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## Alteration fingerprint of the early Yanshanian granite-related high-temperature hydrothermal uranium mineralization in the Nanling Metallogenic Belt, Southeast China

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### ABSTRACT

In the Xiazhuang and Zhuguang uranium ore fields of the Nanling Metallogenic Belt, southeast China, granite-related hydrothermal uranium deposits formed in two major mineralisation stages: (i) an early Yanshanian high-temperature stage (175–145 Ma) concomitant with the early Yanshanian magmatic event; and (ii) a late Yanshanian low-temperature stage (110–50 Ma) that occurred during the Cretaceous-early Cenozoic crustal extension in eastern Asia. To date, the Baishuizhai occurrence (175±16 Ma) and the Shituling and Zhushanxia deposits (162±27 and 165–146 Ma, respectively) represent the early Yanshanian uranium mineralisation in the belt. The Zr-Th-Ta-bearing disseminated-to vein-type uranium mineralisation is cogenetic with a hydrothermal alteration assemblage of epidote, chlorite, muscovite, adularia, illite, calcite, apatite, APS and titanite. The ore trace element signature and the propylitic and potassic alteration are both in agreement with relatively high temperatures (>250°C), corroborated by temperatures of 316–455 °C estimated from chlorite. This early mineralisation stage appears to be related to the intrusion of the early Yanshanian granites where the mineralising fluids could partly to totally derive from the granites in a high-temperature hydrothermal system. This would be to date, the first description and known occurrences for a new type of hydrothermal uranium deposit associated with granites worldwide.

### INTRODUCTION AND GEOLOGICAL SETTING

The South China Uranium Province accounts for the largest amount of explored uranium deposits and resources in China (~50% of identified uranium resources; [1-4]). It includes three major types of uranium deposits, from the most to the least economic: (i) granite-related vein-type deposits, (ii) volcanic-related vein-type deposits and (iii) black shale-related deposits (i.e., C-Si-pelite type; [1, 5, 6]). Some small sandstone-type uranium deposits are also hosted in several Mesozoic-Cenozoic basins of the province. In addition to uranium, the province is also renowned for W, Sn, Bi, Sb, Mo, Au, Ag, Cu, Pb and Zn deposits [2, 3, 6], some of which belonging to the world-class category in terms of grade and tonnage.

Granite-related hydrothermal uranium deposits from the Xiazhuang (eastern part of the Guidong batholith) and Zhuguang ore fields (OF) within the Nanling Metallogenic Belt (NMB) formed in two major mineralisation stages [5]: (i) an early Yanshanian high-temperature stage (175–145 Ma) concomitant with the early Yanshanian magmatic event that occurred in South China during the Jurassic; and (ii) a late Yanshanian low-temperature stage (110–50 Ma) that occurred during the Cretaceous-early Cenozoic crustal extension in eastern Asia. To date, the early Yanshanian stage is only represented by the Baishuizhai occurrence (175±16 Ma) and the Shituling (162±27 Ma) and Zhushanxia (165–146 Ma; [7]) deposits located in the Xiazhuang OF [5]. These early Yanshanian deposits are mainly hosted in Triassic granites (e.g., Baishuizhai and Maofeng plutons) emplaced during the Indosinian orogeny, among which peraluminous S- and L-type leucogranites and highly fractionated high-K calc-alkaline A2-type granite constitute the most favourable U sources [5]. The primary uranium mineralisation mainly occurs as Zr-Th-Ta-bearing uraninite and pitchblende disseminated in the host-granite or as vein filling fractures. Large amounts of secondary uranium mineralisation are

also characteristics of these deposits. Preliminary description of the alteration mineral assemblage including hydrothermal epidote, chlorite, muscovite, K-feldspar, apatite etc. presented in [5] and ore-forming fluid temperatures ranging from 290 to 338 °C at the Shituling deposit [8] were strong evidence for a high-temperature hydrothermal system. Now, this work aims to better characterise the genetic conditions of the early Yanshanian uranium stage through detailed petrographic and mineralogical studies carried on the alteration minerals associated with the uranium mineralisation.

## MATERIAL AND METHODS

Six mineralised samples were collected from the Baishuizhai occurrence (XB1) and the Shituling (XS1, XS2) and Zhushanxia (ZSX1, ZSX2, ZSX3) deposits in the Xiazhuang OF. The textural and paragenetic relationships of the alteration minerals associated with the early Yanshanian uranium mineralisation were determined through detailed petrographic studies by optical reflected light microscope and scanning electron microscope (SEM). The chemical composition of the alteration minerals was analysed by electron microprobe (EMP) and their trace element concentrations were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

## RESULTS

### 1. PETROGRAPHY AND MINERAL ASSEMBLAGE OF THE ALTERATION

The hydrothermal alteration of the host granites associated with the early Yanshanian uranium mineralisation can be pervasive (e.g., Baishuizhai) or confined in the vicinity of fractures (e.g., Shituling and Zhushanxia). The alteration mineral assemblage identified in the studied deposits includes epidote, chlorite, calcite, adularia, muscovite, illite, quartz, apatite, titanite, aluminium phosphate-sulphate (APS) minerals, albite and Fe-oxide. Sulphide minerals such as pyrite, chalcopyrite, galena, molybdenite, sphalerite, bismuthinite and greenockite are also frequently observed. These alteration minerals either occur disseminated in the altered host-granite (e.g., Baishuizhai) or along the mineralised veins (e.g., Shituling). This typical mineralogy characterise extensive propylitic (epidote-chlorite-calcite±albite) and potassic (adularia-muscovite-illite) alterations and silicification (quartz). In the Baishuizhai occurrence, the magmatic feldspars are completely replaced by muscovite, illite and quartz, which is characteristic of greisenisation.

### 1. CHEMICAL SIGNATURES OF THE ALTERATION MINERALS

Among the alteration minerals that were identified, epidote, chlorite and muscovite occur in the three studied deposits and show specific major, minor and trace element compositions, although chlorite is rare in samples from the Shituling deposit. Epidote from Baishuizhai is characterised by its Mn content (16.3–17.5 wt%) whereas epidote from Shituling and Zhushanxia presents similar compositions ranging from 22.9–36.4 wt% CaO, 11.4–25.9 wt% Al<sub>2</sub>O<sub>3</sub> and 5.7–13.4 wt% FeO. All epidotes are characterised by variable concentrations of Ti (27–1215 ppm), V (10–819 ppm), Zn (6–309 ppm), Y (0.1–99 ppm), Sn (5–89 ppm) and Zr (limit of determination (LOD)–8 ppm). It can be noted that only epidote from Baishuizhai returned heavy REE concentrations up to 7 ppm Lu, 11 ppm Er and 33 ppm Yb. Epidote from Shituling and Zhushanxia also has additional concentrations of Sr (5–287 ppm), W (3–56 ppm) and Nb (9–42 ppm). Chlorite from Baishuizhai and Zhushanxia is Fe-dominant (18.9–31.4 wt% FeO; 9.0–16.9 wt% MgO) giving a chamosite composition. Trace elements of petrogenetic interest are Ti (70–1559 ppm), Zn (473–1450 ppm), Li (441–1024 ppm), V (25–425 ppm), Rb (4–170 ppm), Sn (2–58 ppm), Cs (9–51 ppm), Nb (LOD–31 ppm) and Zr (LOD–12 ppm). The calculated temperatures from the chlorite compositions (Al IV thermometer, after [9]) range from 316 to 455 °C (n= 19). Muscovite from the three studied deposits shows relatively homogeneous composition with 46.2–53.2 wt% SiO<sub>2</sub>, 27.4–33.8 wt% Al<sub>2</sub>O<sub>3</sub> and 3.1–11.5 wt% K<sub>2</sub>O contents. It has variable Rb (120–2856 ppm), Ti (37–2319 ppm), Cs (29–1667 ppm), Li (43–1084 ppm), Sn (LOD–628 ppm), Sr (LOD–252 ppm), Nb (LOD–451 ppm), W (LOD–111 ppm), Zr (LOD–57 ppm) and Ta (LOD–31 ppm) concentrations. Titanite from the Zhushanxia deposit (average of 34.4 wt% TiO<sub>2</sub>, 30.9 wt% SiO<sub>2</sub> and 29.4 wt% CaO) shows minor Al<sub>2</sub>O<sub>3</sub> (0.9–1.4 wt%) and FeO (0.1–0.8 wt%) contents and has variable W (160–2010 ppm), Zr (42–878 ppm), Y (81–352 ppm), Sn (47–248 ppm), Nb (100–190 ppm) and Ta (4–12 ppm) concentrations. Finally, apatite from the Shituling and Zhushanxia deposits presents a fluorapatite composition with 52.2–58.5 CaO wt%, 38.0–43.3 wt% P<sub>2</sub>O<sub>5</sub> wt% and 1.6–2.2 F wt% contents. Trace elements with significant concentrations are Sr (615–3640 ppm), Y (69–777 ppm), Rb (2–151 ppm), Th (1–130 ppm), W (3–70 ppm) and Sn (2–19 ppm).

## DISCUSSION AND CONCLUSIONS

The alteration mineral assemblage from Baishuizhai, Shituling and Zhushanxia including epidote, chlorite, K-bearing silicate, titanite and apatite associated with Zr-Th-Ta-bearing uranium oxides characterise an extensive propylitic and potassic alteration strongly suggesting high temperature conditions. The high temperature of the hydrothermal system was thus confirmed by temperature estimates ranging from 316 to 455 °C calculated with the Al IV thermometer in chlorite [9], which is also corroborated by temperatures of 290–338 °C determined from fluid inclusions for the ore-forming fluid of the Shituling deposit [8]. The chemical signatures of the alteration minerals showing characteristic concentrations of incompatible elements (K,

Cs, Li, Rb, Sr, Y, Zr), rare metals (Sn, W, Nb, Ta) and occasionally heavy REE indicate highly differentiated crustal source-rocks [10, 11] such as peraluminous leucogranite or highly fractionated high-K calc-alkaline granite [5], widely represented in the NMB, and also suggest the contribution of magmatic-derived fluids. For instance, hydrothermal titanite largely occurs in alteration zones associated with the intrusion of igneous rocks. It is a common alteration product highlighting late magmatic to post-crystallisation hydrothermal alteration in porphyry Cu and Fe-Cu-Au-W-Mo skarn mineralising systems [12, 13]. Moreover, the Zr content in titanite, up to 878 ppm in titanite from Zhushanxia, also reflects the magmatic contribution as a source of fluid for the hydrothermal system [13]. The greisenisation characterised in Baishuizhai constitutes another strong evidence for the contribution of magmatic-derived fluids to the hydrothermal system. It is indicative of late magmatic alteration of the host-granite that most likely occurred during the cooling stage of emplacement of the early Yanshanian granite in the district. As they are generated during the final stage of granite crystallisation, the late magmatic fluids responsible for the greisenisation tend to be enriched in incompatible elements [10, 11], and also known to be at the origin of W-Sn-Mo-(U) etc. mineralisation in the province [2, 3, 6, 14]. Then the significant and systematic record of this suite of elements in the studied alteration minerals would be the marker of the contribution of such fluids. In the Xiazhuang OF, the early Yanshanian uranium mineralisation is also associated with minor tungsten occurrences such as wolframite in the Shituling deposit [15] and sheelite in the Zhushanxia deposit (up to 0.3% W; [7]), indicating possible genetic relations between uranium and tungsten mineralisation. Finally, the occurrence of fluorapatite (up to 2.2 wt% F) in the Shituling and Zhushanxia deposits together with calcite in the three studied deposits suggest that the hydrothermal solutions were enriched in fluoride and carbonate ions that can form complexes able to transport metals including uranium [5].

Therefore, the early Yanshanian uranium stage appears to be strongly related to the intrusion of the early Yanshanian granites providing: (i) the heat source for the high temperature hydrothermal system, (ii) magmatic-derived fluids that can mix with hydrothermal fluids already present in the basement and (iii) major sources for incompatible elements and rare metals that are concentrated in the alteration minerals and the uranium mineralisation. This model is new for hydrothermal uranium deposits related to granites and seems to represent the only occurrence of this type in the world. At the scale of the NMB, the alteration fingerprint that was characterised in this study for the early Yanshanian uranium event presents numerous similarities with the genetic model proposed for the giant W-Sn event in South China [5, 6, 14], also related to the intrusion of the early Yanshanian granites (peak at 160–150 Ma). Further studies will be conducted in order to characterise the spatial-temporal relations between the U and W-Sn mineralising systems in the NMB.

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## Country or International Organization

East China University of Technology

**Primary author:** Dr BONNETTI, Christophe (State key laboratory breeding base of nuclear resources and environment, East China University of Technology)

**Co-authors:** Dr RIEGLER, Thomas (iCRAG, School of Natural Sciences, Department of Geology, Trinity College Dublin); Mr LIU, Xiaodong (East China Institute of Technology)

**Presenter:** Dr BONNETTI, Christophe (State key laboratory breeding base of nuclear resources and environment, East China University of Technology)

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