

## **Mannardite as the main vanadium-hosting mineral in black shale-hosted vanadium deposits, South China**

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### **ABSTRACT**

Black shale-hosted vanadium (V) deposits account for about 80% vanadium resources in the world, but only <2% vanadium in the black shale can be extracted mainly due to insufficient recognition on the occurrence mode of vanadium. It is commonly agreed that most vanadium in the black shale is hosted in clay minerals and organic matters, but it is not clear how the other parts of vanadium exist and whether there exists a vanadium mineral, which has limited our understanding of metallogenic mechanism of black shale-hosted vanadium deposits. The Jiujiang Basin at the Lower Yangtze Block is a significant black shale-hosted vanadium metallogenic district. In this work, we conducted systematic studies of mineralogy, lithology and geochemistry on the occurrence of vanadium hosted in the black shales. Electron probe microanalysis (EPMA), Raman spectroscopy, and X-ray diffraction (XRD) show that the main vanadium-hosting mineral in the black shale is mannardite, with a structural formula of  $[\text{Ba}_{0.96}\cdot\text{H}_2\text{O}](\text{Ti}_{5.87}\text{V}_{1.87}^{3+}\text{V}_{0.11}^{4+}\text{Si}_{0.07}\text{Cr}_{0.07}\text{Fe}_{0.02}^{3+})\text{O}_{16.00}$ , space group  $I4_1/a$ , unit-cell parameters  $a = b = 14.346(7)$  Å,  $c = 5.899(1)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $Z = 4$ . Data from EPMA, TESCAN integrated mineral analyzer (TIMA), and whole-rock geochemistry indicate that 12.32–44.06% (average 24.95%) vanadium exists in mannardite. Most vanadium atoms in mannardite occupy its structural sites as trivalent vanadium ( $\text{V}^{3+}$ ), forming chemical bonds with O atoms as  $\text{VO}_2$ , whereas a minor amount of vanadium atoms replace titanite atoms ( $\text{Ti}^{4+}$ ) as quadrivalent vanadium ( $\text{V}^{4+}$ ) by isomorphism. Mannardite precipitates under a strong reductive condition with sufficient trivalent vanadium species, titanium and biogenic barium (bio-barite). Our first identification of mannardite in black shale-hosted vanadium deposits thus sheds light on the occurrence mode of vanadium and the metallogenic mechanism of black shale-hosted vanadium deposits.

**Keywords:** Black shale-hosted vanadium deposit, mannardite, occurrence mode, metallogenic mechanism, Jiujiang Basin, South China