Application of MLA in analysis of limonite bearing-zinc ore

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Abstract: In this paper, based on the analysis of oxidized ore from a mine in Guangxi, the composition and content of elements and minerals, and the chemical composition of main minerals were studied by mineral liberation analyser method. The results show that the ore is a zinc-rich limonite, the content of the main mineral limonite is 47%, the majority of limonite is monomer, a few limonite is associated with clay, dolomite and so on, and cemented by clay. Zinc occurs mainly in the form of minerals such as smithsonite and hemimorphite, while a large amount of zinc occurs in limonite in the form of dispersion. The content of smithsonite is 8.73%, most of them are crust-like, colloidal ring-like, and are associated with limonite. The content of hemimorphite is 3%, most of them are single particle. This study will lay a mineralogical foundation for the follow-up development and utilization of this type of ore.

1. Introduction
Mineral liberation analyser is the most advanced automatic quantitative analysis system in the world, which has been applied in mining, metallurgy, materials and other fields[1,2]. It consists of a scanning electron microscope with an advanced energy spectrum and a software package. The design idea is to use backscatter electron image to distinguish different phases, to use energy spectrum analysis to identify minerals quickly and accurately, and to make full use of modern image analysis technology to obtain process mineralogical parameters. Its characteristic is to be making full use of backscatter electronic images, using modern image analysis techniques extensively. There are flexible and changeable in energy spectrum analysis models. It pays attention to the design of software from the thinking of process mineralogy, establishes the standard mineral sequences for test samples, and separates between the analysis test and the data processing and so on. Mineral liberation analyser is widely used in mineralogical analysis of various metallic minerals and coal[3-7]. In this study, the MLA method is used to analyze the composition and content of elements and minerals, and the chemical composition of main minerals.

2. Experimental sample and analytical test conditions
The ore sample was obtained from a mine in Guangxi. The process of MLA Analysis samples preparation are as following. Firstly, the study ore is crushed to -0.2mm, take up 100g representative samples after mixing and shrinking. Secondly, the samples were cold setting with epoxy respectively after grading and drying, and were made 30mm diameter photomask. At last, the pieces were ground
and polished to prepare qualified analysis samples for MLA analysis. The total number of particles analyzed was about 230,000. The analysis equipment is FEI MLA650 which analysis test condition parameters are working voltage 20KV, high vacuum mode and BSED probe.

3. Results and discussion

3.1 Element composition and content

The results of element composition and content of the sample are shown in Table 1.

| Element   | Zn   | Pb  | Fe₂O₃ | Cd   | MnO | S     | Al₂O₃ | SiO₂ |
|-----------|------|-----|-------|------|-----|-------|-------|------|
| Content/% | 8.60 | 1.67| 44.16 | 0.038| 0.31| 0.47 | 5.32 | 22.99|

| Element   | CaO | MgO | K₂O | Na₂O | P   | TiO₂ | BaO |
|-----------|-----|-----|-----|------|-----|------|-----|
| Content/% | 1.71| 1.02| 1.03| 0.08 | 0.091| 0.24 | 0.14|

3.2 Mineral composition and content

The mineral composition and content of the sample are shown in Table 2. It can be seen from Table 2 that the main minerals are limonite with a content of about 47%, followed by zinc minerals, mainly smithsonite and hemimorphite, a small amount of sphalerite and zinc mica, and a variety of lead oxide minerals with the lower content, including cerussite, galena, pyromorphite, hydrophotolite, hydrophobite, lead vitriol, plumbarite and so on. The other sulfides are mainly pyrite with less amount. Gangue minerals are mainly clay illite, sericite, chlorite, followed by quartz, dolomite and so on. Furthermore, a small amount of silver acanthite was found in the sample.

| Mineral     | Content /% | Mineral     | Content /% | Mineral     | Content /% |
|-------------|------------|-------------|------------|-------------|------------|
| acanthite   | 0.002      | pyrite      | 0.612      | psilomelane | 0.443      |
| limonite    | 57.439     | quartz      | 5.280      | plumbarite  | 0.003      |
| cerussite   | 0.824      | albite      | 0.13       | jarosite    | 0.175      |
| galena      | 0.002      | sericite    | 3.058      | lead vitriol| 0.252      |
| pyromorphite| 0.035      | chlorite    | 0.115      | rutile      | 0.147      |
| hydrophotolite| 0.083    | stilpnomelane| 0.220     | barite      | 0.033      |
| hydrophobite| 0.128      | tourmaline  | 0.013      | gypsum      | 0.011      |
| sphalerite  | 0.235      | illite      | 11.698     | gibbsite    | 0.177      |
| hemimorphite| 2.999      | apatite     | 0.152      | slag        | 1.743      |
| smithsonite | 8.728      | calcite     | 0.582      | iron filings| 0.494      |
| zinc mica   | 0.532      | dolomite    | 3.453      | others      | 0.202      |

3.3 The chemical composition of the major minerals

3.3.1 Limonite

The content of limonite is 47%, most of limonite is monomeric (Fig.1(a)), a few limonite is associated with clay and dolomite (Fig.1(b)), and some siderite is closely associated with limonite (Fig.1(c)). In addition, in the local fracture zone, it can be seen that limonite, dolomite and so on are broken granular and cemented by clay (Fig.1(d)).
Fig. 1 SEM BSE images of limonite

The composition of limonite was analyzed by SEM in Table 3. As can be seen from Table 3, the limonite generally contains iron, zinc and lead, with an average of Fe₂O₃ 86.64%, ZnO 6.61% and PbO 2.05%.

Table 3 Results of energy spectrum analysis of limonite.

| Measuring Point | ZnO | PbO | Fe₂O₃ | SiO₂ | Al₂O₃ | K₂O | CaO | P₂O₅ | MgO | TiO₂ |
|-----------------|-----|-----|-------|------|-------|-----|-----|------|-----|------|
| 1               | 4.62| 2.01| 90.87 | 2.07 | 0.21  | 0.01| 0.21| 0.00 | 0.00| 0.00 |
| 2               | 2.33| 0.52| 93.89 | 1.81 | 0.88  | 0.11| 0.15| 0.25 | 0.06| 0.00 |
| 3               | 2.53| 1.59| 85.47 | 5.64 | 3.24  | 0.87| 0.06| 0.15 | 0.26| 0.19 |
| 4               | 9.21| 1.57| 84.85 | 2.93 | 0.80  | 0.04| 0.28| 0.32 | 0.00| 0.00 |
| 5               | 5.38| 0.72| 90.19 | 1.75 | 1.57  | 0.01| 0.18| 0.03 | 0.17| 0.00 |
| 6               | 4.17| 2.70| 88.33 | 2.46 | 0.74  | 0.25| 0.39| 0.74 | 0.22| 0.00 |
| 7               | 3.07| 1.20| 92.99 | 1.71 | 0.76  | 0.10| 0.10| 0.07 | 0.00| 0.00 |
| 8               | 4.38| 1.57| 89.40 | 2.57 | 1.56  | 0.16| 0.13| 0.08 | 0.15| 0.00 |
| 9               | 8.95| 0.68| 85.80 | 3.34 | 0.73  | 0.11| 0.15| 0.19 | 0.05| 0.00 |
| 10              | 3.29| 12.72| 80.47 | 0.86 | 0.66  | 0.32| 0.16| 1.27 | 0.25| 0.00 |
| 11              | 5.64| 3.02| 87.29 | 2.76 | 0.97  | 0.12| 0.20| 0.00 | 0.00| 0.00 |
| 12              | 5.97| 2.13| 88.24 | 3.18 | 0.23  | 0.03| 0.19| 0.01 | 0.02| 0.00 |
| 13              | 28.74| 0.90| 66.09 | 3.17 | 0.65  | 0.03| 0.28| 0.14 | 0.00| 0.00 |
| 14              | 6.46| 1.18| 83.63 | 3.12 | 5.19  | 0.26| 0.14| 0.00 | 0.02| 0.00 |
| 15              | 1.53| 0.07| 91.30 | 3.53 | 2.89  | 0.39| 0.12| 0.02 | 0.15| 0.00 |
| 16              | 9.41| 0.16| 87.40 | 2.69 | 0.19  | 0.01| 0.13| 0.01 | 0.00| 0.00 |
| Average         | 6.61| 2.05| 86.64 | 2.72 | 1.33  | 0.18| 0.18| 0.21 | 0.08| 0.01 |

Fig. 2 is the X-ray spectrum of limonite particles in the sample. It can be seen from Fig. 2, there are obvious impurity peaks such as Zn and Pb in the limonite particles, which indicates that the limonite contains dispersed zinc and lead.
3.3.2 Sphalerite
The content of sphalerite is about 0.24%. The results of multi-point analysis of chemical composition energy spectrum are shown in Table 4. As can be seen from Table 4, the sphalerite contains on average 65.06%Zn, 1.60%Fe, 32.85%S and 0.31%Cd. Sphalerite is mostly monomeric (Fig.3). Sphalerite and limonite can also be found in association or inclusion.

Table 4 Results of energy spectrum analysis of sphalerite.

| Measuring Point | Zn  | Cd  | Fe  | S    | Al  | Si  |
|-----------------|-----|-----|-----|------|-----|-----|
| 1               | 65.35 | 0.38 | 1.25 | 32.83 | 0.08 | 0.11 |
| 2               | 65.41 | 0.36 | 0.89 | 33.10 | 0.11 | 0.13 |
| 3               | 64.21 | 0.28 | 2.61 | 32.76 | 0.03 | 0.11 |
| 4               | 65.22 | 0.20 | 1.67 | 32.66 | 0.18 | 0.07 |
| 5               | 64.87 | 0.29 | 1.52 | 33.08 | 0.16 | 0.08 |
| 6               | 65.29 | 0.34 | 1.66 | 32.66 | 0.01 | 0.04 |
| Average         | 65.06 | 0.31 | 1.60 | 32.85 | 0.10 | 0.09 |

3.3.3 Smithsonite
The content of smithsonite is 8.73%, which is the most zinc mineral. The results of multi-point analysis of chemical composition energy spectrum are shown in Table 5. From Table 5, the smithsonite contains varying amounts of iron and other impurities, with average ZnO55.00% and FeO6.75%. It can be seen from Fig.4, most of smithsonite is in the shape of crust and colloidal ring, and most of them are associated with limonite ((a) with a banded structure, (b) mainly monomeric, (c) limonite inclusions in the rings and clay filling in the crystal cavities).
### Table 5 Results of energy spectrum analysis of smithsonite.

| Measuring Point | Chemical composition and content/% |   |   |   |   |   |   |   |   |
|-----------------|-----------------------------------|--|--|--|--|--|--|--|--|
| 1               | ZnO 40.39 FeO 21.01 CdO 0.25 PbO 0.52 CaO 0.80 MnO 0.09 SiO2 1.25 Al2O3 0.67 CO2 35.02 P2O5 0.00 |
| 2               | ZnO 46.37 FeO 14.95 CdO 0.43 PbO 0.00 CaO 0.47 MnO 0.00 SiO2 1.29 Al2O3 0.12 CO2 36.22 P2O5 0.15 |
| 3               | ZnO 54.04 FeO 7.38 CdO 0.55 PbO 0.00 CaO 0.76 MnO 0.00 SiO2 0.89 Al2O3 0.61 CO2 35.77 P2O5 0.00 |
| 4               | ZnO 54.12 FeO 7.82 CdO 0.25 PbO 0.39 CaO 1.04 MnO 0.00 SiO2 0.75 Al2O3 0.23 CO2 35.22 P2O5 0.18 |
| 5               | ZnO 55.05 FeO 1.78 CdO 0.28 PbO 0.00 CaO 1.05 MnO 0.13 SiO2 1.89 Al2O3 2.56 CO2 37.26 P2O5 0.00 |
| 6               | ZnO 55.52 FeO 7.54 CdO 0.26 PbO 0.00 CaO 0.14 MnO 0.00 SiO2 0.28 Al2O3 0.11 CO2 36.15 P2O5 0.00 |
| 7               | ZnO 57.40 FeO 4.79 CdO 0.37 PbO 0.00 CaO 0.30 MnO 0.00 SiO2 0.40 Al2O3 0.20 CO2 36.54 P2O5 0.00 |
| 8               | ZnO 58.85 FeO 3.86 CdO 0.35 PbO 0.00 CaO 1.51 MnO 0.00 SiO2 0.22 Al2O3 0.08 CO2 35.13 P2O5 0.00 |
| 9               | ZnO 60.10 FeO 1.25 CdO 0.32 PbO 0.00 CaO 2.00 MnO 0.00 SiO2 0.48 Al2O3 0.57 CO2 35.28 P2O5 0.00 |
| 10              | ZnO 60.40 FeO 2.78 CdO 0.35 PbO 0.00 CaO 0.40 MnO 0.00 SiO2 0.43 Al2O3 0.42 CO2 35.22 P2O5 0.00 |
| 11              | ZnO 62.75 FeO 1.04 CdO 0.11 PbO 0.00 CaO 1.05 MnO 0.00 SiO2 0.15 Al2O3 0.09 CO2 34.81 P2O5 0.00 |
| **Average**     | ZnO 55.00 FeO 6.75 CdO 0.32 PbO 0.08 CaO 0.87 MnO 0.02 SiO2 0.73 Al2O3 0.51 CO2 35.69 P2O5 0.03 |

Fig. 4 SEM BSE images of smithsonite

#### 3.3.4 Hemimorphite

The content of hemimorphite is less than that of smithsonite, which is about 3%. The results of multi-point analysis of chemical composition energy spectrum are shown in Table 6. As can be seen from Table 6, the hemimorphite contains a small amount of impurities such as Fe, Al, K and Ti, with an average ZnO 71.05%. The majority of hemimorphite are monomer particles (Fig. 5).

### Table 6 Results of energy spectrum analysis of hemimorphite.

| Measuring Point | Chemical composition and content/% |   |   |   |   |   |   |   |
|-----------------|-----------------------------------|--|--|--|--|--|--|--|
| 1               | ZnO 68.52 FeO 4.48 K2O 0.38 TiO2 0.16 Al2O3 3.39 SiO2 23.07 P2O5 0.00 |
| 2               | ZnO 65.58 FeO 3.80 K2O 0.76 TiO2 0.50 Al2O3 5.38 SiO2 23.98 P2O5 0.00 |
| 3               | ZnO 70.49 FeO 0.00 K2O 0.22 TiO2 3.96 Al2O3 1.57 SiO2 23.76 P2O5 0.00 |
| 4               | ZnO 74.59 FeO 3.01 K2O 0.00 TiO2 0.02 Al2O3 0.32 SiO2 22.06 P2O5 0.00 |
| 5               | ZnO 72.88 FeO 2.40 K2O 0.12 TiO2 0.10 Al2O3 1.14 SiO2 23.36 P2O5 0.00 |
| 6               | ZnO 74.22 FeO 1.30 K2O 0.00 TiO2 0.01 Al2O3 0.47 SiO2 23.39 P2O5 0.61 |
| **Average**     | ZnO 71.05 FeO 2.50 K2O 0.25 TiO2 0.79 Al2O3 2.05 SiO2 23.27 P2O5 0.10 |
3.3.5 Zinc mica
The sample contains a small amount of zinc mica, which is a mica group mineral containing zinc. The results of multi-point analysis of its chemical composition are shown in Table 7. It can be seen from Table 7, the composition of the mica is complex, with an average ZnO36.42%.

Table 7 Results of energy spectrum analysis of zinc mica.

| Measuring Point | Chemical composition and content/% |
|-----------------|-----------------------------------|
|                 | ZnO  | FeO  | PbO  | K₂O  | CaO  | MgO  | TiO₂ | Al₂O₃ | SiO₂ | P₂O₅ |
| 1               | 19.42| 14.44| 0.42 | 2.40 | 0.29 | 0.00 | 0.35 | 37.44 | 25.24| 0.00 |
| 2               | 35.26| 14.37| 0.73 | 1.71 | 0.88 | 0.36 | 0.00 | 18.47 | 28.22| 0.00 |
| 3               | 41.23| 5.00 | 0.24 | 1.15 | 0.00 | 0.00 | 0.36 | 26.88 | 24.76| 0.38 |
| 4               | 42.58| 2.66 | 1.77 | 0.67 | 0.00 | 0.00 | 0.18 | 30.48 | 20.54| 1.12 |
| 5               | 43.62| 3.64 | 0.49 | 0.92 | 0.28 | 0.00 | 0.16 | 25.12 | 25.09| 0.68 |
| Average         | 36.42| 8.02 | 0.73 | 1.37 | 0.29 | 0.07 | 0.21 | 27.68 | 24.77| 0.44 |

3.3.6 Cerussite
The content of lead mineral is much less than that of zinc mineral. The content of cerussite is 0.82%. As can be seen from Table 8, cerussite contains a small amount of impurities such as Fe, Zn. The average PbO82.22%. The majority of cerusite is monomer particles (Fig.6).

Table 8 Results of energy spectrum analysis of cerussite.

| Measuring Point | Chemical composition and content/% |
|-----------------|-----------------------------------|
|                 | PbO  | ZnO  | FeO  | CO₂  |
| 1               | 82.91| 0.06 | 0.38 | 16.65|
| 2               | 82.48| 0.01 | 0.97 | 16.54|
| 3               | 82.46| 0.14 | 0.55 | 16.85|
| 4               | 82.23| 0.52 | 0.53 | 16.72|
| 5               | 81.04| 0.86 | 1.26 | 16.84|
| Average         | 82.22| 0.32 | 0.74 | 16.72|
4. Conclusions

(1) The composition and content of elements and minerals, and the chemical composition of main minerals were studied by mineral liberation analyser method. This study will lay a mineralogical foundation for the follow-up development and utilization of this type of ore.

(2) The ore is a zinc-rich limonite, the content of the main mineral limonite is 47%, the majority of limonite is monomer, a few limonite is associated with clay, dolomite and so on, and cemented by clay.

(3) Zinc occurs mainly in the form of minerals such as smithsonite and hemimorphite, while a large amount of zinc occurs in limonite in the form of dispersion. The content of smithsonite is 8.73%, most of them are crust-like, colloidal ring-like, and are associated with limonite. The content of hemimorphite is 3%, most of them are single particle.

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