Study on the Interaction between Galena and Sphalerite During Grinding Based on the Migration of Surface Components

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ABSTRACT: In Pb–Zn ore flotation, unintentional activation of sphalerite often leads to difficult separation of Pb and Zn minerals, during which grinding plays a key role in unintentional activation. Therefore, the aim of this study was to evaluate the surface component changes of two different mineral particles and to propose the interaction between galena and sphalerite during mixed grinding using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The results show that after mixed grinding of the galena and sphalerite, the Pb content on the sphalerite surface increased with the decrease of Zn and Fe contents on the sphalerite surface. The lead ions from galena were obviously absorbed onto the sphalerite surface, while the zinc and iron ions from sphalerite were not obviously migrated to the galena surface. Principal component analysis (PCA) of a dataset composed of 206 positive ion peaks of galena and sphalerite indicates that the surface components of galena and sphalerite migrated from either side to different degrees. This study successfully identified an important factor for unintentional activation of lead and zinc minerals during flotation: homogenization of surface components of different minerals during grinding.

1. INTRODUCTION

Galena (PbS) and sphalerite (ZnS) are abundant in the earth and usually exist together in the same deposit. Most lead–zinc ores are processed by differential flotation, in which galena is recovered first followed by sphalerite. The addition/presence of lead ions (Pb2+) in ore pulp can directly promote the sphalerite flotation. Lead ions were considered to be able to substitute Zn in the sphalerite lattice to form PbS9 or to be adsorbed on the sphalerite surface in the form of PbS9 at near-neutral pH conditions. Liu et al. showed that zinc and lead ions can be released from sphalerite and galena during grinding, respectively. Rao and Natarajan found that lead ions could be detected on the surface of sphalerite after it contacted galena in deionized water. It is widely believed that grinding has a significant effect on the flotation of sulfide minerals. More active sites in newly generated surfaces during wet grinding of sulfide minerals lead to alterations of the chemical properties of mineral surfaces. Peng et al. suggested that the grinding environment played a key role in flotation separation of galena and pyrite, and this role was closely associated with the lead and iron species presented on the mineral surfaces. Xia et al. showed that the amount of copper ions adsorbed on the sphalerite surface was related to the grinding environment, and the oxidation of cathode mineral during grinding was an important factor in the flotation separation of sphalerite and chalcopyrite. Various electrochemical models have been proposed to explain the interactive influence between different sulfide minerals during the grinding process. Because the solutions of sphalerite and galena have different potentials, a direct contact of these minerals in aqueous systems would initiate a galvanic effect. Researchers have reported the effect of component migration between different minerals on their flotation. Hart et al. applied the principal component analysis (PCA)-assisted time-of-flight secondary ion mass spectrometry (ToF-SIMS) on the concentrate and tailing samples collected from the mineral
processing plant; their results indicated that the transfer of Cu and Ni between chalcocite and heazelwoodite resulted in inadvertent activation of heazelwoodite and depression of the chalcocite. Zanin et al.\textsuperscript{28} also applied ToF-SIMS to survey the surface chemistry of molybdenite in the concentrate from the copper–molybdenum flotation circuit; the results indicated
Figure 3. (a) Digital photograph magnified 100 times of the composite sample of galena and sphalerite after separate grinding; (b–e) images of Pb\(^+\), Zn\(^+\), and Fe\(^+\) and overlay of Zn\(^+\)–Pb\(^+\), respectively.

Figure 4. (a) Photograph magnified 100 times of the composite sample of galena and sphalerite after the mixed grinding; (b–e) images of Pb\(^+\), Zn\(^+\), and Fe\(^+\) and the overlay of Zn\(^+\) and Pb\(^+\), respectively.
higher concentrations of Ca, Fe, Mg, and K on the surface of slow floating molybdenite minerals compared to the fast floating grains. However, up to now, no systematic study has been carried out on the component migration between different minerals. In view of the fact that the grinding process is the initial stage of intense mineral mixing, in this study, the migration of surface chemical components of the mixed sample (galena and sphalerite) after mixed grinding was investigated using the ToF-SIMS. Because of the sampling depth of 1–3 nm and the ion imaging of sub-micron-resolution, ToF-SIMS is particularly suitable for analyzing the chemical component.

In the present work, a PCA model was also established based on the spectral data of ToF-SIMS to qualitatively analyze the variation of the surface components of galena and sphalerite after grinding.

2. RESULTS AND DISCUSSION

2.1. Imaging Analysis. Figure 1a shows a digital photograph of the sphalerite sample magnified 100 times, in which the green square area was the analysis area of 500 μm × 500 μm. The picture was taken with a pixel density of 256 × 256 and a horizontal resolution of less than 5 μm. Figure 1b–e shows the ion images of Pb+, Zn+, and Fe+ and the overlay of Zn+–Fe+ obtained from the analysis area. In the ion images, bright color indicated the area of high intensity, whereas dark color indicated the area of low ion intensity. The intensity was positively correlated with the content of the elements or molecules, and it was affected by the surface roughness of the samples. Ion intensity was usually lower in areas where the surfaces were concaved. The results in Figure 1 show that the Zn+ and Fe+ distributions on the sphalerite surface were similar, with a small amount of unevenly distributed Pb+. Fe+ is generally released from the lattice of sphalerite, but the Pb+ present may be released from galena associated with sphalerite. Both Zn+ or Fe+ distribution can be used to identify sphalerite particles.

Figure 2 shows the ion images of the galena surface. Figure 2 shows that compared with the sphalerite crystal in Figure 1, the signal intensity of Pb+ on the galena surface was obviously stronger, while that of Fe+ and Zn+ were obviously weaker. In fact, there was almost no signal of Zn+. Pb+ distribution can thus be used to identify galena particles in the samples.

Figure 3 shows the ion images of the mixed samples after separate grinding of galena and sphalerite. Partial galena and sphalerite particles can be distinguished by observing Figure 3a, in which some silver-gray and reflective particles are galena, while some light brown particles are sphalerite. From the ion images of Pb+, Zn+, and Fe+, the intensities distribution of Zn+ and Fe+ were similar and showed marked variation from the Pb+ distribution. However, compared with Figure 3, the intensity of Pb+ was higher in the region with high Zn+ distribution, indicating that Pb+ migrated from the galena surface to the sphalerite surface during the mixed grinding. Ion images of Pb+ and the overlay of Zn+ in Figure 4e were markedly different from those in Figure 3e, and the distribution region of the sphalerite changed from red to magenta, which was the overlay of red (Zn+) and blue (Pb+); suggesting that a certain amount of Pb+ were adsorbed on the sphalerite surface, that is, Pb+ released from the galena surface migrated to the sphalerite surface during the mixed grinding.

2.2. Statistical Analysis. Through the ion-imaging analyses of ToF-SIMS, we qualitatively determined the migration and adsorption of Pb+ on the sphalerite surface during grinding. This conclusion is consistent with the early findings that sphalerite is easily activated by the presence of lead ions in ore pulp during the flotation of Pb–Zn ore. However, the changes in the contents of Pb+, Zn+, and Fe+ on the surfaces of galena and sphalerite are still not clear, and until now, no research has reported the effect of sphalerite on the surface component of galena. In order to study the migration of Pb+, Zn+, and Fe+ on the surfaces of galena and sphalerite during grinding, SurfaceLab 6.8 (ION-TOF GmbH, Münster, Germany) was used for Zn+–Pb+ overlay images, delineating 6 regions of interest (ROIs) of galena and ROIs of sphalerite. Then, the mass spectra of each ROI were obtained by data reconstruction of each ROI, which is shown in Figure 5. Based on the intensities of Pb+, Fe+, and Zn+ peaks in the mass spectra, the normalized intensities of Pb+, Fe+, and Zn+ in Figure 6 were obtained.

Figure 6 shows the statistical intensities of Pb+, Zn+, and Fe+ on the sphalerite and galena surfaces. It can be seen from Figure 6 that compared with the galena in the separate grinding sample, the Pb+ intensity on the surface of galena in the mixed grinding sample decreased, with a slight increase of Zn+ intensity and no significant change of Fe+ intensity. Meanwhile, compared with the sphalerite in the separate grinding sample, the Pb+ intensity on the sphalerite surface in the mixed grinding increased, with a

Figure 5. Schematic diagrams of the ROI data reconstruction.
significant decrease of Fe+ and Zn+ intensities. These results show that during mixed grinding, the lead ions released from the galena surface migrated to and were adsorbed on the sphalerite surface; however, the zinc and iron ions released by sphalerite were hardly adsorbed on the galena surface. This indicates that the homogeneity in grinding was related to the elements the mineral contains. The decrease of Pb+ intensity on the galena surface shows that sphalerite also changed the surface component of galena during the mixed grinding to a certain extent.

The amounts of Zn2+ and Pb2+ released from sphalerite and galena during grinding were determined by Liu et al.11 and Bai et al.,12 respectively, and their studies showed that the concentrations of Zn2+ and Pb2+ released by 2 g sphalerite and 2 g galena in the presence of 40 mL of deionized water after grinding for 10 min were $8.79 \times 10^{-6}$ and $6.54 \times 10^{-6}$ mol/L, respectively. In the present work, 1 g sphalerite and 1 g galena were mixed and ground in the presence of 2 mL deionized water for 2 min. Ideally, the highest concentrations of Zn2+ and Pb2+ in the solution should be within the order of $10^{-5}$ mol/L. Based on this, the Eh–pH diagrams of Pb2+ and Zn2+ were drawn as shown in Figure 7. Figure 7 shows that Zn2+ and PbOH+ are stable ions at near-neutral pH conditions. Therefore, according to the analysis results of Figure 6, it can be inferred that Zn2+ hardly interacts with the galena surface, while PbOH+ is easily adsorbed on the sphalerite surface.

### 2.3. PCA Analysis

Although galena and sphalerite in the study were highly pure natural minerals, yet the surface changes of the minerals during grinding were still likely to be very complex.59 Recent studies have shown that galena and sphalerite contain rich fluid inclusions that can be destroyed by grinding, and the components will be released into the ore pulp, which affects the subsequent surface adsorption and flotation.51,52,53 In addition, the dissolution of the minerals, as well as the effects of O2 and H2O, also affects the mineral surface component.54,55...58 Therefore, the changes in the surface component during grinding may not be fully reflected by only analyzing the chemical changes of Pb, Zn, and Fe on the surfaces of galena and sphalerite.

It is difficult or even impossible to accurately analyze the chemical states of Pb, Zn, and Fe on the surfaces of galena and sphalerite or to completely determine the surface components of galena and sphalerite. However, with the aid of the positive/negative mass spectra of ToF-SIMS, a detailed analysis that contains almost all the components of material surface can be obtained, which enables us to comprehensively study the surface components of sphalerite and galena. Figure 5 shows the positive ion mass spectra of sphalerite and galena in the mass range of 52–212 m/z. It is not difficult to find that the positive ion mass spectra of sphalerite and galena contain multiple mass peaks. This implies that the comprehensive surface components of materials can be obtained in theory through the spectral analysis of ToF-SIMS, which is impossible to accomplish with complete mass spectrum analysis. To simplify the data interpretation as well as to classify and discriminate similar compounds, multivariate statistical analysis such as PCA, which has a wide range of applications in processing complex ToF-SIMS data, was employed.46–48 Unsupervised PCA is commonly applied to ToF-SIMS dataset to reduce the data, to recognize similarities and differences, and to categorize the spectra into distinguishable groups.49 In order to determine the changes in the surface components of the two minerals during grinding, a PCA model was established in this section to evaluate the interaction of galena and sphalerite.

Figure 8 shows the results of the PCA based on ToF-SIMS spectral data. The results of the PCA consist of scores and...
PC2 is the main distinction between the galena in the mixed grinding sample and other samples. The galena in the mixed grinding sample has the smallest negative PC2 scores (Figure 8a), corresponding to the organic peaks, such as C_3H_3+, Zn+, Fe+, PbOH+, PbO_2+, and Pb_2O_+ with the smallest negative PC2 loadings (Figure 8c), implying that the organics were adsorbed to the galena surface during the mixed grinding. It can be speculated that these organics may mainly be derived from fluid inclusions in sphalerite because the galena in the mixed grinding sample was distinguished from other separately ground galena samples. The sphalerite samples have both positive and negative scores on PC2, and no significant differences were observed on PC2, reflecting some minor differences in the sphalerite sample group.

The results of Figure 6 show that the intensities of Zn+ and Fe+ on the galena surface changed unobviously, but the intensity of Pb+ decreased obviously. Combined with the results of PCA, the adsorption of organics on galena surface may be also a reason for the decrease of the Pb+ intensity. In summary, the PCA results reflect that the surface components of sphalerite and galena after the mixed grinding became more similar, which indicates that the components of sphalerite and galena migrated to each other’s surface during the mixed grinding.

3. CONCLUSIONS

The change of surface components of sulfide minerals during grinding is an important factor affecting the selective flotation separation of galena and sphalerite. Therefore, in this study, we used ToF-SIMS to demonstrate that there is an interaction between galena and sphalerite during the mixed grinding. The following conclusions are drawn:

Compared with the galena in the separate grinding sample, the Pb+ intensity on the surface of galena in the mixed grinding sample decreased, with a slight increase of Zn+ intensity and no significant change of Fe+ intensity. Meanwhile, compared with the sphalerite in the separate grinding sample, the Pb+ intensity on the sphalerite surface in the mixed grinding increased, with a significant decrease of Fe+ and Zn+ intensities. A PCA model was successfully established, and its results indicate that the surface components of the galena and sphalerite became similar in the mixed grinding sample, while the surface properties of sphalerite/galena in the separate grinding sample are near to the surface properties of pure sphalerite/galena in the scores plot.

4. MATERIALS AND METHODS

4.1. Materials. In this study, galena and sphalerite samples were obtained from the natural deposits of Qinghai and Guangxi in China, respectively, as shown in Figure 9. Galena and sphalerite crystals were manually selected and then cleaned with deionized water in an ultrasonic cleaner to remove the surface
impurities of the samples. After natural air-drying for 1 h, the samples were ground using a three-head grinder with agate mortars and pestles (XPM-Φ120 × 3, China) and thereafter dry-screened (+0.180 to −0.425 mm size fraction). Quartz sand, anhydrous alcohol, and deionized water were used to clean agate mortars and pestles before grinding. The samples (+0.180 to −0.425 mm size fraction) were cleaned with deionized water three times in an ultrasonic cleaner, each time for 2 min with the liquid poured out after standing for 1 min. The resulting samples were air-dried for 1.5 h and then were sealed in spiral glass bottles. The results of chemical analysis show that the galena contained 86.16 wt % Pb, 13.41 wt % S, 0.11 wt % Fe, and 0.13 wt % Zn, while the sphalerite contained 64.83 wt % Zn, 31.8 wt % S, 1.97 wt % Fe, and 0.09 wt % Pb, indicating that galena and sphalerite samples have high purity.

4.2. Sample Preparation. Two grams of galena, 2 g of sphalerite, and 2 g of mixed samples (consisting of 1 g galena + 1 g sphalerite) were ground with a three-head grinder, respectively. The grinding procedure performed for each sample is as follows. The sample and 2 mL of deionized water were added to the agate mortar in turn and then ground for 2 min. Finally, 15 mL of deionized water was used to rinse the solution from the agate mortar and pestle into the funnel filter. Afterward, the filtered samples were naturally dried for 2 h and then were immediately used for ToF-SIMS analysis. Quartz sand, anhydrous alcohol, and deionized water were used to clean agate mortars and pestles before each grinding.

4.3. Time-of-Flight Secondary Ion Mass Spectrometry Analysis. ToF-SIMS analyses were conducted using a ToF-SIMS V (ION-TOF GmbH, Münster, Germany) instrument. The powder sample was glued to the double-sided conductive adhesive, purged with nitrogen gas to remove fine particles from the large particle surface, and thereafter transferred to the instrument sample loading chamber. After keeping in vacuum for 13 h, the sample was transferred to the instrument analysis chamber. The pressure in the analysis chamber was maintained below 5 × 10⁻⁶ mbar to avoid contamination. A pulse of 15 keV Bi⁺ primary ion beam was used, the Bi⁺ beam was rastered over a 500 × 500 μm² area in a sawtooth mode of 256 by 256 pixels, giving a pixel size of <5 × 5 μm. The process was stopped after 112 s of analysis. The positive spectra were calibrated using C⁺, CH₃⁺, and C₂H₅⁺ before further analysis. Data acquisition and subsequent data processing were performed using SurfaceLab 6.8 (ION-TOF GmbH, Münster, Germany). The total accumulated primary ion dose for data acquisition was about 1.26 × 10¹¹/cm², which was within the static SIMS regime.

4.4. Multivariate Statistical Analysis. For mixed minerals, the overlay of Pb²⁺ and Zn²⁺ image was divided into 6 ROIs for galena and 6 ROIs for sphalerite, respectively. For single minerals, the 500 × 500 μm analysis region was also divided into 6 ROIs with equal area; the spectra of each ROI were obtained by data reconstruction using SurfaceLab 6.8. The selection of the mass peak was determined by peak search program. The mass peaks that meet the following conditions were selected: mass range, 20–450 m/z; peak area, >5000 counts. A total of 206 positive ion peaks were selected. The intensity of each peak was normalized against the total ion intensity statistics of its spectrum, and then the data matrix was scaled by Poisson scaling and mean centering. Finally, PCA was performed using SIMCA 14.1 (MKS Umetrics, Sweden) software.

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