1 Introduction

Lead and zinc sulfide deposits are the main deposits type in the nature. Although lead and zinc have similar geochemical properties and behaviors, and they are referred to as twin close intergrowth minerals, the phenomenon of mineral assemblage zoning (lower or center of ore-body is rich in zinc, the upper or outside is rich in lead) (Fig.1) occurs widespread in these deposits. It is indicated that paragenesis and separation had happened in the process of sulfide precipitation.

Many researchers have studied the mechanism of the paragenesis and separation of lead and zinc by the experiments of solubility (Anderson, 1975; Nriagu, 1971; Bourcier, 1988; Ruaya, 1986; Seward, 1984; Barrett, 1977; Reed, 2006; Shang, 2003). However, these researches focus on their properties and behaviors in the process of migration. There is lack of detail research in the physiochemical conditions of the formation of mineral assemblage in the process of precipitation.

The Zhaotong large-type lead-zinc deposit is one of the representatives deposits in northeastern Yunnan, China. The major minerals are often characterized by zoning as shown in Fig.2 from the floor to the roof of the ore - bodies.

Demonstrating the Zhaotong lead and zinc deposit as a case study, the pH-logfo\textsubscript{2}, logfo\textsubscript{2} -logfs\textsubscript{2}, pH-logphas diagrams and ore-forming physiochemical conditions have been constructed and studied. Based on the phase diagrams, therefore, the pH, a\textsubscript{p}, f\textsubscript{o2} and fs\textsubscript{2} conditions of the migration and precipitation, as well as the processes and the zoning mechanism of the metallic minerals have been discussed in this paper.

2 Methods

Base on the detailed field geological work, we have constructed the pH-logfo\textsubscript{2}, logfo\textsubscript{2} -logfs\textsubscript{2}, pH-logphase diagrams and ore-forming physiochemical conditions.
diagrams (Fig.3) in the Zn-Pb-O-S-Fe hydrothermal system by using the test results of fluid inclusion (Han et al. 2007) as references.

In order to draw these phase diagram, in terms of the paragenetic assemblage relationship of the minerals, the chemical equations of the ore minerals should be established at first. The Nernst equation can be used to calculate the pH, log$f_{\text{O}_2}$ and log$f_{\text{S}_2}$ of the reaction equations (Lin,1985).

\[
\begin{align*}
\text{Eh} &= \text{Eh}_0 + \frac{RT}{nF} \ln \left( \frac{\text{oxidation state}}{\text{reduction state}} \right) \\
\text{Eh}_0 &= \frac{\Delta G_{R,T}^\theta}{nF}
\end{align*}
\]

Then the $f_{\text{O}_2}$ and $f_{\text{S}_2}$ are calculated by using the formula below:

\[
\Delta G_{R,T}^\theta = -2.303RT \log f_{\text{O}_2}
\]

The pH-log$f_{\text{O}_2}$, log$f_{\text{O}_2}$-log$f_{\text{S}_2}$ phase diagram are drawn on the basis of calculation.

3 Results

Taking the 473 K phase diagram as example, the phase diagrams are demonstrated the physiochemical conditions of the metallic mineral assemblage, such as pH, log$a$, log$f_{\text{O}_2}$ and log$f_{\text{S}_2}$. It is shown that metallic mineral zoning of the Pb-Zn sulfide deposits was resulted from the multi-controls of pH, $a$, $f_{\text{O}_2}$ and $f_{\text{S}_2}$, especially the $f_{\text{O}_2}$ and $f_{\text{S}_2}$which are the key controlling factors.

4 Conclusions

In essence, the lead-zinc zoning phenomenon in Pb-Zn sulfide deposits is paragenesis and separation of lead and zinc in the process of sulfide precipitation. This rule is controlled by the geochemical environment. The zoning phenomenon formed at the different conditions. Because of galena and sphalerite as distinguishable mineral, the important significances of the law are not only in the theory, but also in the ore exploration.

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