

# Research progress in metallogenic chronology of Mississippi valley-type (MVT) Pb-Zn deposits

**Huiguo Liu**

Guizhou Vocational Technology Institute, Guiyang, Guizhou 550023, China.

huiguo\_liu@outlook.com

**Abstract.** MVT Pb-Zn deposits are one of world's important Pb-Zn deposits. Their lead and zinc account for approximately 20% of global lead and zinc resources. After constant explorations, researchers have made substantial progress in geological features, geochemical characteristics, ore-forming material sources, and transport and deposition mechanisms for ore-forming fluids, chronology restriction, and geochemical kinetic background for ore genesis of MVT Pb-Zn deposits over the past decades. This paper discusses problems with chronological research by summing up previous outcomes.

## 1. Introduction

As a type of Pb-Zn deposits with striking epigenetic characteristics produced in carbonatite, MVT deposits are well-known for their typical development in the Mississippi River of the United States. This kind of deposits has been studied since one century ago. Earlier studies mainly recorded features of hydrothermal genesis in investigating these deposits and defined the deposits as post-magmatic hydrothermal deposits or tele-hydrothermal deposits. By 1970s, many scholars further explored these deposits according to theories of strata-bound ore deposits. They deeply analyzed and summarized their metallogenic background, their associations with magma rocks, spatial distribution, ore-controlling factors and features (Garven, 1985; Ge et al., 1992; Appold et al., 1999). In particular, many new data, including lead isotopes, sulfur isotopes, fluid inclusions and metallogenic fluids, were obtained from the perspective geochemistry and mineralogy of deposits by performing hydrothermal experiments. Lots of geological and geochemical data of deposits have fully demonstrated that the genesis of these deposits is not associated with magma or hydrothermal liquids of magma. Nowadays, it is acknowledged that these deposits are epigenetic under the control of stratigraphic horizons, arising from filling and metasomatism of underground brine between space of carbonatite, including voids, cracks, karst caves, surface of unconformity and intercalated crushed zones. With the increase of market demands for lead and zinc in the world, people have paid more attention to explore MVT Pb-Zn deposits over the past years. In this paper, MVT deposits are studied from the perspective of their metallogenic chronology, in hope of better understanding these deposits.

## 2. Structural Settings and Metallogenic Environment

MTV Pb-Zn deposits were considered to be irrelevant to plate tectonics and it was considered that these deposits would be metallogenic as long as there was carbonatite on meseta. However, since 1980s, more and more studies have suggested that most MVT Pb-Zn deposits of the world have



formed when extensive ore-forming fluids flow through foreland basins with the drive of gravity of adjacent orogenic belts and their metal sulfide deposits (Garven, 1985; Ge et al, 1992, Appold et al, 1999). Although surrounding rocks, basin brine, driving forces of fluids and areas where ore body deposits are critical for genesis of deposits, all of these conditions are finally caused by activities of tectonic structures inside these structures, so it is important for studying genetic causes of deposits and guiding prospecting by exploring tectonic backgrounds. These years, some research has suggested that MVT Pb-Zn deposits mostly form in foreland basins of orogenic belts, a few of them form in thrust-nappe belts and rarely in extensional tectonic structures of continents. This view was questioned at first when it was just proposed, but has been widely acknowledged at last.

### 3. Research on Metallogenic Chronology

With the development of high-precision high-resolution mass spectrometers and advanced super clean laboratories, people have studied dating techniques of deposits increasingly more intensively and several radioisotope dating methods have been made available for more widespread uses. Concerning many problems about metallogenic epoch of MVT Pb-Zn deposits, relatively satisfactory results have been obtained. The dating methods are not only applicable to certain extent, but also have their respective limitations. Hereunder, some major dating techniques will be discussed.

#### (1) Paleomagnetic method

The application of paleomagnetic techniques is a major progress in dating of MTV Pb-Zn deposits. Further magnetization occurs in chemical reactions related to fluids, so paleomagnetic fields may be recreated in surrounding rocks with the transport of ore-forming fluids of MVT Pb-Zn deposits. More favorably, these deposits generally develop in unperturbed and structurally stable on carbonatite meseta, which is ideal for palingenestic dating. However, precision of magnetometer was always just measured based on theories for certain period. The magnetometers haven't been put into practices and widely utilized until the emergence of low-temperature magnetometers. Symons et al (1996) summarized paleomagnetic dating methods and several practical instances. They pointed out that these methods would be applicable if only there were magnetic minerals for recording directions of geomagnetic field such as magnetic iron ores, red iron ores and pyrrhotite ores whatever the content.

#### (2) $^{40}\text{Ar}$ - $^{39}\text{Ar}$ ( $^{40}\text{K}$ - $^{39}\text{Ar}$ ) Method

Over the past decades, it has been the most widespread for dating hydrothermal genesis of K-included hydrothermal minerals by  $^{40}\text{Ar}$ - $^{39}\text{Ar}$ . concerning this dating method, the measured objects mainly include alkali feldspar, mica, hornblende, illite and quartz.  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  method performs many other methods in following aspects: Evolution histories of minerals can be usually reflected from plateau ages on age spectra obtained from multi-stage heating.  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  method is incomparable to other methods in this aspect.  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  is more precise than  $^{40}\text{K}$ - $^{39}\text{Ar}$  in dating. Only a small amount of samples is needed by this method that very few problems are caused by non-homogeneity of samples. For  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  method, the experiment performed by Kontak et al. (1994) is the most typical case of dating MVT Pb-Zn deposits. In their experiments, they finally exactly confirmed the metallogenic age of the MVT deposits to be  $\pm 27\text{Ma}$  by measuring plateau ages of sedimentary clastic rocks related to the deposits in Gays River, which was consistent with 300-320Ma determined by paleomagnetic measurements. This indicates that the deposits formed in the paleozoic period of Pennsylvania and their genesis was associated with Alleghanian orogeny.

#### (3) U-Pb Method

In the metallogenic epoch, uranium-bearing minerals such as zircon, rutile, edwardsite, allanite, sphene and apatite involved in hydrothermal genesis in altered belts or ore bodies were mostly measured by single-grain U-Pb method. However, very few uranium-bearing minerals suitable for U-Pb dating form during metallogenic genesis, so this method isn't used so widely as  $^{40}\text{Ar}$ - $^{39}\text{Ar}$ , Rb-Sr and Sm-Nd for studying metallogenic epoch. Many scholars measure epoch of MVT Pb-Zn deposits by U-Pb method. Brannon et al (1992) measured that the age of calcite (a gangue mineral) in MVT Pb-Zn deposits of east Kansas and Canning basins by  $^{232}\text{Th}$ - $^{208}\text{Pb}$  and  $^{238}\text{U}$ - $^{206}\text{Pb}$ , confirmed to be  $351 \pm 15\text{Ma}$ .

#### (4) Rb-Sr Method

Rb-Sr method has been proven to be effective for directly measuring the mineralization age of MVT Pb-Zn deposits. Nakai et al. (1990) firstly reported Rb-Sr isochron age of sphalerite in Coy Deposit of East Tennessee Mine to be  $377 \pm 29$  Ma. This result was in disagreement with previous view that the genesis of MVT Pb-Zn deposits in middle and eastern parts of the United States was associated with late paleozoic alleghanian orogeny before 330-250 Ma. Besides, Nakai et al. (1990) proposed a new metallogenic model for basin compaction. Furthermore, they measured the Rb-Sr isochron age of sphalerite in Immel Deposit of east Tennessee Mine to be  $347 \pm 20$  Ma, which was in line with the metallogenic epoch of the Coy Deposit, so this demonstrated that the deposit of that mine formed between 350-380 Ma and its genesis was connected with mid paleozoic acadian orogeny. Brannon et al. (1992) measured the Rb-Sr isochron ages of sphalerite in Upper Mississippi Valley by Rb-Sr method and concluded that they were  $269 \pm 6$  Ma and  $270 \pm 4$  Ma, which formed a sharp contrast with Nakai's  $377 \pm 29$  Ma. Nevertheless, Brannon et al. (1992) considered that the completely different age of two metallogenic provinces in North America indicated that in those areas, MVT Pb-Zn deposits formed through multiple stages, including at least two metallogenic epochs, and they were mostly associated with major tectonic movements of the same stage. In China, Li et al. (2004) clarified the mineragenetic epoch of No.6 Ore Body of Qilin Plant in Huize Pb-Zn Deposit of Yunnan Province to be  $225.11 \pm 2.9$  Ma and  $225.9 \pm 3.1$  Ma respectively. Thus, they concluded that Pb-Zn metallogenesis inside metallogenic provinces of Sichuan, Yunnan and Guizhou provinces was associated with movement of basaltic magma in Emei Mountain.

However, isochron age of most MVT Pb-Zn deposits hasn't been reasonably determined because sphalerite samples are not closed after their metallogenesis, or inclusions of clay minerals exist in sphalerite, or fluid inclusions still exist in residual facies of sphalerite. So far, the causes of this phenomenon are still unclear. At present, Institute of Geology and Geophysics, Chinese Academy of Sciences has successively measured single-grain mica and single-grain pyrite from the perspective of Rb-Sr isotopes and according to chemical procedures of ultra-low backgrounds using advanced and high-precision IsoProbe-T thermal ionization mass spectrometers. To certain extent, this measurement method not only satisfies basic closure requirement for Rb-Sr dating, but also increases precision of Rb-Sr measurement and reduces lower limit of tests. With the promotion of this research outcome, worthy lessons may be learnt from it for Rb-Sr dating of low-temperature hydrothermal Pb-Zn deposits.

#### (5) Sm-Nd Method

Although this is a relatively new and effective dating method, it is not commonly used for dating MVT Pb-Zn deposits. Halliday et al. (1990) reported the application of Sm-Nd method in exploring metallogenic causes of MVT Pb-Zn deposits in Pennines in the north of England. Although they failed to clarify the exact metallogenic age, they concluded after comparing  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  and Rb-Sr ages that the metallogenic age was about 200 Ma, and the metallogenesis of these deposits was associated with regional tectonic movements between the carboniferous period and carbonic period. By analyzing Sm-Nd isotopes of fluorite in MVT Pb-Zn deposits of Illinois-Kentucky mine, Chesley et al. (1994) concluded that the metallogenic age of this mine was  $277 \pm 16$  Ma and thus inferred that the metallogenesis of the deposit was attributable to large-scale fluid movement arising from the movement of the Allegheny River. Li et al. (2004) measured metallogenic epoch of No.6 and No.1 ore bodies of Qilin Plant with Rb-Sr isochrone of calcite (a gangue mineral). Their results suggested that the metallogenic epoch of both mine concessions was the same. The metallogenic epochs were  $226 \pm 15$  Ma and  $225 \pm 38$  Ma respectively for the deposit of the Qilin Plant and the deposit of the mine. The measured age was close to the metallogenic epoch of extensive basalt in the southwest of Emei Mountain within the error scope. They provided chronology evidences for proving associations between metallogenesis of Pb-Zn deposits and movement of basaltic magma on Emei Mountain.

#### (6) Fission Track Dating

Fission track dating is simple, feasible, sensitive and applicable to widespread objects, particularly suitable for measuring young samples. This dating method shall be adopted on the premise that

uranium and fission tracks are closed and measured minerals are generally hypothesized to be associated with mineralization in terms of their annealing.

#### 4. Conclusion

In spite of some doubts about dating of MVT Pb-Zn deposits, Leach et al (2001) discovered in summarizing ages of major MVT Pb-Zn deposits in the world that among 10 deposits measured by paleomagnetism and isotope to identify their ages, 8 results were consistent. This suggests that the paleomagnetic and isotopic dating results are generally the same among most deposits. Only evidences haven't been found for demonstrating that the research data couldn't reflect metallogenic ages in 3 deposits measured by isotopic dating and 4 deposits measured by paleomagnetic dating. Thus, it is clear that after decades of explorations, some progress has been made in exploring metallogenic ages of MVT Pb-Zn deposits. The methods introduced above are effective for exactly measuring ages of the deposits under certain conditions.

#### 5. Conferences

- [1] Garven G. The role of regional fluid inclusions: a new tool in constraining source regimes and its implications for the genesis of Mississippi Valley-type deposits. *Economic Geology*, 1985, 80: 307-324.
- [2] Ge S and Garven G. Hydromechanical modeling of tectonically-driven groundwater flow with application to the Arkoma basin. *J. Geophys. Res.*, 1992, 97: 9119-9144.
- [3] Appold M S and Garven G. The hydrology of ore formation in the Southeast Missouri district: numerical models of topography-driven fluid flow during the Ouachita orogen [J]. *Economic Geology*, 1999, 94: 913-936.
- [4] Symons D T A, Sangster D F, Leach D L. Paleomagnetic dating of Mississippi Valley-type Pb-Zn-Ba deposits. In: Sangster D F, ed. *Carbonate-hosted lead-zinc deposits*. Society of Economic Geologists Special Publication, 1996, 4: 515-526.
- [5] Kontak D J, McBride S, Farrer E. <sup>40</sup>Ar-<sup>39</sup>Ar dating of fluid migration in a Mississippi Valley-type deposit: Gays River Zn-Pb deposit, Nova Scotia. *Economic Geology*, 1994, 89: 1501-1517.
- [6] Brannon J C. Alleghenian age of the Upper Mississippi Valley zinc-lead deposits determined by Rb-Sr dating of sphalerite. *Nature*, 1992, 356: 509-511.
- [7] Nakai S, Halliday A N, Kesler S. Rb-Sr dating of sphalerites from Tennessee and the genesis of Mississippi Valley-type ore deposits. *Nature*, 1990, 346: 354-357.
- [8] Halliday A N, Shepherd T J, Dickin A P. Sm-Nd evidence for the age and origin of a Mississippi Valley-type ore deposit. *Nature*, 1990, 344: 54-56.
- [9] Chesley J T, Halliday A N, Kyser T K. Direct dating of Mississippi Valley-type mineralization: use of Sm-Nd in fluorite. *Economic Geology*, 1994, 89: 1192-1199.
- [10] Li W B, Huang Z L, Chen J, Han R S. Rb-Sr dating of mineral assemblage from the Huize giant Zn-Pb deposit, Yunnan province. *Acta mineralogical sinica*, 2004, 24 (2): 112-116.
- [11] Leach D L, Bradley D C, Lewchuk M T. Mississippi Valley-type lead-zinc deposits through geological time: implications from recent age-dating research. *Mineralium Deposita*, 2001, 36: 711-740.