Cadmium and lead distribution in pyrite ores: Environmental concerns over geochemically mobile fractions

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The pyrite ores are strategic industrial resources which generally serve as raw material for producing sulfuric acid. However, during the mining and industrial processing activities, associated toxic elements of cadmium (Cd) and lead (Pb) could be released into the surroundings, posing a significant threat to local environment and human health. In this study, the Institute for Reference Materials and Measurement (IRMM) sequential extraction scheme was used to investigate the geochemical fractionation of Cd and Pb in pyrite ores from a mining area located in Yunfu, western Guangdong, China. The results showed that most of Cd and Pb (>90%) were predominantly found in the geochemically mobile fractions, indicating that Cd and Pb were readily bioaccessible thus easily assimilated and accumulated by organisms. FESEM-EDS results showed that the studied pyrite ores were mainly composed of O, S, and Fe, while the XRD characterizations suggested that FeS₂ and SiO₂ were the major minerals. The high-resolution transmission electron microscope and element mapping characterization further confirmed that FeS₂ was the main mineral of pyrite ores which contained relatively enriched toxic heavy metals (e.g., Pb and Cd). The findings highlight that an extremely large amount of geochemically mobile heavy metals can be released into the environmental media during the mining and utilization processes of pyrite ores based on IRMM sequential extraction protocol. Therefore, proper countermeasures against environmental risks of utilizing pyrite ores should be taken to mitigate the impacts on local ecosystem and human health.

Keywords: Heavy metals, Pyrite ores, Geochemical fractions, Sequential extraction

1. Introduction

The environmental risks over utilization of minerals containing highly toxic metals have been receiving increased attention. For instance, heavy metals that are toxic even present in a low concentration, such as cadmium (Cd) and lead (Pb), could be released into the water, soils, and atmosphere from various industrial activities such as mining and smelting (Liu et al., 2019a; Wang et al., 2021). Excessive intake of Pb can lead to destruction of biological activity (Zhou et al., 2020), while high Cd poisoning can induce kidney disease, bone damage, and hematuria (Sasmaz et al., 2019). These elements can migrate and tend to be accumulated in the environment, which could consequently be subjected to further geochemical dispersal, transport, and transformation, posing a significant threat to both environmental quality and human health.

Geochemical fractionation of heavy metals in environment is the dominant factor influencing their reactivity (Peng et al., 2018; Lian et al., 2019) and bioavailability (Bastami et al., 2018; Ibrahim et al., 2020). Therefore, better understanding of geochemical fractionation is essential to control and remediation of heavy metal pollution. Sequential extraction techniques can provide referential indications regarding the bioavailability, toxicity, as well as mobility of heavy metals (Tessier et al., 1979; Huang et al., 2018). Tessier et al. (1979) proposed the first methodology named “sequential extraction” for analyzing the chemical phase distribution of heavy metals in soils and sediments. Kersten and Förstner (1986) further improved the analytical methods for identifying the chemical fraction of heavy metals in coastal sediments. However, the lack of the reference materials limits the verification of the effectiveness and comparability of this method. Subsequently, the Commission of the European...
Communities issued the standard three-step Institute for Reference Materials and Measurement (IRMM) sequential extraction scheme with certification of related reference materials (Ure et al., 1993; Luo et al., 2019). Due to the simplicity and reliable reproducibility, the standard procedure has been widely used in the fraction identification of heavy metals in the environmental matrix such as sediments, soils, and solid wastes.

The IRMM sequential extraction was widely applied to investigate the geochemical fractionation of heavy metals in soils and sediments (Gomez-Gonzalez et al., 2015; Huang et al., 2018; Liu et al., 2019b, 2020a; López-Arce et al., 2019; Li et al., 2020; Lin et al., 2020; Wang et al., 2020). For instance, Wang et al. (2020) reported that Cd in river sediments affected by Pb-Zn smelting activities mainly existed in acid extractable fraction. The geochemical fractionation of Cd, Cr, Cu, Ni and Pb in sediments of the Hooghly (Ganges) River Estuary, eastern part of India was studied by Mondal et al. (2020), and the results indicated that Cd primarily existed in the acid extractable fraction while Pb was dominant in the reducible fraction. Liu et al. (2020) found that the ratio of labile fractions (sum of the first three fractions) of Cu, Cd and Pb in the subtropical watershed was much higher than that from the temperate watershed. The distribution pattern of eight toxic elements (V, Pb, Cd, Cr, Co, Ni, Cu, and Zn) in river sediments collected in Selangor, Malaysia, was comprehensively investigated and several important findings were provided based on the sequential extraction method (Nemati et al., 2011). However, to our best knowledge, few systematical studies regarding the geochemical fractionation of toxic elements (Cd and Pb) in pyrite ores were conducted, and the release risk arising from labile geochemical fractions has been not yet well understood.

Therefore, the objectives of this work are to shed special light on the environmental aspects of pyrite ores during mining/smelting process by (1) investigating the geochemical fraction of heavy metals typical of Cd and Pb in pyrite ores via the IRMM sequential extraction method and (2) revealing the exposure flux/release risk of mobile fractions of typical toxic elements from pyrite ores.

2. Sampling and the analytical methods

2.1. Sample collection and pretreatment

Three types of pyrite ores (bulk, floatation, and powder) were obtained from Yunfu, Guangdong Province, China. The collected samples were ground and then sieved through 100-mesh sieve prior to further analysis. All glassware and polyethylene containers were washed with 5% (wt) HNO₃ for 48 h, then cleaned with ultrapure water, and finally dried for use.

2.2. Characterizations of pyrite ores

The mineralogy of the pyrite ores was characterized using powder X-ray diffraction (XRD, PW3040/60), and the results were analyzed with the software of Jade 6.0. Field Emission Scanning Electron Microscope combined with an Energy Dispersive Spectrometer (FESEM-EDS, JSM-7001F, JEOL, Japan) was employed to analyze pyrite ores morphology and elemental composition. Furthermore, the mineral composition and elemental distribution features of pyrite ores were characterized by a 200 kV Field Emission Transmission Electron Microscope (FETEM, JEOL JEM-2100F, JEOL, Japan) equipped with EDS element mapping.

2.3. Determination of metal contents

Aliquot of 0.2 g of pyrite ores was digested in X-press digestion vessel in a microwave digestion system with 6 mL 68% HNO₃, 2 mL 30% H₂O₂, and 2 mL 40% HF. After digestion, the sample was cooled down to room temperature and then redigested with addition of 4 mL saturated HBO₃ solution for 15 min, in order to remove excessive HF. Subsequently, the digested solution was diluted to 100 mL and preserved in 4 °C before analysis.

Content of the studied heavy metals in samples was determined based on an IRMM sequential extraction method which was verified by a standard reference (GBW073011). Specially, 0.5 g of each pyrite ore sample was used to extract four geochemical fractions of heavy metals (acid extractable, reducible, oxidizable, and residual fraction). The acid extractable fraction was obtained employing 20 mL CH₃COOH (0.11 mol/L, pH = 2.8). The reducible fraction was obtained using 20 mL NH₂OH-HCl (0.50 mol/L, pH = 1.5). The oxidizable fraction was determined employing 5 mL H₂O₂ (0.50 mol/L) and 25 mL CH₃COONH₄ (1 mol/L). The residual fraction was obtained after the digestion of the residue using HNO₃·HF.

2.4. Geochemical fractionation analysis

Geochemical fractionation of Cd and Pb in the pyrite ores was determined based on an IRMM sequential extraction method which was verified by a standard reference (GBW073011). Specially, 0.5 g of each pyrite ore sample was used to extract four geochemical fractions of heavy metals (acid extractable, reducible, oxidizable, and residual fraction). The acid extractable fraction was obtained employing 20 mL CH₃COOH (0.11 mol/L, pH = 2.8). The reducible fraction was obtained using 20 mL NH₂OH-HCl (0.50 mol/L, pH = 1.5). The oxidizable fraction was determined employing 5 mL H₂O₂ (0.50 mol/L) and 25 mL CH₃COONH₄ (1 mol/L). The residual fraction was obtained after the digestion of the residue using HNO₃·HF.

3. Results

3.1. Characterization of the pyrite ores

As displayed by FESEM-EDS analysis (Figure 1), pyrite ores were mainly composed of O, S, and Fe. The XRD characterizations (Figure 2) showed that the major minerals in the pyrite ores were pyrite (FeS₂) and quartz (SiO₂), with small amounts of szomolnokite (FeSO₄·H₂O), consistent with the FESEM-EDS analysis. The presence of szomolnokite may be due to the reactions occurring under weathering conditions (Oliveira et al., 2016). Ti is usually found in sulfur-containing minerals owing to its chalcophile property (Liu et al., 2020b; Voegelin, 2015; Wei et al., 2020; Yin et al., 2021). Further analysis by TEM-SAED (Figure 3) showed that metals like Pb and Cd were enriched in varying degrees in accordance with their brightness. The identified lattice fringes from high-resolution transmission electron microscope (HRTEM) image (Figure 3a) and SAED pattern corresponding to (220) and (111) planes (Figure 3b) were identified as the isometric system of pyrite. In addition, (113) and (220) planes were identified as the isometric system of Fe₃O₄ (Figure 3d).
3.2. Geochemical fractionation of the hazardous elements in pyrite ores

The results of geochemical fractionation of Cd and Pb in pyrite ores were shown in Figure 4. Even though in all types of pyrite ores, Cd and Pb were found in acid extractable, reducible, oxidizable and residual fraction at different levels, the geochemical fractions of Cd and Pb exhibited similar distribution patterns among different pyrite ores.

Cadmium in the pyrite ores was mainly present in acid extractable fraction (>85%), with reducible fraction less than 10%, oxidizable fraction below 1%, and residual fraction around 4%. Lead in the pyrite ores predominantly existed in acid extractable fraction (>55%), followed by...
reducible fraction (approximately 30%), and the oxidizable fraction occupied the lowest proportion (approximately 3.6%). The distribution of Cd and Pb in the four geochemical fractions generally followed the order as acid extractable fraction > reducible fraction > residual fraction > oxidizable fraction.

4. Discussion

4.1. Geochemical fractionation of the heavy metals in the pyrite ores

The mobility, toxicity, and bioavailability of heavy metals in the environment usually depend on their chemical forms (Huang et al., 2018). Thus, geochemical fractionation of metals in the pyrite ores could determine their environmental behaviors. The acid extractable fraction of the studied heavy metals in the pyrite ores refers to the part that is easily adsorbed onto the mineral microstructure layers, or bonded with carbonates, which tends to release into the environment media upon the decomposition of carbonate and/or the disappearance of Van der Waals force between the mineral structure layers (Zhang et al., 2007a, 2007b). Hence, the acid extractable fraction is most active and bioavailable, which can be readily released into the surroundings by means of rainfall, especially in the acid-rain region. As shown in Figure 4, more than 85% of Cd existed in acid extractable fraction. This finding is consistent with previous sequential extraction results (Burgay et al., 2020; Wang et al., 2020), which can be explained by the presence of Cd carbonate minerals in pyrite ores (Gujre et al., 2021). Cadmium in this fraction can be readily released into the environment via the process of ion exchange and decomposition of the Cd-carbonate phase (Jung et al., 2019), which may pose a great threat and should receive attention. The acid extractable fraction of Pb accounted for approximately 56%; a relatively high acid extractable fraction proportion of Pb was also found in the soil polluted by dust from a lead-acid battery plant by Liu et al. (2018).

The reducible fraction is mainly related to the Fe-Mn (hydr)oxides, and the studied heavy metals can be readily released into the environment under certain circumstances (Kang et al., 2019). In a natural ecological environment, acid rain and sulfuric acid oxidized by special bacteria can lead to the reducible fraction transferring into the environment. Reducing substances can react with the high-valence elements of the reducible fraction, further facilitating the release of toxic heavy metals. As displayed in Figure 4, approximately 9% of Cd and 30% of Pb in this fraction may be released into the environment. This finding is in accordance with the results by Mondal et al. (2020), who found that about 8% of Cd...
comprised the reducible fraction in sediments of the Hooghly (Ganges) River Estuary. High percentage of the reducible Pb may be ascribed to the formation of stable complexes between Pb and Fe-Mn (hydr)oxides in the process of (hydr)oxides co-precipitation (Zhang et al., 2017).

The oxidizable fraction is primarily related to the organic matter and sulphides in pyrite ores (Gao et al., 2015). Metals in this fraction can be oxidized and released into the environment under oxidating conditions (Al-Mur, 2020). Approximately 1% of Cd and 3.6% of Pb in this fraction may be leached out of the pyrite ores and migrate into the environment. Similar results have been found in previous studies. For example, the mean percentage of Cd in the oxidizable fraction was 3.7% in the suspended particulate matter of the Yellow River Estuary (Gao et al., 2015). The average ratios of Cd and Pb in the oxidizable fraction were 5.1% and 2.0% in intertidal surface sediments of Donghai Island, China, respectively (Zhang et al., 2016).

The residual fraction is present mainly in the lattice of the silicate, primary and secondary minerals, which is usually retained in the pyrite ores as an impurity embedded in the silicate (Nkinahamira et al., 2019). It is relatively stable and inactive, displaying lithophile nature, which suggests that metals in this fraction are not available for uptake by microorganism and plants (Prabakaran et al., 2019). Approximately 4% of Cd and 10% of Pb existed in residual fraction in the studied pyrite ores. The ratios of residual fraction of Cd and Pb are much lower than the results by Sundaray et al. (2011), who reported that the residual fraction dominated the Cd (53.9%) and Pb (66.5%) distribution in Mahanadi river-estuarine sediments.

4.2. Environmental implications and release flux of heavy metals in the pyrite ores

The labile fraction refers to the sum of the three geochemical fractions, that is, acid extractable fraction, reducible fraction, and oxidizable fraction. Approximately 95% of Cd and 90% of Pb in the studied pyrite ores were in labile fractions. Under natural environmental conditions, the acidification of pyrite ores could occur by means of rainwater especially acid rain. In particular, most of Cd and Pb in the pyrite ores can be readily released into the surroundings, causing serious pollution of the downstream rivers, sediments, and soils in the mining and peripheral areas. Therefore, the potential hazardous of pyrite ores to the surrounding is considerably high. It should be noted that the content level is not the decisive factor for the risk and threat posed by these heavy metals in the pyrite ores, but their chemical reactivity and geochemical affinity. In a previous study on the leaching experiment of pyrite ores, Li et al. (2010) reported that Cd detected in the leachate was mainly acid extractable and the pH value of the leachate altered slightly in the first 16 weeks. The reason was mainly ascribed to the dissolution of carbonates which acted as a buffer in the leachate. After 20 weeks, the oxidation

![Figure 4. The geochemical fractionation of the heavy metals in pyrite ores. (a)~(b): the contents of geochemical fractions of Cd and Pb, and (c)~(d): the ratio of geochemical fractions of Cd and Pb in pyrite ores including acid extractable fraction, reducible fraction, oxidizable fraction, and residual fraction. DOI: https://doi.org/10.1525/elementa.2021.00093.f4](http://online.ucpress.edu/elementa/article-pdf/9/1/00093/456229/elementa.2021.00093.pdf)
of pyrite dominated reaction, and pH value decreased significantly, resulting in remarkable release of the heavy metals including Cd, Pb, Zn, and Cu (Li et al., 2010). The release flux of a certain heavy metal could be roughly estimated according to labile geochemical fractions. Taking an average annual production of pyrite ores as 3 Mt, for example, assuming the average contents of Cd and Pb as 4.5 mg/kg and 1313.2 mg/kg, respectively, the estimated annual release of Cd and Pb to the environment would be 12.8 t and 3545.6 t, respectively. The estimated release flux of Cd and Pb would lead to significant damage to the ambient environment if proper countermeasures are not taken.

5. Conclusions
The results of the geochemical fractionation of Cd and Pb in the pyrite ores showed that dominant portion (>90%) of Cd and Pb was observed in the geochemically mobile fractions. The distribution of geochemical fractions of studied metals was generally similar among different types of pyrite ores. It implied that these heavy metals were homogeneously formed and incorporated into the pyrite ores under similar hydrothermal ore-forming conditions. Remarkably high ratios of Pb and Cd in the geochemically mobile fractions in the pyrite ores suggest a high potential environmental risk derived from utilization of these ores in the process of mining and smelting activities. Therefore, proper countermeasures toward pollution mitigation should be initiated.

Data accessibility statement
All the data have been presented in the manuscript.

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Competing interests
The authors have no competing interests to declare.

Author contributions
JC and SR contributed equally to this work.
Contributed to the data analysis and interpretation: JC, SR, CW, LW, JW, JL.
Contributed to acquisition of data: CW (sequential extraction), SR (characterizations).
Contributed to the project administration and funding acquisition: JW, JL.
Drafted and/or revised the article: JC, SR, YL, YZ, YJ, JS, LW, JW, YW, JL, YC.
Approved the submitted version for publication: all coauthors.

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