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Geology and Genesis of the World-class Donggou Porphyry Molybdenum Deposit, Henan Province, East Qinling Metallogenic Belt, Central China

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1 Geological characteristics of Donggou Porphyry Mo Deposit

Donggou porphyry deposit is located in the East Qinling molybdenum belt, the southern margin of the North China craton, to the north of nearly EW-trending Machaoving fault. The Mesoproterozoic Xiong'er Group of volcanics, as well as the early Cretaceous Donggou granite porphyry crop out in this area. The Mo orebodies are host in the contact zone between Donggou granite porphyry and the Xiong'er Group, ranging from 46.6 to 253.9 m in thickness, averaging 189.9m, with a subhorizontal beds' shape. The ore has disseminated, veinletdisseminated, vein and film structures. The proven and inferred reserves of Donggou deposits are 62.5×10⁴t, averaging 0.113%. The mineralization processes could be divided into two different periods: the late magmatic period and the hydrothermal period. In the magmatic period, the alkaline-rich fluids widely altered the granite porphyry, causing widespread potassic alteration, along with locally silicification, magnetite veins and biotite patches. The hydrothermal period could be divided into four stages as: 1) quartz-K-feldspar stage (I), forming K-feldspar veins, quartz-K-feldspar veins, and milky quartz veins; 2) quartz-molybdenite stage (II), with quartzmolybdenite quartz veins; 3) sericite stage (III), with pyritesericite veins, pyrite-quartz veins, and molybdenite; 4) quartzcalcite stage (IV) , forming calcite veins, fluorite veins, and pyrite-chlorite veins.

2 Geochronology of Emplacement of Intrusions and Mineralization

The Donggou granite porphyry is flesh-red and has a

massive structure and a porphyritic texture. The phenocrysts consist of quartz and perthite, and the matrix is composed of perthite, quartz and plagioclase with minor biotite; the accessory minerals include magnetite, anatase, sphene, rutile and zircon. Geochemistry characteristics suggest that the rock is K-rich aluminous-peraluminous A type granite, which formed in the extension environment. The SHRIMP U-Pb zircon dating data range from 112 to 117Ma

Eight molybdenite-bearing samples yielded Re-Os model ages of $114.8\pm1.9-118.5\pm1.8$ Ma, with a mean weighted age of 116.81 ± 0.83 Ma, and isochron Re-Os age of 116.4 ± 1.9 Ma, roughly the same as the SHRIMP U-Pb zircon dating of Donggou granite porphyry.

3 Fluid inclusion Microthermometry and Laser Raman Spectroscopy

The K-feldspar-quartz stage (I): Fluid inclusions are mainly NaCI–H₂O fluid inclusions (W type) and minor CO₂-bearing fluid inclusions (C type) and polyphase brine inclusions (S type), boiling assemblages were locally observed. Homogenization temperatures range from 280° C to 483°C, peaking 350~390°C, averaging 365°C. The salinities range from 7.1~16 wt percent NaCl equiv and 31.8~44.9 wt percent NaCl equiv. The W type and S type fluid inclusions have density ranging from 0.55~0.86g/cm³ and 1.02~1.14g/cm³, the minimum pressures are 60 to 123 MPa, and the formation depth is 2.5~5.0 km, averaging 3.7 km.

Polymetallic sulfide stage (II+III): W type fluid inclusions and minor S type fluid inclusions and C type fluid inclusions, the boiling assemblages were observed as well. Homogenization temperatures range from 175° C to

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429° C, peaking 290~330° C, averaging 311° C. The salinities range from $3.5\sim14.7$ wt percent NaCl equiv and $30\sim44.4$ wt percent NaCl equiv. The W type and S type fluid inclusions have density ranging from $0.61\sim0.95$ g/cm³ and $0.99\sim1.10$ g/cm³, respectively. The minimum pressures are 56 to 86 MPa, and the formation depth is $2.3\sim3.5$ km, averaging 2.8 km.

Quartz-calcite stage (IV): the W type fluid inclusions are the only fluid inclusion type that found in this stage. Homogenization temperatures range from 125° C to 257° C, peaking $150{\sim}200^{\circ}$ C, averaging 176° C. The salinities range from $0.5{\sim}8$ wt percent NaCl equiv, along with the density ranging from $0.83{\sim}0.97$ g/cm³, averaging 0.92g/cm³. The minimum pressures are 10 to 45 MPa, and the formation depth is $0.4{\sim}1.8$ km, averaging 0.92 km.

The Laser Raman spectroscopy shows that the gas components of fluid inclusions in the K-feldspar-quartz stage are characterized by CO_2 , with liquid components as water. The polymetallic sulfide stage displays fluid inclusions are strongly characterized by CO_2 weak water spectrum for the gas components, and strong water spectrum for the liquid components. Quartz-calcite stage only displays water spectrum for both gas and liquid spectrum. In conclusion, for the whole ore-forming process, potassic-quartz and later polymetallic sulfide stage have a large mount of CO_2 , forming H₂O-NaCl-CO₂ system, but no CO_2 was found in the calcite-quartz stage, forming an H₂O-NaCl systems.

4 Characteristics of Stable Isotopes

The $\delta^{18}O_{quartz}$ values for I stage, II +III stage, and IV stage range from 2.9‰~7.4‰, 8.6‰~9.1‰, 8.6‰~ 9.1‰, the calculated $\delta^{18}O_{H2O}$ values are 5.6‰~4.2‰, 2‰~2.6‰, and -4.6‰~-2.2‰; with corresponding δD values are -86‰~-73‰, -85‰~-69‰, and -92‰~-81‰.. The plot of δD versus $\delta 18O_{H2O}$ shows the fluids for the I stage fall within the range of primary magmatic water and vicinity, whereas for the II +III stage and IV stage samples plot close to the primary magmatic water, suggesting the involvement of meteoric water for the later stages. The fourteen samples of sulfides have $\delta^{34}S$ values ranging from +7.5‰~+9.4‰, averaging +8.56‰. The narrow range of $\delta^{34}S$ values of all the samples implies that all the sulfurs soured from a common source. By comparing with sulfur isotope data for known reservoirs, it is suggestive that sulfur derived form magma source.

5 Conclusions

The Donggou Mo deposit is host in the contact zone between the Donggou granite porphyry and Xiong'er group. The ores occur as veinlets, stockworks and films. Hydrothermal alteration can be recognized as potassic alteration, silicification alteration, sericite alteration, epidotie-chlorite alteration, fluorite alteration, and calcite alteration. The geochronological data suggested that the emplacement of granite porphyry and mineralization both formed in the early Cretaceous period. Prior to the main mineralization stage (massive K-feldspar alteration stage and quartz-K-feldspar stage), molybdenum was transported as KHMoO₄ complexes in the CO₂-H₂O-NaCl system of the exsolved fluids that caused by the emplacement of Donggou magma, this fluid was alkali rich and in characteristic of high fO₂.

While fluid flowed through the contact zone of Donggou porphyry and wall rock of the Middle Proterozoic Xiong'er Group volcano rocks, metasomatism occurred, forming the massive K-feldspar and magnetite bearing K-feldspar veins. In the main mineralization stage (molybdenum-quartz stage and sericite alteration stage), fluid mixing (meteoric water adding), fluid boiling, waterrock reaction, caused induced pH, reduced fO2 and increased of reduction sulfur in ore-forming fluid. These pH and oxygen fugacity condition changed within fluid caused the KHMoO₄ complexes to become unstable and resulted in Mo precipitating as MoS₂ along the rocks near the contact zone of fractures, formed molybdenite veins finally, as well as the formation of the silicification and sericite alteration. After the mineralization stage (quartzcalcite stage), the ore-forming fluid was lack of metal mineral, with the combination of further added meteoric water, fluid of H₂O-NaCl system is in low temperature, and low salinity, and just precipitate of quartz and calcite.

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