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## Redox State of the Granitic Rocks and Formation of the Scheelite Skarn in the Xintianling Deposit, Nanling Range, South China

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### 1 Introduction

The ore-element associations are closely associated with the relative oxidation state and the degree of fractional crystallization. Study on the redox state of granite is a valid reference on discriminating rock types and prospecting ore elements. In general, Mo, Cu and Au mineralization is associated with oxidized granite, whereas Sn is related to the reduced granite (Blevin and Chappell, 1992). Tungsten occurs as W<sup>6+</sup> in evolved granitic melt, which is weakly controlled by redox state. In Australia and Japan, tungsten deposits could occur as W-Mo-Cu and W-Sn-F series, corresponding oxidized and reduced granites, respectively (Blevin and Chappell, 1992; Kwak and White, 1982).

Most skarn minerals have compositional variations that can yield significant information about the skarn evolution and can be used to differentiate skarn types. Garnet and pyroxene compositions in skarns are particularly important as they can indicate redox condition of a skarn system. Stable isotope are of great help in understanding the origin of specific hydrothermal ore deposits.

The Xintianling granite complex, associated with a large scheelite skarn deposit, is situated in the middle Nanling Range, South China. This skarn deposit is the third largest tungsten deposit in China, ranking only second to the Dahutang and Shizhuyuan deposits. In this study, we systematically analyzed the whole-rock geochemistry, Sr-Nd-Hf-Pb isotopes, and chemical compositions of rock-forming and accessory minerals to

constrain the petrogenesis of the granitic rocks in the Xintianling deposit. Meanwhile, the redox state of the granitic rocks is evaluated based on the magnetic susceptibility, magnetite/ilmenite ratios, Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios of biotite and Ce abnormalities of zircons. We also observed the paragenesis of different skarn minerals, and analyzed mineral chemical compositions together with C-H-O-S isotopes to discuss the physico-chemical conditions of skarn.

### 2 Geological Setting

The Xintianling scheelite skarn deposit contains 80.9 Mt @ 0.36% WO<sub>3</sub>, 21.8 Mt @ 0.022% Mo and 9.5 Mt @ 0.033% Bi. The scheelite skarn are associated with medium-grained biotite monzogranite and fine-grained biotite granite (~165 Ma), both of which are cut by late-stage granite porphyry dyke (147 Ma). The sedimentary sequence exposed in this area is primarily Carboniferous limestone, dolomitic limestone, dolomite, sandstone and shale.

### 3 Petrogenesis and Redox State of the Granitic Rocks

Geochemical, whole-rock Sr-Nd, and zircon Hf isotopic data indicate that biotite granites and granite porphyry are S-type and A<sub>2</sub>-type granites, respectively. The Xintianling biotite granites and granite porphyry are formed by Paleoproterozoic immature graphite-absent metagreywacke and Mesoproterozoic granulitic restite in

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the lower crust undergone an early event of melt extraction, respectively. These processes are induced by upwelling of asthenospheric mantle and delamination of lithospheric mantle and produced vast Sn-W and W (Sn) granitic intrusions in South China.

In their accessory mineral composition, the two facies of Xintianling granite have an association of magnetite + ilmennite (pyrophanite) + titanite + allanite. The high average magnetite content of 0.86 wt% is distinctive and somewhat different from most W-bearing granites in the Nanling Range. The Xintianling biotite monzogranite and granite are characterized by high magnetite/ilmenite ratios, high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios of biotite, remarkable Ce abnormalities of zircon and high magnetic susceptibility. These features confirm the high oxidation state of the Xintianling granite and suggest that the oxygen fugacity has no distinct influence on the enrichment of tungsten, but it explains the lack of tin mineralization. The oxidized Xintianling W-bearing granites distinctly differ from reduced Qitianling Sn-bearing granites, indicative of that the Xintianling stock is an independent pluton.

#### 4 Formation of the Scheelite Skarn

Skarn in Xintianling deposit formed in four stages: stage I (grandite-diopside), stage II (scheelite-hornblende-actinolite-andradite), stage III (scheelite-tourmaline-epidote-fluorite-quartz vein), stage IV (molybdenite-

quartz vein and calcite-spessartine-sulfide vein substages). Scheelite mineralization occurred mainly in stage II. Molybdenite Re-Os dating yields an isochron age of  $161.8 \pm 2.2$  Ma for the Xintianling scheelite skarn, consistent with the zircon U-Pb age of the host biotite granites, indicating a direct genetic relationship. C-O isotopes of calcite veins indicate that the carbon of skarn was derived by mixing of magmatic carbon and sedimentary carbon. H-O isotopes of scheelite quartz veins demonstrate that the ore-forming fluid was derived by magmatic water and lesser meteoric water. Sulfur of the ores is originated from magmatic and sedimentary sulfur. Pb isotopes indicate that the skarn orebodies were derived from crustal materials.

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