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# Mineralogical and geochemical evidence for biogenic and petroleum-related uranium mineralization in the Qianjiadian deposit, NE China

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ABSTRACT

The sandstone-hosted Qianjiadian uranium deposit, hosted in the Upper Cretaceous Yaojia Formation in the Qianjiadian area, Songliao Basin, NE China, has been studied for over twenty years. However, there exists debate on whether mineralization fluid is low-temperature groundwater in favor of biogenic mineralization or diabase-related magmatic hydrothermal fluid for this deposit and other adjacent geologically linked sandstone-hosted uranium deposits (Baixingtu, Baolongshan and Huitianzhao deposits) in the North China. This study provided new data from petrographic and geochemical analyses, geochronology of uranium minerals (the EMPA chemical dating method) and petroleum hydrocarbon biomarkers in host sandstones. Two types of host sandstone were recognized. In calcareous sandstones, pitchblende coexists with colloform pyrite and poikilitic calcite cement while quartz and feldspars were extensively corroded. In non-calcareous sandstones, coffinite coexists with colloform pyrite and only feldspars were slightly corroded. This suggests that pitchblende formed in high pH ($pH > \sim 9$) fluid, while the pH of ore-forming fluid for coffinite was lower ($pH = 7–9$). Besides, EMPA chemical dating revealed two stages of uranium mineralization. Stage-A occurred in 43–28 Ma with pitchblende as the only uranium mineral species. Stage-B occurred in 19–3 Ma with the formation of both pitchblende and coffinite. The uranium mineralization was biogenic under low-temperature groundwater condition and thus not from a diabase-related mafic magmatic hydrothermal fluid based on the following lines of evidence: (i) some coffinite occurs as phosphorus-rich microorganism-like microspherules structure; (ii) pyrite aggregates were generated from bacterial sulfate reduction as indicated by the $\delta^{34}S$ values as low as −41.4‰; (iii) calcite cement in calcareous sandstone contains only single phase aqueous inclusions, and have $\delta^{13}C$ values as low as −11.2‰, indicating that part of the carbon was derived from organic matter oxidation; (iv) the organic matter oxidation is further supported by hydrocarbons extracted from petroleum inclusions within calcite cement, showing occurrence of $C_{26}$–$C_{31}$ 17α, 21β 25-norhopanes, typically resulting from heavy biodegradation.

## 1. Introduction

The mineralization mechanism for sandstone-hosted uranium deposits has been generally attributed to U(VI) reduction by abiotic and organic matters under low temperature conditions (Granger and Warren, 1969; Reynolds et al., 1982). The viewpoint of abiological reduction of U(VI) by pyrite, mackinawite, aqueous sulfides, adsorbed or structural Fe(III) in clays and reduced organic functional groups (e.g., thiols) (Granger and Warren, 1969; Reynolds and Goldhaber, 1983; Wersin et al., 1994; Hua et al., 2006; Cumberland et al., 2016) has been overwhelmed by the cognition of biomineralization, including U(VI) biosorption and bioaccumulation, and bioreduction of U(VI) to U(IV) (Cai et al., 2007a,b; Burgos et al., 2008; Campbell et al., 2012; Newsome et al., 2014; Cumberland et al., 2016), because U(VI)

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abiological reduction is too slow to be efficient as shown by low-temperature laboratory experiments (Nakashimima et al., 1984; Lovley and Phillips, 1992; Abdelouas et al., 1998). In contrast, experiments have confirmed that sulfate-reducing bacteria and iron-reducing bacteria are capable of utilizing U(VI) as a preferred electron acceptor in respiration, leading to direct reduction of U(VI) to U(IV) at low temperature (< 80 °C; Lovley et al., 1991; Lovley and Phillips, 1992; Abdelouas et al., 1998; Sani et al., 2004; Spear et al., 1999). However, only morphological evidence alone for biogenically precipitated uranium minerals was provided in some uranium deposits (Milodowski et al., 1990; Min et al., 2005a,b), which was subsequently followed by robust and integrated mineralogical and geochemical lines of evidence from mineralized microfossils, nanocrystals, carbon and sulfur isotopes and biomarkers for biogenicity of coffinite in Dongsheng deposit (Cai et al., 2007b; Cuney, 2010). It was thought that Mesozoic intracontinental sedimentary basins in northern China were all potential for biogenic sandstone-hosted uranium deposits due to favorable geological settings (Bonnetti et al., 2015, 2017b).

Hydrothermal uranium mineralization with high-temperature metamorphic or magmatic fluids was the main cause for synmetamorphic, intrusive, vein-type and unconformity-related uranium deposits (Mercadier et al., 2011; Frimmel et al., 2014). Recently, earlier biogenic and later hydrothermal mineralization has been proposed as the origin of roll-front uranium deposit in the Lake Eyre Basin, Australia, based on in situ chemical and sulfur isotope analysis of pyrites (Ingham et al., 2014). While in tabular-type uranium ore deposits in the Hangjinqi deposit, Ordos basin, Zhang et al. (2017) proposed that hydrothermal mineralization occurred since 39 ± 2 Ma and was limited to local areas with biogenic mineralization ongoing since 97 ± 2 Ma based on REE and V, Fe and Y distribution measured from coffinite. The trace elements of uranium minerals are significant for constraining the genetic conditions of uranium deposits (Bonhoure et al., 2007; Mercadier et al., 2011; Depiné et al., 2013; Frimmel et al., 2014), especially that the REE pattern has been demonstrated as the most efficient tool, in which LREE-enriched and flat chondrite-normalized REE patterns indicate uranium mineralization by meteoric fluid infiltration and hydrothermal fluid activity, respectively (Mercadier et al., 2011; Zhang et al., 2017).

The sandstone-hosted Qianjiadian uranium deposit, located in the SW Songliao Basin, NE China, has been studied for over twenty years. However, the mineralization mechanism for this deposit and the adjacent geologically similar uranium deposits, e.g. Baixingtu, Baolongshan and Huitianzhao deposits, still remain controversial on whether low-temperature groundwater in favor of biogenic mineralization or diabase-related magmatic hydrothermal fluid dominated the ore-forming process (Luo et al., 2007, 2012; Wu et al., 2011b, 2012; Xu et al., 2011; Cai et al., 2013; Weng et al., 2015; Bonnetti et al., 2017b). The carbonate cements, colloform and framboidal pyrite aggregates, authigenic kaolinite and hematite in host sandstones from Baixingtu, Baolongshan and Huitianzhao deposits in the Qianjiadian Sag were regarded as the products of hydrothermal alteration resulted from mafic magmatism and the uranium was provided by upwards migrating hydrothermal fluid leaching uranium-rich basement rocks (Wu et al., 2011b, 2012; Xu et al., 2011; Cai et al., 2013; Weng et al., 2015). However, no geochemical evidence has been provided to support the hydrothermal fluid origin for the mineral assemblage or endogenetic uranium mineralization. By contrast, biogenic uranium mineralization process for the Baixingtu deposit has recently been proved with integrated mineralogical, geochemical and isotopic analyses, including pyrites of framboidal aggregates and in replacement of organic matter, which coexists with uranium minerals, having light sulfur isotope compositions characterized by $\delta^{34}S$ values from −72.0‰ and −6.2‰ (Bonnetti et al., 2017b). The uranium ore-bearing Yaojia Formation has undergone heating below 80 °C (Xi et al., 2015), which is favorable for microbes to survive (Wenger et al., 2002; Hoefs, 2015). Petroleum emplaced into Yaojia Formation from Lower Cretaceous source rocks (Tian et al., 2001; Liang, 2003; Li et al., 2008) during intermittent faulting activities since the end of Late Cretaceous (Luo et al., 2007; Li et al., 2012a) may be also involved in the uranium mineralization process and served as part of energy sources for microbial metabolism and carbon sources for calcite cement as revealed in Ordos Basin (Cai et al., 2007b). Therefore, the contradictory opinions on dominant uranium mineralization fluid of either low-temperature groundwater in favor of biogenic mineralization or diabase-related magmatic hydrothermal fluid in the Qianjiadian Sag, especially the Qianjiadian deposit, are necessary to be studied with more detailed and comprehensive analyses.

Geochronology of sandstone-hosted uranium deposits is more difficult than other types of deposits because (i) it is always unpractical to find sufficient quantities of coarse-grained uranium minerals for U-Pb isotopic analysis, (ii) it generally has a long-term and multi-stage ore-forming process (Zhang et al., 2017), and (iii) lead is incompatible with the structure of uranium minerals and these minerals are susceptible to alteration (Janeczek and Ewing, 1992; Alexandre and Kyser, 2005). Therefore, previous U-Pb isotopic dating based on whole rock was seriously interfered by pre-ore stage detrital grains and cements, resulting in older ages than real ones. Even though the interference by pre-ore stage minerals could be eliminated, the result from whole rock analysis is also a mixed age of multiple ore-forming events. Chemical U-Th-Pb dating using electron microprobe analysis (EMPA) is an effective way for uranium mineral geochronology (Bowles, 1990, 2015). It can provide a minimum age of uranium mineralization and is advantageous with its high spatial resolution and low cost (Kempe, 2003; Alexandre and Kyser, 2005; Cross et al., 2011). The EMPA chemical dating allows minerals of ages from 2 Ma to about 700–1000 Ma to be determined reliably (Bowles, 2015). This method has been applied to the dating of various minerals, such as zircon, xenotime (Suzuki and Adachi, 1991), monazite (Montel et al., 2000; Cocherie et al., 2005; Schulz and von Raumer, 2011; Bonnetti et al., 2017a), thorite, huttonite (Jercinovic and Williams, 2005) and apatite (Hu et al., 2013). The chemical ages of sandstone-hosted uranium minerals have also been studied with EMPA data in Deditius et al. (2008), Frimmel et al. (2014), Bonnetti et al. (2017b) and Zhang et al. (2017).

In this study, a series of analyses have been performed on the mineralized sandstones from the Qianjiadian uranium deposit, aiming to, (i) learn about the diagenetic minerals and paragenetic sequence, (ii) investigate the geochemistry of ore-forming fluid, (iii) find out the potential evidence for biogenic and petroleum-related mineralization, (iv) constrain the mineralization geochronology and, finally, (v) reveal the uranium mineralization mechanism and ore genesis model.

## 2. Geological setting

### 2.1. The Songliao Basin

The Songliao Basin is a Cretaceous rift structure located in northeast China, which is also one of the largest lacustrine basins in the world with a total area covering approximately 260,000 $km^2$ (Fig. 1A; Ren et al., 2002; Li et al., 2012a; Song et al., 2014). It is geographically surrounded by the Great Xing'an Range in the west, the Lesser Xing'an Range in the north and the Zhangguangcai Range in the east (Fig. 1A; Wu et al., 2011a; Deng et al., 2013). Based on the spatial distribution of rises and depressions originated during the thermal subsidence phase in the Late Cretaceous, the Songliao Basin can be divided into seven major structural units: the Northern Plunge, the Central Depression, the Northeastern Uplift, the Southeastern Uplift, the Western Slope, the Southwestern Uplift and the Kailu Depression (Fig. 1A; Zhu et al., 2014).

The basement of Songliao Basin is mainly composed of Precambrian to Palaeozoic metamorphic rocks (Pei et al., 2007; Wang et al., 2006; Wu et al., 2001), Palaeozoic to Mesozoic granites (Zhang et al., 2010; Wu et al., 2011b), Palaeozoic sedimentary strata (Li et al., 2012a; Zhou et al., 2012) and Late Jurassic intermediate to felsic volcanic rocks