP–AES; ICPE-9000, Shimadzu) and ICP–mass spectrometry (ICP–MS; iCap Qc, Thermo Scientific). Standard solutions were prepared using Anion mixture standard solution I (FUJIFILM Wako Pure Chemical), ICP multi-element standard solution IV (Merck), and Indium standard solution (Kanto Chemical).
Solid (ore and sediment) samples dried at room temperature were pulverized using a Multi-Beads Shocker (PV1001(S), Yasui Kikai) and sieved through a 53 μm stainless steel sieve. Bulk chemical compositions were determined using glass-bead XRF (MagiX PRO, Spectris). The detailed methodology and analytical conditions for XRF analysis are described by Chikanda et al. (2019). Bulk mineralogical compositions were analyzed using an X-ray diffractometer (Multiflex, Rigaku) equipped for graphite monochromatic CuKα radiation at 40 kV and 30 mA. Samples were scanned from 2° to 70° at a scan rate of 0.02°/s. Fine fractions (<2 μm) of the samples were separated by centrifugation at 3,000 rpm for 40 min after being dispersed ultrasonically in deionized water. Sediment samples of preferred orientation were prepared to identify clay minerals by mounting them on glass slides at room temperature with and without ethylene glycol treatment at 60°C overnight. These samples were analyzed using XRD (RINT1200, Rigaku) equipped for CuKα radiation at 30 kV and 20 mA, and were scanned from 2° to 40° at a scan rate of 1.0°/min.

Bulk concentrations of As, Cu, and Zn were determined by total digestion of 0.4 g of each sample by 15 ml of a 3:1 mixture of HNO₃ (ultrapure grade; Kanto Chemicals) and HF (TAMAPURE AA-100, Tama Chemicals) at up to 180°C for 15 min using a microwave assistant digestion system (ETHOS, Milestone), and analyzed by ICP–MS (iCap Qc, Thermo Scientific) after diluting the solutions by a factor of 10,000.

Sequential extraction of As from the solid samples was conducted using the modified method of Javed et al. (2013). Arsenic was sequentially extracted from sediment samples using various acids, such as sodium acetate, sodium dihydrogen phosphate, ammonium oxalate, Ti-citrate-ethylenediaminetetraacetic acid-bicarbonate, hydrogen fluoride, nitric acid, and hydrogen peroxide. It is divided into first (F1) to tenth (F10) fractions: F1, soluble in distilled water; F2, exchangeable and loosely adsorbed; F3, strongly adsorbed; F4, carbonate bounded; F5, co-precipitated with amorphous Fe, Al, and Mn oxyhydroxides; F6, co-precipitated with crystalline Fe, Al, and Mn oxyhydroxides; F7, associated with As-oxide and silicate clays; F8, co-precipitated with pyrite and amorphous orpiment; F9, associated with organic matter and secondary sulfides; and F10, residual.

4 | RESULTS

4.1 | Physicochemical characteristics of water samples

Water temperature in Nan-tank-pauk stream ranged from 20.8 to 22.8°C in the wet season (November), and from 22.6 to 26.5°C in the dry season (April–May; Table S1), which reflects the higher air temperature in the dry season. All of the pH values measured during the study were in the neutral to slightly alkaline range in both seasons. The pH gradually increased from 7.3 to 8.2 in the downstream direction in the wet season, with pH at the most downstream site (S8) being higher than that in the dry season (7.9; Table S1; Figure 2a). The pH of water in the DM was ~8.5 in both seasons. Eh values were relatively constant at ~450 mV in the wet season but increased gradually from ~360 to ~450 mV in the downstream direction in the dry season (Table S1). EC was also constant at...
48–50 mS/m in the wet season but showed a decrease from 57 to 50 mS/m in the downstream direction in the dry season (Figure 2b). In the wet season, turbidity increased markedly from 0.05 FTU at the most upstream site (S1) to 13.1 FTU in the upper and middle reaches of the stream before the entry of tributaries from the mine area (S3 and S4) and further increased downstream to 31.8 FTU at S8 (Table S1; Figure 2c). In the dry season, turbidity was more variable but generally increased in the downstream direction, similar to the pattern observed for the wet season. The turbidity of DM waters was much higher (28 FTU) in the dry season compared with the wet season (0.3 FTU). Turbidity in both tributaries in the wet season was fairly low (<10 FTU; Table S1). DO values were relatively constant at 7–9 mg/L in Nan-tank-pauk stream, except for the most upstream (S1) and upper-middle stream (S3) sites, which showed slightly lower DO values of ~6 mg/L in both the wet and dry seasons (Table S1).

4.2 Major and trace elements in water samples

Results of major cation and anion concentration analyses show that all of the water samples were dominated by calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), and HCO$_3^-$ (Table S2; Figure 3). No significant change in cation or anion concentrations was observed in the downstream direction in Nan-tank-pauk stream (Figure 3a,b), or between the wet and dry seasons. Ratios of Mg$^{2+}$ to Ca$^{2+}$ were higher in waters of the DM and the two tributaries compared with the main stream (Figure 3c,d). In Nan-tank-pauk stream, Ca$^{2+}$ and Mg$^{2+}$ concentrations were fairly uniform, although overall somewhat higher in the wet season (~65 and ~30 mg/L, respectively) than in the dry season (~50 and ~27 mg/L, respectively; Table S2; Figure 4a). Anions other than HCO$_3^-$ were minor in all of the water samples. No significant change in nitrate (NO$_3^-$) concentration was observed in the downstream direction in Nan-tank-pauk stream (Figure 4b). Although sulfate ions (SO$_4^{2-}$) were a minor component, their concentration showed a slight increase downstream from the middle reaches (S4) in Nan-tank-pauk stream; for example, from ~2 to ~3.5 mg/L in the wet season (Figure 4c). SO$_4^{2-}$ concentrations were very low (<4 mg/L) in both the DM and the two tributaries (Table S2). Calculated charge imbalance values were within ±16% for all of the water samples.

Results of trace-element analyses of water samples show that concentrations of metal and hazardous elements were all lower than 4 μg/L, except for Fe, which was 36.3 μg/L in the DM in the dry season. Other elements detected by ICP-MS analysis include Mn, Fe, Cu, Zn, As, Pb, and U (Table S2). Zinc was detectable in Nan-tank-pauk stream only in the wet season, and its concentration tended to decrease in the downstream direction (Figure 5a). In the wet season, concentrations of other elements (As, Cu, and Fe) were fairly uniform along the stream even below the mining area. Iron concentrations in Nan-tank-pauk stream were ~6 to ~11 μg/L. Arsenic, Cu, and Fe concentrations were lower in the DM and the two tributaries than in Nan-tank-pauk stream. However, during the dry season, their concentrations in Nan-tank-pauk stream tended to gradually increase in the
downstream direction, although the maximum concentrations were < 3 μg/L for As and Cu, and < 30 μg/L for Fe (Figure 5b). Concentrations of these elements were higher in the DM than in Nan-tank-pauk stream. Uranium was only detectable in the dry season, whose concentrations were ~0.2 μg/L.

### 4.3 Mineralogy and bulk chemical compositions of ore and sediment samples

Results of XRD analysis show that hematite ores (H1 and H2) are composed predominantly of hematite with minor goethite (Table 1). Limonite ores (L1–L9) are dominated by goethite with minor hematite and variable amounts of quartz. Some limonite ore samples also contain a manganese oxide (birnessite; e.g., L3 and L6) and barite (e.g., L9), and samples L5 and L8 also contain micaceous clay. The DM sediment sample (DM) is composed of quartz, calcite, manganese oxide, and dolomite, as well as micaceous clay. The mineralogical composition of sample S5, which was obtained from the middle reaches of Nan-tank-pauk stream close to the DM, is similar to that of DM. The most downstream sample (S8) shows a composition similar to that of sample S5 but with more quartz and minor manganese oxide and micaceous clay (Table 1).

Results of XRF analysis show that all of the ore samples are enriched in Fe (61–99 wt% as Fe₂O₃; Table S3). Hematite ore samples H1 and H2 in particular show a high Fe₂O₃ content (99 wt%). Limonite ore samples contain variable amounts of SiO₂ (1–12 wt%) and Al₂O₃ (0.4–3.0 wt%). Only limonite ore sample L9 contains a significant amount of BaO (8.6 wt%). Although Fe (hydr) oxide minerals were not identified (by XRD) in sediment sample DM, this sample contains ~6 wt% of Fe₂O₃. All of the ore samples are depleted in Na₂O, K₂O, CaO, and CaO.
Results of ICP-MS analysis after acid digestion show variable but generally low contents (<1 wt% or 10,000 mg/kg) of hazardous elements in the ores, except for As, which constitutes 2.06 wt% of sample L1 (Table S3). Arsenic contents in the ore samples show highly variable from low (17.8 mg/kg) in sample L4 to high (>1,000 mg/kg) in samples L1, L5, and L9 (Figure 6). Sample L3 contains relatively high Cu contents (2,600 mg/kg), whereas most other ore samples contain 100 to 1,000 mg/kg Cu. Zinc concentrations are <100 mg/kg in all of the ore samples. Uranium concentrations in the ores were ~40 mg/kg in average (Table S3). No significant differences in the concentrations of As, Cu, Zn, and U are observed between hematite and limonite ores. Sediment samples from the DM and Nan-tank-pauk stream (S5 and S8) also show low contents of these elements, although the As content of DM is slightly higher (92 mg/kg) than in S5 and S8 (Table S3; Figure 6).

### 4.4 Sequential extraction of As

Sequential extraction results for As show that four fractions are the dominant phases in both hematite and limonite ores (Figure 7a): F6 (co-precipitated with crystalline Fe, Al, and Mn hydroxides), F7 (associated with As-oxide and silicate clays), F9 (associated with organic matter and secondary sulfides), and F10 (residual). These fractions constitute more than 90% of all the As in the ore samples. Two hematite ore samples (H1 and H2) and one limonite ore sample (L4) contain significant amounts of As in fractions F9 and F10, which are essentially insoluble fractions. Arsenic in other limonite samples is hosted mostly (>65%) in fractions F6 and F7. In particular, samples L1, L5, and L9, which have high total As contents, are dominated by fraction F7 (>50%) followed by fraction F6 (>20%). Labile fractions F1 (soluble in distilled water) and F2 (exchangeable and loosely adsorbed) are very low (<0.3%) in all ore samples.

Compared with the ore samples, the sediment samples show slightly different patterns with respect to As fractions (Figure 7b). Fractions F9 and F10 are the
dominant phases for sample S8, which has the lowest As concentration of the sediment samples. This fraction dominance is similar to that of ore sample L4, which also has a low total As concentration. Other sediment samples (DM and S5) have F6 as a significant As-bearing phase in addition to fractions F9 and F10.

5 | DISCUSSION

5.1 | Bedrock control on water chemistry and turbidity in Nan-tank-pauk stream

All pH values measured at the study sites were in the nearly neutral to slightly alkaline range in both seasons (Table S1), which indicates an absence of the acidic pollution that can be caused by mining activities, such as acid mine drainage (AMD). The dominant cations and anions were Ca²⁺, Mg²⁺, and HCO₃⁻ (Figure 3), typical of water in an area with carbonate bedrocks (Appelo and Postma, 2005). The relatively high EC values in the stream water are also consistent with the carbonate bedrock geology (Ito et al., 2017). Dissolution of carbonate minerals in the bedrock provides high concentrations of Ca²⁺ and Mg²⁺ (Figure 4a), as well as high alkalinity from HCO₃⁻. The pH values in Nan-tank-pauk stream gradually increased in the downstream direction in both the wet and dry seasons (Figure 2a), which is likely due to the input of surface and/or ground waters that had undergone greater reaction with the bedrock downstream or to degassing of CO₂ from stream water with a high HCO₃⁻ concentration by aeration via the following reaction:

\[
\text{HCO}_3^- \rightarrow \text{CO}_2(g) + \text{OH}^-.
\]  

The stronger increase in pH in the downstream direction in the wet season suggests a greater influx of water into the lower reaches from the highland region where surface and/or ground water had reacted with the carbonate bedrock. Regardless of the along-stream pH gradient, the relatively high pH values indicate that the waters have a buffering capacity, imparting a tolerance to contamination by acidic water in the case that contamination might occur (Galvez and Sebastien, 1998).

Turbidity also gradually increased in the downstream direction in both the wet and dry seasons (Figure 2c). The increase in turbidity was not caused by mining activity because the increase was continuous in the downstream direction, and the mining operation is currently suspended. The source of turbidity is likely to have been suspended particulates produced by erosion, agricultural activities on farmland, and dust. The higher turbidity in the wet season compared with the dry season suggests that erosion played an important role in the production of turbidity. Turbidity in the DM waters differed substantially between the wet and dry seasons (Figure 2c). In the
dam, the high turbidity in the dry season reflects the low water level resulting from low precipitation and the consequent sampling depth closer to the bottom sediments.

5.2 | Present and past anthropogenic influences on stream water and sediment chemistries

Water chemistries measured during this study indicate that mining activity at Pinpet has no influence on Nan-tank-pauk stream waters. All of the chemical parameters lie within the water quality range specified in the World Health Organization (WHO) standard for drinking water (e.g., 75 mS/m for EC; WHO, 2004) and the Food and Agriculture Organization standard (e.g., 35 FTU for turbidity; Ayers and Wescot, 1985). All of the measured metal and ion concentrations were also below the WHO standards as well as the national quality standards for drinking water proposed by the Ministry of Health and Sports of Myanmar (e.g., 1.0, 0.05, 3.0, and 2.0 mg/L for Fe, As, Zn, and Cu, respectively). In the wet season, no significant external input of metal ions was observed, except for Zn at S2 (Figure 5b), which may have been caused by automobile exhausts from the nearby main road (Akhter and Madany, 1993; Al-Khashman, 2004). Most metal concentrations were higher in the dry than in the wet season and increased in the downstream direction in Nan-tank-pauk stream. However, the increases were gradual starting from S2 or S3, suggesting that the increase was caused by multiple sources and not a point source such as the mine site. We suggest that the increase in Fe and As concentrations are geogenic and attributable to an increased amount of fine (<0.2 μm) Fe-bearing particulates from eroded materials or dust. Previous studies (Smedley and Kinniburgh, 2002; Campbell and Nordstrom, 2014) have shown that As is strongly associated with Fe oxides in the natural environment. The coherent behaviors of Fe and As in Nan-tank-pauk stream suggest that the source and transport processes of these two elements are essentially identical, with As likely being strongly adsorbed onto the surfaces of Fe-oxide particles or incorporated into the crystal structure.

NO$_3^-$ concentrations ranged from 3 to 7 mg/L, which are relatively high values for aquatic plants and animals, particularly in the downstream reaches of Nan-tank-pauk stream in the wet season, although these values still lie within the WHO environmental standard for drinking water (50 mg/L; WHO, 2004) and the U.S. Environmental Protection Agency (EPA) environmental standard (10 mg/L; US EPA, 2012). The observed values are likely due to increased agricultural runoff in the harvest season (August–September). High concentrations of NO$_3^-$ can cause eutrophication. However, DO values were all well above 5 mg/L (Table S1) and at levels suitable for aquatic life and indicating no or negligible anthropogenic influence. Although SO$_4^{2-}$ concentrations were also low (<8 mg/L), these concentrations showed a slight increase in the middle reaches of Nan-tank-pauk stream at S3 and S4 (Figure 4c) in both the wet and dry seasons, which could be related to mining activity (i.e., the ores are still exposed at the surface), as the change occurred near the mine. As discussed in more detail in Section 5.3, the ores are composed of Fe oxides and hydroxides (Table 1). Although there was no substantial contribution of sulfate ions from the mine site, the slight increase detected may have been caused by impurities in the ores.

As mining activities at Pinpet are currently suspended, it might have been expected that no significant impact on the water chemistry of Nan-tank-pauk stream would be detected. In contrast, chemical compositions of sediments in the stream could record past anthropogenic influences because hazardous elements in the stream water may be sequestered and accumulated within sediments. However, bulk chemical compositions of the sediments (Figure 6) indicate no such contamination, with As, Zn, and Cu concentrations in the sediments being similar to those in uncontaminated sediments (Martin and Whitfield, 1983; Kabata-Pendias, 2011). Results of sequential extraction for sediments of sample S5, which is close to the mine site and DM, show that ~50% of As is associated with strongly adsorbed or amorphous or crystalline Fe, Al, and Mn oxyhydroxides (Figure 7b). The As host phase fraction pattern of S5 is similar to that of sediments from the DM, but different from that of sediments from the most downstream site (S8), which is ~10 km from the mine site. This suggests that a significant proportion of sediments at S5 were transported from the DM, at least for As-bearing minerals. However, this influence was not sufficient to change the bulk chemical compositions of the sediments at S5. Furthermore, because most fractions of As in sediments were found to be insoluble phases, the chemical impacts of sediment-hosted As on the surrounding environment are likely to be minimal.

5.3 | Geochemical characteristics of Pinpet Fe ores and potential environmental risk

Ores in the Pinpet deposit are composed mainly of Fe oxides and hydroxides (i.e., hematite and goethite). Although the origin and formation processes of ores in the Pinpet deposit are poorly understood, significant sulfide mineralization was not detected in our study. Exposure of sulfide minerals, particularly pyrite, at the surface by
mining activities is known to cause serious environmental issues, such as the occurrence of AMD (Akcil and Koldas, 2006). However, geochemical characteristics of the studied ore samples indicate that there should be no concern regarding AMD in the Pinpet mine, as supported by chemical compositions of water, including pH, and of sediments in the DM. No significant mineralization of U (>100 to 1,000 mg/kg) was also recognized in the Pinpet deposit as found in some IOCG deposits (Hitzman and Valenta, 2005).

Therefore, the primary environmental concern associated with the Pipet deposit is high concentrations of As in some ores (Figure 6). Although As concentrations are quite variable in the ore samples, those samples with high concentrations are likely to have undergone enrichment by hydrothermal fluids during activity on WNW–ESE-trending faults, which also caused remineralization of goethite to hematite (Zay Ya, unpublished data). Therefore, it is possible that a substantial As-rich zone is distributed in the deposit. However, our sequential extraction results indicated that most (>90%) of the As is hosted in insoluble fractions, namely F6 (co-precipitated with crystalline Fe, Al, and Mn hydroxides), F7 (associated with As-oxide and silicate clays), F9 (associated with organic matter and secondary sulfides), and F10 (residual). Together with the results of mineralogical analysis (Table 1), As in samples L1, L5, and L9, which have high total As concentrations, is inferred to be hosted predominantly by Fe hydroxides (i.e., goethite; F6) and clay (i.e., micaceous clay; F7). Because these phases are strongly bound to the minerals (i.e., more tightly than strong adsorption, F3), As is likely to be incorporated into the crystal structure, as commonly observed in other studies (Erbs et al., 2010). Therefore, it is unlikely that As at Pinpet will be released into the aquatic environment by interacting with water during future ore beneficiation through the DM could have delivered Fe and As into sediment of sample S5, which has a higher As concentration than downstream sediment (sample S8).

Because As is also hosted in Fe hydroxides, it could be further concentrated during ore beneficiation. Arsenic can be released to the air as a volatile component during smelting. Thus, appropriate treatment of the volatile component will be necessary during smelting should mine operations be restarted.

6 CONCLUSIONS

This study conducted a geochemical investigation of stream waters in Nan-tank-pauk stream and its tributaries, which flow through and near the Pinpet Fe mine area in southern Shan State, Myanmar. No significant contamination of surface water caused by mining activity or hematite and limonite ore beneficiation processes was found in the wet or dry seasons. All pH values measured at the study sites are neutral to slightly alkaline. Water alkalinity and Ca²⁺ and Mg²⁺ ion concentrations indicate that the chemical compositions are controlled by carbonate bedrock. All heavy metal and hazardous element concentrations are within the WHO standards for drinking water. Although Fe and As concentrations in the dry season increased in the downstream direction to 36 and 3.1 μg/L, respectively, these increases are inferred to be attributable to a geogenic source, namely the transportation of fine Fe-bearing particulates from eroded materials or dust.

Bulk chemical compositions of sampled sediments in Nan-tank-pauk stream indicate no significant past contamination by hazardous elements. Arsenic, Zn, and Cu concentrations in the sediments are similar to those in uncontaminated sediments, although some sediments in the DM were probably transported to the middle reaches of Nan-tank-pauk stream. Bulk mineralogical and chemical analyses of ore samples showed that hematite and limonite ores are mainly composed of Fe oxides and hydroxides (i.e., hematite and goethite), and that some limonite ore samples contain high amounts of As (up to ~2 wt%). However, sequential extraction results indicate that most (>90%) of the As in these As-rich ores is hosted in insoluble fractions, probably in the crystal structure of Fe hydroxides and clays. Therefore, arsenic is unlikely to be released into the aquatic environment by interacting with water during future ore beneficiation processes should mining be re-established at Pinpet.

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**SUPPORTING INFORMATION**
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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