Study on Provenance and Mineralization Chronology of Porphyry Molybdenum Ore

Xudong Xiao 1,*, Jiuqiang Tao 2, Zhongqun Wang 1, Neng Zheng 1

1 Jiangsu Nanjing Institute of Geo-Engineering Investigation, China.
2 Guizhou Land and Mineral Resources Reserve Bureau, Guiyang, China.

*Corresponding author email: 108320210@qq.com

Abstract. Porphyry molybdenum deposit is one of important molybdenum deposit types in the world, and the quantity of molybdenum resources accounts for 90% of global molybdenum resources. In recent decades, important progress has been achieved in terms of geologic features, geochemical features, mineralization metal resource, mineralization fluid resource and evolution of porphyry molybdenum ore as well as Mo element migration and sedimentation mechanism, mineralization age clarifying and geochemical dynamics of deposit formation. Based on synthesizing predecessors’ achievements, mineralization metal resource and mineralization chronology are introduced in this paper, and new materials are provided for the research on porphyry molybdenum ore. The research indicates that, provenance system of porphyry molybdenum ore is very complicated, and Re-Os and Os-Os are effective age measurement methods.

Keywords: Porphyry molybdenum deposit; provenance; mineralization age.

1. Introduction
Porphyry molybdenum ore refers to the deposit which has space and formation cause relation with superficial - super-superficial moderately acid porphyry intrusive body, consists of disseminated or veined (net) disseminated ores, and surrounding rocks mostly present obvious face-type hydrothermal alteration. Porphyry molybdenum ore provides 90% metal molybdenum resources in the world, so its industrial significance is very important. Hence, it is favored by numerous geologists. The theoretical research on porphyry molybdenum ore has been based on the study of porphyry copper for many years. There are just a few researches on independent formation reasons for porphyry molybdenum ore and mineralization laws at home and abroad. In fact, the differences of copper and molybdenum in geochemical behaviors lead to different mineralization features, and the two have respective features in the aspects of deposit production environment, ore-contained porphyry system evolution, evolution of mineralization fluid system, development of hydrothermal alteration system and metal sedimentation mechanism. Thus, it is very necessary to deeply study mineralization of porphyry molybdenum ore. Metal source of molybdenum ore mineralization and mineralization chronology are studied, and Predecessors’ research progress is summarized in this paper, in the hope of promoting exploration of porphyry molybdenum ore forming process.
2. Brief introduction to porphyry molybdenum ore

Large quantities of researches indicate that the emplacement of porphyry containing ore is usually shallow, generally 1~4km. The scale is not large, and the diameter is generally <2km. There is the feature of multi-period emplacement. Not just does emplacement phase space coexist before mineralization, in mineralization period and after mineralization, but also cryptoexplosion breccia in the later period is usually developed together. The main lithofacies is from neutral diorite to acid granitic porphyry, but porphyry component in island arc environment tends to be neutral, while porphyry in mainland environment (continental margin and collision zone) tends to be acid. These reflect felsic magma passing through the thick crust experienced more sufficient crystallization differentiation. On the whole, porphyry containing ore in island arc environment is usually calcium alkaline, while porphyry containing ore in mainland environment is mostly alkaline with high potassium and calcium, and some are potassic alkaline and mugearite. Such regular or implied magmatic source area of porphyry containing ore differs. Or these the thickened crust generates mixed dyeing for protomagma components.

Mother rocks of porphyry molybdenum deposit include granodiorite and alkaline granite with high silicon content, and mostly present stock output. In rare cases, batholiths output is also shown (such as Endako deposit in Canada and Mount Tolman deposit in US). Porphyritic texture is also seen for the stock (the matrix is from cryptocrystalline to fine-grained phaneromer), round-oval shape is shown on the plane. The diameter of stock us generally 500~1500m. Huge underlaying batholiths may exist in the lower part of stock. Alkaline calcium – alkaline porphyry molybdenum ore is related to alkaline, alkaline calcium and alkaline magma series with high potassium and calcium content. Symbiotic magmatic rocks are characterized by rich Rb and low Sr. High magmatic differentiation index (91~94) reflects these rocks are the product of magma experiencing high differentiation. Calcium alkaline porphyry molybdenum ore is related to calcium alkaline and alkaline magma series with high potassium and calcium. Mother magma usually forms batholiths, and the main components include quartz diorite and granite. In particular, granodiorite and quartz monzonite are most common. Molybdenum mineralization is mostly related to alaskite with excessive aluminum and silicon and aplite, and represents the output of magma crystallization differentiation in the last stage. Symbiotic magmatic rocks are characterized by rich Sr, moderate Rb and poor Nb and Sn (Westra et al., 1981).

3. Study on mineralization matter sources

Internalization matter sources of porphyry deposit are greatly similar to the sources of mineralization magma. Westra et al. (1981) proposed a source mode related to oceanic crust sheet subduction. When the depth of subducted oceanic crust sheet is 120~240km, the subducted sheet is partly melted to produce the initial magma of calcium alkaline porphyry molybdenum ore. The initial magma will suffer a little transformation of overlying mantle wedge, but molybdenum should mainly come from the subducted sheet. However, since 1.7 billion years, abnormal Mo, W and F enrichment has happened to various rocks of crust in different periods and in Rocky Mountains region, Colorado. This implies the resource regions of these rocks and elements should be continental lithosphere rather than subducted sheet and asthenosphere, because subducted sheet and asthenosphere will generally shift in every plate movement period, while continental lithosphere is relatively stable (White et al., 1981). The formation of enriched upper mantle caused by subduction may not be the necessary factor of porphyry molybdenum ore formation.

Wallace (1978) considered that, the formation of calcium alkaline – alkaline porphyry molybdenum ore has nothing to do with have nothing to do with subduction, but arises from mainland crust. Magma stems from the lower crust; mineralization metal stems from the upper crust; F stems from mantle. But, the upper crust source of metal contradicts against isotope data. Through comparing lead isotope components of mineralization rock mass of Henderson deposit and surrounding rocks, Stein et al. (1985) thought that, mineralization metal element is homologous with magma rather than magma gaining the element in the surrounding rocks of the upper crust. $^{87}\text{Sr}/^{86}\text{Sr}$ specific value (0.705~0.710) of mineralization rock mass of Climax, Questa, Henderson and other deposits is much lower than that
(0.8~1.0) of Precambrian surrounding rocks, close to current mantle value (0.704). $^{206}\text{Pb}/^{204}\text{Pb}$ specific value (17.93 on the average) of Climax, Henderson, Emmons and other deposits is relatively low, and $^{208}\text{Pb}/^{204}\text{Pb}$ specific value (3.96 on the average) is relatively high, indicating lower crust source of metal (White et al., 1981).

In conclusion, porphyry molybdenum ore system likely originated from neutral magma produced by upper mantle or middle-lower crust melting. The basic magmatic hearth (from asthenosphere or mantle melting) which provides thermal energy and volatile matter exists in the lower part. The magma with neutral components rises to the upper crust to form magma chamber. Crystallization differentiation makes magma evolve to felsic component from neutral components. The basic magma from asthenosphere continuously intrudes into the bottom of magma chamber and provides lots of volatile matters (F, Cl, S, CO$_2$ and so on). These volatile matters have important significance for molybdenum enrichment (White et al., 1981). For example, high F content in magma can increase water content in magma and reduce crystallization temperature of magma (Westra et al., 1981) so that magma convection can proceed more sufficiently and lots of ore-containing fluids are enriched on the top of magma chamber.

Predecessors have carried out large quantities of researches and discussion on mineralization matters and mineralization magma source of molybdenum deposit in eastern Qinling Mountains, China. It is generally believed that, the sources of diagenesis and mineralization matters are complex, ranging from mantle change to crust. Through the research on S, C, Pb and Sr isotopes, Huang et al. (1985) considered that, diagenesis and mineralization matters mainly come from mantle. Lu et al. (2008) thought that, mineralizing rock mass of molybdenum ore belt in eastern Qinling Mountains mainly comes from the lower crust. Chen (2000) considered that, mineralizing rock mass mainly comes from continental crust remelting caused by A-type subduction of continental crust sheet in eastern Qinling Mountains.

Re-Os isotope system is a strong tracer agent of sulfide deposit formation and also a highly sensitive indicator for crust matter mixture degree in mineralization process. Re is a basic field element and tends to be enriched in mantle or basic-ultrabasic rocks. Thus, some scholars advocate that Re content in granite and deposit can be used as the tracer agent of diagenesis and mineralization matters (Mao et al., 1999; Li et al., 2003). Through contrasting the content of Re in molybdenite of molybdenum deposits in China, Mao et al. (1999) held that, the change law of Re content in molybdenite of deposits in which granite of M, I and S types serves as mother rocks is $n \times 10^{-4} \rightarrow n \times 10^{-5} \rightarrow n \times 10^{-6}$, that is, the decrease in order of magnitudes is shown. But, the conclusion that Re content in molybdenite is used to judge mineralization magma source is not consistent with the conclusion drawn from the study on isotope and geochemistry of element. The control factors of Re content change in molybdenite are complex and diversified. The series change of Re content may be closely related to its output state, and it seemingly cannot effectively reflect the source of mineralization matters. For the conclusion that Re content in molybdenite traces the source of mineralization matters, the following problems deserve to be discussed. Firstly, the sources of diagenesis and mineralization matters are same, which is default in this paper. Besides, Carbonic acid dyke, granite I and granite S represent the formation reasons of mantle source, shell mantle mixed source and shell source. Secondly, the number of samples used to gain the statistic law is insufficient (Yang et al., 2011).

For the samples containing $^{188}\text{Os}_{\text{common}}$, the initial specific value of $^{187}\text{Os}/^{188}\text{Os}$ and $^\gamma_{\text{Os}}$ value can be used to trace the source of mineralization matters. In the application process, the initial specific value of $^{187}\text{Os}/^{188}\text{Os}$ and Os content can be combined to overall judge the source of mineralization matters (Zhang et al., 2012).

4. Mineralization chronology research
Re-Os isotope system is based on $^{187}\text{Re}$ presenting $^{187}\text{Os}$ after $^\beta$ decay. Since Re has sulphur affinity, Re-Os isotope system is the best age determining means for metal sulfide deposit. Molybdenite is the most common ore mineral in porphyry molybdenum deposit. Because Re and Mo own similar ion radius, Re replaces Mo to enter molybdenite lattice in the form of isomorphism in molybdenite forming process. Molybdenite has been the sulfide which is richest in Re so far, and the common Os can be ignored,
relative to $^{187}$Os formed by radiation. Thus, the content relation between $^{187}$Os and $^{187}$Re in molybdenite can provide the forming age of deposit. This not just contributes to understanding geological background of deposit formation and regional mineralization law, but also can be used as an important parameter of inversion of regional tectonics evolution or mineralization dynamics background (Huang et al., 1994; Du et al., 2001; Qu et al., 2003; Mao et al., 2004). Li et al. (2004) measured Re-Os isotopic age determination for 4 deposits including Nannihu Molybdenum Deposit and Leimengou Molybdenum Deposit in Nanyuan, North China Platform, Henan Province, and drew the conclusion that, the age of molybdenite Re-Os mode is 144.8±2.1-132.4±2.0Ma. Besides, they considered that, the corresponding geochemical dynamics backgrounds are intracontinental extension process after collision and orogenesis between North China Craton and Yangtze Craton, and Eastern China tectonic system conversion period.

Meng Xiang et al. (2012) adopted LA-ICP-MS zircon U-Pb age measurement technology ad gained the conclusion that, fine-grain quartz syenite containing ore and medium-grain quartz syenite in Shapinggou porphyry molybdenum deposit formed in 122.51±0.81Ma-121.5±1.3Ma respectively; orthophyre formed in 120.7±1.1Ma; the age mode of Re-Os isotope in molybdenite is 100±1.8-113.6±1.7Ma. The time difference between diagenesis and mineralization is about 7Ma, indicating that the time period of ore-containing hydrothermal solution activity is long. This may be the important factor for the formation of Shapinggou super-large porphyry molybdenum deposit.

Molybdenite Re-Os age determining method is widely applied in geology, and meanwhile it experiences theoretical and practice test all the time. At present, for the problems existing in age determination of Re-Os isotope system, numerous improvement measures have been taken to improve data analysis quality. For instance, Li et al. (2010) adopted dense HNO$_3$ to decompose molybdenite samples, which greatly simplifies chemical preparation process of Re and Os. And, according to the feature that normal Os content level in molybdenite can be ignored relative to $^{187}$Os, normal Os standard is used as the diluent to achieve online calibration of Os isotope mass fractionation in instrument measurement process and improve data analysis quality. In recent years, great breakthroughs have been achieved to improve the selection of Os standard reference material used to accurately determine Re and Os diluent, chemical constituent determining method, the study on Re-Os standard reference material and age calculation method for molybdenite mode containing common Os, which has greatly promoted the application of Re-Os isotope system in age determination and mineralization mater source tracing and ensured accuracy of Re-Os age determination (Du et al., 2009, Li et al., 2012).

Os-Os age determining method is another age determining method of Re-Os isotope system. Compared with Re-Os method, it needs neither to add the diluent nor to determine Re isotope composition. Therefore, there is no undermixing problem, and the influence is also little. Two independent and comparable ages of $^{186}$Os and $^{188}$Os can be gained to verify result reliability (Zhang et al., 2012). Maybe due to the problem of radioactivity protection, Os-Os method is rarely applied and reported at home and abroad (Xie et al., 2002). If radioactivity protection problem can be solved, the application of Os-Os method will be greatly promoted and the development of Re-Os isotope system will be driven.

5. Conclusion

Based on predecessors’ researches, it is believed that, 1) porphyry molybdenum ore system likely originated from neutral magma generated by the upper mantle or middle-lower crust melting, and the basic magmatic hearth which provides thermal energy and volatile matter exists in the lower part; 2) predecessors’ researches show that the sources of diagenesis and mineralization matters are complex, ranging from mantle change to crust; 3) numerous deposit examples indicate that Re-Os and Os-Os are effective methods to determine the age of molybdenum ore.

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