Research on provenance of MVT Pb-Zn deposits

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Abstract. Based on previous research materials, provenance of MVT Pb-Zn deposits are explored. The results suggest that in China, MVT Pb-Zn ores form when deep met allogenic materials are transported to shallow zones through large deep zones and taken away after they are leached by fluids. All typical MVT Pb-Zn ores present features of crust sources all over the world.

1. Introduction
Produced in carbonatite and with evident epigenetic characteristics, MVT Pb-Zn deposits are well-known for their typical development in Mississippi River, the United States. This category of deposits has been explored for over a century (Garven, 1985; Ge, 1992; Appold, 1999; Leanch et al., 2005). Over the past few years, people have paid more attention to research on MVT Pb-Zn deposits with the growing demands for lead and zinc in the world. Based on previous research, the author analyzes material sources of MVT Pb-Zn deposits, in order to make basic materials available for future research on this kind of deposits.

2. Provenance of MVT Pb-Zn deposits
Concerning MVT deposits, people have acknowledged that metals of fluids originate from sedimentation basins or effects of leaching produced by brine in passing by the water bearing bed. It has been recognized that solubility of metals is impacted by temperature, pressure and fluid composition, particularly by fluid ligands of basins (Basukli et al, 2004). Many scholars consider that joint effects of content, temperature, pH value and element activity are decisive factors for formation of ligands and capacities of metal ions in solutions (Leach et al., 2005). Although both sulphides and organic metal complex compounds are likely to carry metal ions, the solubility of sulphides is low and organic matter is not common in MVT deposits. Owing to high content of chlorides in fluids, complex compounds of metal chlorides are most likely to transport metals of fluids. Since ore-forming fluids are cryogenic (<200 °C) with a narrow range of changes, pH value of fluids is influenced by carbonatite of wall rocks, and the effects of temperature and pH value upon Pb and Zn solubility of ore-forming fluids are far weaker than reduction of sulphur activity (Plumlee et al, 1994), such reduction is highly effective for controlling content of Pb and Zn in ore-forming fluids.

Nowadays, content of metals is extremely high in brine of oilfields, where pH value of brine is rarely below 4 but mostly above 4.5 to 6 (Emsbo, 2000). In such brine, the content of Pb and Zn can be a high date, negatively correlated to content of reduced sulfur. In line with characteristics of MVT ore-forming fluids, oilfield brine has become convincing evidences for brine metallogenesis of MVT Pb-Zn deposits. However, it is still difficult to clarify how to transport ore-forming fluids and contributions of intruded or surrounding strata.
Sangster et al (1990) have summarized characteristics of lead isotopes in 17 MVT Pb-Zn deposits and mines. In the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ dot plot (Fig.1), lead isotope values make up a narrow band, which may be represented by a straight line with a slope of 0.096. Such distribution is considered to be the result of the mixing between leached lead from Precambrian basements and lead from secondary radioactivity of overlaying sediments.

Apart from Pine Point, composition of lead isotopes is associated with age differences between crystalline basements and met allogenic adjacent rocks in most MVT Pb-Zn deposits. In case of greater age differences, there will be more lead isotopes in radioactive sources that enter the deposits. The extent to which radioactive lead is blended into the deposits is dependent upon geological and geochemical changes to ore-forming materials during their transport and deposition. For instance, homogeneous composition of lead isotopes in Pine Point suggests that these isotopes would be the single sources of lead, or multi-source lead is homogenized in the process of extracting or transporting ore-forming fluids. The ratio of lead isotopes from radioactive sources varies so greatly that its dots form a line. Such changes indicate that lead comes from multiple sources, including further alternation of lead-included adjacent rocks on impervious strata, multi-source rocks or multiple sources of brines.

After statistically analyzing test results of 570 lead glance and sphalerite (Fig 2), Leach et al. (2005) have reported that lead tends to be from basements in many MVT Pb-Zn deposits (or ore concentration areas). For instance, the value of $\mu$ is relatively high in Bushy Park, Pering, Gays River, and Midlands Region, Lennard Shelf, Upper Mississippi Valley, Southeast Missouri regions and Tri-State regions, where lead is supposed to be from upper crusts.

![Fig 1 Growth of Lead Isotopes in 17 MVT Deposits and Mines [Sangster et al (1990)]](image-url)
Fig. 2 Composition of Lead Isotopes in 30 MVT Deposits [Leach et al. (2005)]

Lead isotopes of ores and deposits in Sichuan, Yunnan and Guizhou (including Maozu, Qilin Mines, Tianbao Mountain and Dalianis) are mapped upon the $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb. Some of them fall upon the average evolution belt of upper crusts or include lead from crusts, or those under the evolved orogenic belt are partially from the earth’s mantle (Zhang et al., 2005). The projection points are relatively scattered in ore concentration areas of northwestern Hunan Province such as Huayuan, Fenghuang and Longshan, mostly distributed in evolved belts of upper crusts and orogenic belts, and partially allocated in the earth’s mantle and lower crusts (Zhong et al., 2007). As a whole, ore-forming material sources of Chinese MVT Pb-Zn deposits mostly come from basement strata above orogenic belts, and deep metallogenic materials are possibly leached by fluids to form ores when they are transported to shallow zones through large deep fault zones.

3. Feature of S isotope

MVT Pb-Zn deposits are formed by a wide range of sulfur isotopes, which are different from sulfur isotopes of magma. Characteristic distribution of $\delta^{34}$S has been detected in all areas, which apparently reflects formation mechanisms of sulphur sources and H2S. The distribution range of sulphur elements in MVT Pb-Zn deposits is consistent with sulphur deviation of various crust sources, including sulfur-containing organic matters, H2S gas, and sulfate-containing evaporate, basin brine, inter-particle seawater and par genetic sulphate. In general, $\delta^{34}$S of sulfide in MVT Pb-Zn deposits is similar to rock isotopes near the deposits. However, the ratio of such $\delta^{34}$S is lower than that of contemporaneous seawater isotopes in adjacent rocks. Hence, there must be a crust of rocks as a direct source of sulphur for a MVT Pb-Zn deposit, where the sulfur of rocks is available from the seawater. Such typical light sulphur isotopes related to seawater of the depositional period of adjacent rocks shall be attributed to fractionation of sulphur isotopes in the process of reducing various sulphate rocks.

In some areas, the composition of $\delta^{34}$S covers a relatively wide range, which suggests mixing of sulphur from different sources, fractionation of isotopes with the same function as a type of minerals, imbalance between mineral pairs in terms of temperature or chemical environment and kinetic effects. Generally, biological reduction of sulphate is considered to result from a wide range of $\delta^{34}$S. Nevertheless, deposition temperature is mostly higher than that necessary for growth of bacteria, the biological reduction of sulphate is separated from its precipitation in time and space when these compounds deposit.

Although the ratio of sulphur isotopes greatly varies in typical worldwide MVT deposits, such isotopes have been mostly discovered to come from crusts. For a single deposit or area, sulphur would
be from one or more sources such as sulfate-containing evaporite, syngeneic seawater, diagenetic sulfate, sulphur-containing organic matters, and H2S reservoirs and reduced sulfur of anaerobic water in basins. However, sulfate of seawater (wrapped in side various minerals by sediments) or syngeneic seawater is possibly still the major source of sulphur, which is subsequently reduced. Sulphate is reduced by three different mechanisms, including bacterial sulfate reduction (BSR), thermal degradation of sulphur in organic matters and thermochemical sulfate reduction (TSR).

Based on materials about $\delta^{34}S$, it may be known that sulphur of MVT Pb-Zn deposits is mostly from seawater sulphate, mixed with fluids and closely related to reduction with organic matters (Zhou et al., 2011).

4. Conclusions
After a comprehensive analysis, several conclusions are reached as follows: 1) Ore-forming material sources of Chinese MVT Pb-Zn deposits mostly come from basement strata above orogenic belts, and deep metallogenic materials are possibly leached by fluids to form ores when they are transported to shallow zones through large deep fault zones. 2) Sulphur isotopes of typical worldwide MVT deposits are generally from crusts in spite of significant changes to their ratio.

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