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## Discovery and Genesis Discussion on A Early-Cambrian Large-Scale Vanadium Deposit from Eastern Guizhou, China

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Recently the large scale vanadium deposit, of ZhuXi with reserves of nearly 1 tonnes: in black shales was discovered in eastern Guizhou. Sedimentology, trace element geochemistry and isotope geochemistry were applied to reveal the genesis of the ZhuXi vanadium deposit. Results show that the deposit is characterized by hydrothermal sedimentation, and the metallogenic fluid may come from the deep inflow.

### 1 Sedimentary Characteristics and Sedimentary Sequence

The ZhuXi vanadium bearing black shales are at the top of the Liuchapo Fm. and the first section of the Cambrian Jiumenchong Fm. Vanadium mainly occurs in mica, iron oxide, kaolin group minerals in the sandstone, seldom in siliceous rocks which are distributed mainly in the lower section of Liuchapo Fm.. From top to bottom, the ore-bearing rock series is mainly composed of a suite of black clastic sandy to siliceous rock with thickness of 93m-186m. The rock series is in conformable contact with the underlying Doushantuo Fm. and the overlying second section of Jiumenchong Fm., The boundaries of the two are clear. There is a marker bed at the bottom of the Jiumenchong Fm., which is characterized by grayish green pyritic argillaceous siltstone with thickness of 3-18cm. This layer is named as "multimetal layer".

The ore bearing rock series has the structure and construction of hydrothermal deposition. For example, the lamellar structure interbedded by black hydrothermal sedimentary silicalite (Zhang Weihua et al., 2003) and black argillaceous siltstone.

Columnar structure with length of 1.5m and diameter of 15cm was found near the high-carbon layer of Daling profile from Zhenyuan. The direction of the long axis of the

columns parallel to the strata. They are carbonaceous siliceous columns, which has similar appearance to Zunyi nickel-molybdenum mine's pillow structure found by Luo Taiyi (Luo Taiyi, 2003) and Tianzhu barite mine's column found by Yang Ruidong (Yang Ruidong, 2007). A layer of carbonate breccia imbedded in carbonaceous shale of Zhuxi vanadium deposit from Zhenyuan breccia was found, and in which the breccia with size of 3mm-8mm has poor roundness and distributed randomly there. Net-vein structure was also found in Zhuxi mining area, which is characterized by pyrite and calcite veins fracturing into siliceous rocks. Pyrite cluster structure was observed from the front of the sample, while radial arrangement of calcite veins was observed from the back. In addition, banded barite was found in the ore bearing rock series, which is also an important evidence to prove the involvement of hydrothermal deposition.

### 2 C, O Isotope Geochemistry

According to the test results of thirty-five drilling samples: ①The  $\delta^{18}\text{O}_{\text{PDB}}$  value ranges narrowly from -8 ‰ ~-15 ‰; ②The  $\delta^{13}\text{C}_{\text{PDB}}$  values range from -0.1 ‰ ~-16 ‰ by a wide margin, and all show negative anomalies; ③The  $\delta^{13}\text{C}_{\text{PDB}}$  value is relatively high near the ore bed (-1.24 ‰ ~ -6.37 ‰) but lower in the surrounding rock (-4.94 ‰ ~ -16.90 ‰),  $^{13}\text{C}$  values in the ore bed are remarkably higher than in the surrounding rock; ④ The  $\delta^{18}\text{O}_{\text{PDB}}$  value in the ore bed is relatively lower than that in the surrounding rock, both show narrow range; ⑤ The C isotope value of ZhuXi vanadium has good correlation with V content, the  $\delta^{13}\text{C}_{\text{PDB}}$  increases with the increase of V content, which indicates that the  $\delta^{13}\text{C}_{\text{PDB}}$  value may be associated with vanadium ore genesis.

Test shows that  $\delta^{13}\text{C}_{\text{PDB}}$  value ranges from -1.24 ‰ to -6.37 ‰ (-4.82 ‰ on average). This figure is similar to

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inorganic  $\delta^{13}\text{C}_{\text{PDB}}$  value of modern seafloor hydrothermal vents (Exly et al., 1986; Merlivat and Chen, 1988). In the  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  diagram, vanadium deposit concentrate in the range of hydrothermal sedimentary range. Similarly, surrounding rock fall into the range of hydrothermal sediment and the transition band of carbonate thermal decarboxylation, indicating influence from seafloor hydrothermal vent during mineralization process.

### 3 Sedimentary Geochemistry

#### 3.1 Geochemistry of trace elements

Trace element geochemical characteristics of ZhuXi vanadium ore are as follows: ① Multiple elements associated in vanadium ore, and some of them reach industrial grade; ② Correlative change among various elements was observed through the spider diagram, indicating that elements correlated to each other in the genesis; ③ Mo was strongly enriched in the "polymetallic layer" with content far above the industrial grade (970.1ppm), which indicates that Ni, Mo and V can be enriched together at the lower Cambrian; ④ Significant lower Th/U ratio reflects the addition of mafic-rich materials during siliceous rock formation (McLennan and Taylor, 1980), in the ore bearing rock series of ZhuXi vanadium Th/U ratio is extremely low as 0.026-0.146, which reveals the involvement of mafic-rich source from the deep inflow. Compared with logU-logTh cartesian coordinate graph, the ore-bearing strata fall into the uplift area of East Pacific; ⑤ Co/Zn ratio can be used as a sensitive index to distinguish hydrothermal origin from normal authigenic source (Toth, 1980). The Co/Zn ratio of hydrothermal sources is relatively low (0.15 on average); but Fe-Mn nodules is about 2.5. For the samples studied, the Co/Zn was 0.045 on average, showing clear hydrothermal genesis characteristics.

#### 3.2 Geochemistry of rare earth elements

Rare earth elements content in ZhuXi vanadium ore is relatively high with a large range of  $134 \times 10^{-6}$  to  $488 \times 10^{-6}$ . The  $\delta\text{Ce}$  values are 0.339 to 0.497, showing negative anomalies. The  $\delta\text{Eu}$  values are 0.810 to 0.983, showing weak negative anomalies. REE chondrite normalized distribution curve indicate LREE enrichment, which is similar to the characteristics of Zunyi Huangjiawan Ni-Mo ore (Mao et al. 2001)

### 4 Conclusion

- (1) Vanadium ore is distributed in sandstone, siltstone, silty mudstone, but seldom in siliceous rocks;
- (2) The ore bearing rock series has structures of columnar, pillow and veins, which are similar to those found in Mo-Ni deposit from Zunyi and barite deposit from Tianzhu. Besides, banded barite sediment was observed.
- (3) "Polymetallic layer" was found at the bottom of Jiumenchong Fm., and Mo content reaches industrial grade. Comparative study is needed for this layer and the "Ni-Mo" multi-metal layer at the Cambrian bottom;
- (4)  $\delta^{13}\text{C}_{\text{PDB}}$  value ranges from -1.24 ‰ to 6.37 ‰, which is similar to modern seafloor hydrothermal vents' inorganic  $\delta^{13}\text{C}_{\text{PDB}}$  values. Carbon in marlite from ZhuXi vanadium ore may be inorganic carbon of deep source;
- (5) REE characteristics of the ore bearing rock series is similar to that of the Ni-Mo hydrothermal sediment at the bottom of Cambrian in Guizhou. Extremely low Th/U ratio reflects the join of deep mafic-rich source. And while ore bearing rocks fall into ancient hydrothermal sedimentary area according to logU-logTh diagram.

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