Transformation of Fe-bearing minerals from Dongsheng sandstone-type uranium deposit, Ordos Basin, north-central China: Implications for ore genesis

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Abstract

Iron-bearing mineral assemblages and their distribution patterns directly reflect the redox environment in sediments, which plays a decisive role in the migration and precipitation of U. The Dongsheng sandstone-type U deposit hosted in fluvial and/or deltaic sandstones of the lower member of the Middle Jurassic Zhiluo Formation in the northeastern Ordos Basin has experienced multiple fluid events that impacted the redox conditions. Highly enriched in barren grey sandstones, pre-ore U (U mean = 12.05 ppm) associated with Fe-Ti oxides, clay minerals and organic matter is likely one of the key sources of U for the mineralization. Different contents of Fe-bearing minerals including biotite, Fe-Ti oxides, pyrite, hematite, goethite, and chlorite that were formed or altered under different redox conditions, resulted in sandstone units with distinct colors. The red sandstone is hematite-rich, indicating a highly oxidizing environment. The green sandstone is chlorite-rich

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and formed because of reducing hydrocarbon-rich fluids that overprinted the hematite-rich sandstone. The barren and mineralized grey sandstones consist of pyrite (with a higher content in mineralized sandstones), Fe-Ti oxide minerals, and carbonaceous debris, which are indicators of a reducing environment. Based on the paragenetic relationship and sulfur isotopic compositions of ore-stage pyrite, bacterial sulfate reduction was responsible for the formation of framboidal pyrite ($\delta^{34}S = -31.2$ to -3.8‰), and the sulfur of this pyrite mainly came from the oxidation of pre-ore pyrite ($\delta^{34}S = -19.1$ to +20.3‰). Euhedral and cement pyrite overprinting framboids were produced via Ostwald ripening with $\delta^{34}S$ values ranging from -56.9 to -34.3‰, lower than any values of framboidal pyrite. Therefore, these mineralogical and geochemical characteristics of the Dongsheng deposit suggest U mineralization involved both biogenic and abiogenic redox processes.

**Keywords:** Pyrite, $\delta^{34}S$, Fe-bearing minerals, alteration, sandstone-type U deposit, Ordos Basin

**Introduction**

Large-scale sandstone-type U deposits in China are mainly distributed in sedimentary basins generally parallel to the Central Asian Orogenic Belt (Chen 2002; Huang and Huang 2005; Zhang et al. 2010; Jiao et al. 2015; Zhu et al. 2018). The Dongsheng U deposit, located at the southeastern margin of the Central Asia Uraniferous Province (CAUP; OECD-NEA, IAEA 2010), has experienced multiple low-temperature fluid events responsible for multi-stage mobilization and fixation of U (e.g., Miao et al. 2010; Zhang et al. 2019). Having simple fluid histories quite different from the complex fluid history in the Dongsheng deposit, the ore-forming process of
other sandstone-type U deposits in the CAUP (e.g., the Bayinwula deposit in the Erlian basin, Bonnetti et al. 2015; the Kuji’ertai and Mengqiguer deposits in the Yili basin, Zhang and Liu 2019), is similar to the roll front reported by Shawe and Granger (1965) and Warren (1971). However, the genesis of the Dongsheng deposit remains controversial, with two models proposed including biogenic processes due to confirmed existence of bacteria (Cai et al. 2007a, 2007b; Jiang et al. 2012) and hydrothermal mineralization (Xiao et al. 2004; Zhang et al. 2017).

It has been widely accepted that U mineralization of sandstone-type deposits occurs during infiltration of the low-temperature surface-derived oxygenated groundwater into permeable sandstones. Containing abundant intrinsic or extrinsic reductants (e.g., organic matter, H₂S and FeS₂; Granger and Warren 1969; Goldhaber et al. 1983; Jiao et al. 2018a; Hough et al. 2019; Bonnetti et al. 2020), those permeable sandstones are confined by non- to semi-permeable aquitards (e.g., coal seams and mudstones). In this process, soluble U (VI) is reduced to insoluble U (IV). Additionally, iron is a redox-sensitive element with a high abundance in natural environments (e.g., Soliman and Goresy 2012; Mahoney et al. 2019). The mobilization, migration and fixation of U are often accompanied by variations in the existing forms of Fe species (i.e., different Fe-bearing minerals; Reynolds and Goldhaber 1978; Bonnetti et al. 2015; Rong et al. 2016). Therefore, the distribution and alteration characteristics of Fe-bearing minerals, in turn, reveal the geochemical zoning of the host sandstones, thus helping to decipher the genesis of U deposits. The changes of redox environment can also be indicated by the distribution characteristics of organic materials (e.g., total organic carbon; Spirakis 1996). It is known that
organic materials can not only provide energy for microbial activities involved in the alteration of Fe-bearing minerals (Reynolds et al. 1982; Reynolds and Goldhaber 1983), but also adsorb U under reducing conditions (Douglas et al. 2011; Zhang et al. 2020). Although the metallogenic model for the Dongsheng U deposit is well established, and in outcrops, U anomalies mainly associated with carbonaceous debris (CD) in the yellow sandstone have been reported by Jiao et al. (2018b) and Zhang et al. (2019a), the distribution characteristics of Fe-bearing minerals in different geochemical zones of host sandstones, especially the alteration of these minerals, are poorly understood.

The purpose of this paper is to characterize the role of Fe-bearing minerals in the mobilization and fixation of U in the Dongsheng deposit in the Ordos Basin. Mineralogical, chemical, and sulfur isotopic data are used to evaluate their alteration processes and to characterize the genetic link between Fe-bearing and U-bearing minerals. Here, we propose that biogenic activities and the following abiogenic processes were involved in the U mineralization in the Dongsheng deposit, thereby providing a better understanding for the genesis of U deposits in northern China.

**Geological background**

**The Ordos Basin**

The Ordos Basin is a rectangular, NNE-trending basin located in north-central China (Fig. 1a), covering an approximate area of 250, 000 km² (Deng et al. 2005). Based on the current tectonic configuration, the basin can be divided into six structural domains (Fig. 1a): the Yimeng uplift, the Western fault-folded zone, the Tianhuan depression, the Shanbei slope, the Jinx folded zone, and
The Weibei uplift (Guo and Jiao 2002).

The Ordos Basin developed during five main stages (Sun et al. 1985; Li et al. 1992; Zhang et al. 1995; Zhao et al. 1996; Zhang and Liao 2006; Jiao et al. 2015; Peng et al. 2019): (1) an aulacogen stage characterized by Mesoproterozoic to Neoproterozoic metamorphic rocks, including phyllites, marbles, greenschists and metamorphosed volcanic rocks (Zhang et al. 1980; Jia et al. 1997; Yang et al. 2005); (2) an epicontinental sea stage marked by early Paleozoic limestone, evaporite and gas-rich carbonate rocks of neritic platform facies (Sun et al. 1986; Zhai et al. 2002); (3) a depression stage characterized by late Paleozoic to early Mesozoic coal, limestone, and gas- and oil-bearing sandstone and mudstone (Li et al. 1995; Liu and Yang 2000); (4) an independent intra-continental basin stage characterized by deposition of middle to late Mesozoic sedimentary units dominated by fluvial, deltaic and lacustrine environments, and containing various energy resources including (from oldest to youngest in Jurassic sediments) oil in the Fuxian Formation, oil and coal in the Yan’an Formation, and U in the Zhilu Formation (Qu et al. 2003; Yang et al. 2005; Zhang et al. 2006; Cai et al. 2007a); and (5) a fault depression stage characterized by generation of a series of grabens in the Cenozoic around the basin, thereby destroying the integrity of the basin (Zhao, Z.Y. 1990; Zhao, M.W., et al. 1996; He 2003).

Several NW- and NNE-trending faults are developed in the northern Ordos Basin (Fig. S1; Han et al. 2008), some of which cut through the early Paleozoic to middle Mesozoic sediments (Chen et al. 2005; Deng et al. 2005; Liu et al. 2009). Based on thermal and tectonic history analyses reported by Zhao et al. (1996), the Ordos Basin has undergone a short-lived thermal event in
Middle Jurassic (170-160 Ma), and this event was attributed to the subsurface magmatic intrusion related to the early Yanshanian movement and resulted in the initial formation of hydrocarbons in Paleozoic sediments and migration from them. In addition, the differential uplift and erosion between the eastern and western parts of the basin since 23 Ma led to a regional upward migration of hydrocarbons (Zhao et al. 1996; Zhang et al. 2018), which was indicated by carbon isotope values and fluid inclusion compositions in calcite cement in the Zhiluo Formation (e.g., Cai et al. 2007b).

The Dongsheng uranium deposit

The Dongsheng uranium deposit, located in the northeastern Ordos Basin (Fig. 1a), is hosted in the sandstone of the Middle Jurassic Zhiluo Formation (J2z) deposited as climate changed from semi-humid to semi-arid (Miao et al. 2010; Sun et al. 2017; Jiao et al. 2018a). The Zhiluo Formation unconformably overlying the Middle Jurassic coal-bearing strata of the Yan’an Formation (J2y) is composed of lowstand, transgressive and highstand systems tracts, and the lowstand systems tract consists of two parasequence sets (Jiao et al. 2005a, 2005b). The lower parasequence set (J2z1–1) originated from a braided river (delta) is the primary ore-bearing stratum. The upper parasequence set (J2z1–2) originated from a meandering river (delta) is the secondary ore-bearing stratum. Two main tabular orebodies have been delineated based on their different horizons (i.e., J2z1–1, J2z1–2; Fig. 1b), showing 0.5 to 5 m in thickness and dip direction of northwest-southeast with a burial depth decreasing from 800 to 100 m. The orebodies extend for over 100 km along the redox front and are a few hundred meters to a kilometer wide (Peng et al. 2019). The inferred and indicated
resources total more than 50 kt at 0.03 to 0.1% U (Akhtar et al. 2017; Zhu et al. 2018; Peng et al. 2019). The U mineralization is mainly hosted in coarse to medium-grained sandstones in the middle and upper parts of the fluvial facies (Figs. 1 and 2). Uranium minerals mainly occur as coffinite and uraninite and are associated with CD and pyrite (Jiao et al. 2018a; Yue et al. 2019).

Four facies displaying different colors are identified in the deposit: red sandstone (Figs. 1b-1d and 2a), green sandstone (Figs. 1b-1d and 2b-2c), grey sandstone (Figs. 1b-1d and 2d-2h) and yellow sandstone (Fig. 1c and 1d), classified into: (1) oxidized zone, consisting of red, green and yellow sandstones, (2) mineralized zone hosted by grey sandstones, and (3) reduced zone with barren grey sandstones (Fig. 2). Clay minerals are composed of an assemblage of smectite-kaolinite-chlorite-illite in the sandbodies, with a higher content of chlorite in the green sandstone and a higher content of kaolinite in the mineralized grey sandstone (e.g., Zhang et al. 2019).

**Sampling and analytical methods**

A total of 109 sandstone samples from three regional stratigraphic drill holes (DSA, DSB and DSC) and three drill holes through the Dongsheng U deposit (DS1, DS2 and DS3), and 21 outcrop sandstone samples from Shenshangou area were collected. Detailed sample locations and descriptions are shown in Figures S1-S3 and Tables S1-S2.

Ninety-nine drill core samples (27 red, 33 green and 39 barren grey sandstone samples; Fig. S2) combined with 7 yellow outcrop sandstone samples (Fig. S3) were analyzed for their U and Th contents (Table S1). Three drill holes DSA-DSC were used as a reference to determine the petrographic, mineralogical and geochemical characteristics of the host sandstone before U
mineralization. Thirty-five different colored samples (7 red, 7 green, 7 mineralized grey, 7 barren grey and 7 yellow sandstone samples; Figs. S2 and S3; Table S2) were analyzed for redox-sensitive indicators (i.e., Fe$^{3+}$, Fe$^{2+}$, S$^{2-}$, S$_{\text{total}}$, TOC, ΔEh and pH). The ΔEh and pH of the sandstones were tested with international standards, i.e., ISO11271:2002 and ISO10390:2005, respectively. The analyses of U, Th and redox-sensitive indicators were carried out, by using a HD3025 laser analyzer for U (relative standard deviation (RSD) = 4.18%), a modal 721 spectrophotometer for Th (RSD = 2.60%), a 5mL acid burette for Fe$^{3+}$ (RSD = 0.10 to 1.24%), Fe$^{2+}$ (RSD = 0.22 to 1.35%) and TOC (RSD = 0.10 to 1.30%), a HCS-140 high frequency infrared ray carbon-sulphur analyzer for S$_{\text{total}}$ (RSD = 0.24 to 1.65%), a ESJ200-4 electronic balance for S$^{2-}$ (RSD = 0.18 to 1.40%), an electronic potentiometer for ΔEh (RSD = 0.30 to 1.50%) and a PHS-3C acidimeter for pH (RSD = 0.12 to 1.50%) at the Analyses and Testing Center in No.208 Geological Party, China Nuclear Geology, Chinese National Nuclear Corporation, Baotou, China.

Thirty-five samples (Table S2) were prepared as polished thin sections and characterized, by using a Nikon ME600POL optical microscope and a Zeiss EVO LS 15 scanning electron microscope (SEM) at the Key Laboratory of Tectonics and Petroleum Resources Ministry of Education, China University of Geosciences, Wuhan. Observations were focused on the U-bearing and Fe-bearing minerals to determine their textural and paragenetic relationships. Electron probe microanalysis (EPMA) was chosen to quantify the chemistry of U-bearing and Fe-bearing minerals at the University of Manitoba, Winnipeg, Canada, by using a Cameca SX100 universal electron probe microanalyzer. The EPMA beam size was adjusted between 1 and 10 µm, which depended
on the detail required. The acceleration voltage was 15 kV and the current was 20 nA.

Twenty-two thin sections (5 red, 5 green, 5 mineralized grey, 2 barren grey and 5 yellow sandstone samples; Table S2) were selected for pyrite sectional area counts within a 2 cm² area by SEM. The percentage area covered by pyrite grains in the photomicrographs is measured, by using the software named Image-Pro Plus 6.0. We tried to approximate the average content of pyrite in sandstones using the ratio of cross-sectional area of pyrite to 2 cm² in thin sections (Fig. S4).

In order to preserve isotopic values in their paragenetic context, eleven polished thin sections from grey sandstones (GY-1~GY-9, DSC-08 and DSC-14; Table S2) were prepared for in situ sulfur isotope analyses, conducted with a Cameca 7f secondary ion mass spectrometer (SIMS) at the University of Manitoba, Winnipeg, Canada. Procedures similar to those documented by Hough et al. (2019) were used. All samples were gold coated to prevent surface charging. Sulfur isotope ratios ($^{34}$S/$^{32}$S) were measured, by using a ~1-nA Cs⁺ primary beam accelerated at 10 kV with a spot size of ~15 µm filtered through a 247 µm entrance slit. The sulfur isotope values are reported in per mil relative to V-CDT standards with an analytical uncertainty (1σ) of ± 0.3‰ for $\delta^{34}$S.

**Results**

**Uranium and thorium contents**

Average U contents for red, green and yellow sandstones are 1.55 ppm, 1.32 ppm and 1.81 ppm, whereas the content for barren grey sandstones is 12.05 ppm (Tables S1 and S3). The oxidized and reduced sandstones have similar Th contents but differ in their Th/U ratios (Fig. S5). The mean ratio of Th/U in red, green and yellow sandstones are 7.68, 9.20 and 6.94, whereas the ratio in
barren grey sandstones is 1.06 (Table S3).

**Redox-sensitive indicators of host sandstones**

In contrast to those in red and yellow sandstones, the Fe$^{3+}$/Fe$^{2+}$ ratios are less than 1.0 in both green and grey sandstones (Fig. 3a). The mean ratio of S$_{\text{total}}$/S$^{2-}$ in red sandstones (mean > 6) is much higher than that in yellow sandstones (mean = 1.80), and the mean value in grey sandstones (mean = 1.40) is lower than that in green sandstones (mean = 3.74; Fig. 3a; Table S4). Both the average values of S$^{2-}$ and total organic carbon (TOC) are highest in mineralized grey sandstones, followed by those in barren grey sandstones and yellow sandstones, and decreasing gradually from those in green sandstones to those in red sandstones (Fig. 3b). Notably, there is a positive correlation between TOC and S$^{2-}$ in grey sandstones (Fig. 3b). There are relatively higher values of ΔEh but lower pH in mineralized grey sandstones, and the pH values in all four colored sandstone units are more than 7 (Fig. 3c).

**Occurrence and paragenesis of Fe-bearing minerals**

Macroscopically, the Fe-bearing minerals that can be found mainly include pyrite, limonite and hematite (Fig. 4). Pyrite, generally as nodules with diameter ranging from 2 to 20 mm in drilling cores, is predominantly associated with CD in the grey sandstone and surrounded by limonite when exposed to air for an extended period of time (Fig. 4a). Limonite is a mixture of iron hydroxides, mainly comprised of goethite, and usually occurs as encrustation on pyrite in the yellow sandstone (Fig. 4d). The dark red hematite is mainly distributed in the red sandstone (Figs. 4b, 4c and 4e).

Microscopically, the Fe-bearing minerals appear mainly as authigenic and altered minerals such
as hematite, goethite, pyrite and chlorite, as well as detrital minerals such as Fe-Ti oxides and biotite (Fig. 5; Table S5). Hematite mainly occurs as dark red cements in the matrix or as coatings on mineral surfaces and along microfractures of clastic particles in red sandstones (Fig. 5a). Minor amounts of it occur as subhedral grains with a diameter up to 150 μm (Fig. 5b). Goethite can be observed in both yellow and red sandstones, and occurs primarily as coatings on the surfaces of interstitial materials and detrital particles, or along microfractures of clastic particles (Fig. 5c). Same as with hematite, a small amount of goethite was observed as subhedral grains (Fig. 5d).

Three different morphologies of pyrite in all four colored sandstones were identified: framboidal, euhedral and cement. Framboidal pyrite mainly distributed around CD is the most abundant type of pyrite (Fig. 5e). Densely-packed framboids appear as spherical aggregates of submicrometer-sized pyrite crystals. Euhedral pyrite, generally in the form of discrete cubes, is most closely associated with the matrix of clay minerals (Fig. 5f). Distributed between clastic particles, the pyrite cement shows a texturally homogeneous growth (Fig. 5g).

Chlorite is most abundant in the green sandstone, followed by the grey sandstone. It occurs mainly in one of two habits: pompon-like aggregates coating clastic particles (Fig. 5h), or needle-shaped crystals or squamous aggregates in the matrix (Fig. 5i).

The detrital Fe-Ti oxide minerals were observed in all four colored sandstone units (Fig. 5j). Ilmenite is the original detrital mineral but it usually appears as the remnant grain with residual cores surrounded by Ti oxides (Fig. 5k). These minerals are a mixture of Ti oxide and Fe oxide/hydroxide micrograins, characterized by relatively high U contents (Table S5). Iron-Ti
oxides are more abundant in grey sandstones than in oxidized sandstones in which the Fe-Ti oxides have lower iron contents (Table S5).

Detrital biotite is high in Fe but low in Mg (Table S5), and occurs in all four colored sandstone units (Fig. 5l). The length of the biotite can reach several hundred micrometers, and it generally appears as a deformed grain.

These six Fe-bearing minerals are closely related to each other, mainly manifested as the coexistence of two or more minerals at the micron scale (Fig. 6). Significantly, the types of Fe-bearing minerals occurring along cleavage planes in biotite in different colored sandstones are quite distinct. For instance, pyrite predominates in the grey sandstone (Fig. 6a), hematite in the red sandstone (Fig. 6b), and goethite in the yellow sandstone (Figs. 6c and 6d), whereas in the green sandstone, biotite was partially replaced by chlorite (Fig. 6e). In addition, it can also be observed that chlorite altered from biotite was filled with hematite and pyrite (Fig. 6f). As a clay mineral widely distributed in the matrix, chlorite occurrence is linked to the occurrence of pyrite (Fig. 6g). Generally, pyrite is distributed in the microfractures of or around Fe-Ti oxides (Figs. 6h and 6i).

In red sandstones, framboidal hematite can be observed (Fig. 6j), whereas in yellow sandstones, goethite and pyrite are often found on the same particle (Figs. 6k and 6l), and the goethite around the edge of different morphological pyrite is documented (Fig. S6). In addition, based on our observations and recent work described in detail by Yue et al. (2020), it is common to see the framboidal pyrite overprinted by euhedral pyrite and pyrite cement, respectively, in mineralized grey sandstones (Fig. S7). The simplified paragenetic sequence of Fe-bearing minerals in the
Dongsheng U deposit is illustrated in Figure 7.

Proportions of pyrite

The proportions of pyrite in reduced sandstones are 2 orders of magnitude higher than that in oxidized sandstones. In red, green and yellow sandstone units, the mean area percentages of pyrite are $1.49 \times 10^{-4}$%, $3.31 \times 10^{-4}$% and $5.47 \times 10^{-4}$%, respectively (Table S6). In mineralized grey sandstones, the proportions of pyrite ranging from $3.97 \times 10^{-2}$ to $9.28 \times 10^{-2}$% are higher than those in barren grey sandstones ($1.06 \times 10^{-2}$ to $2.58 \times 10^{-2}$%) whose values represent the initial level of pyrite content.

In situ sulfur isotopes

Sulfur isotopes were analyzed in pyrite from barren samples (pre-ore pyrite) and associated with U (ore-stage pyrite; Fig. 8; Table S7). The pre-ore pyrite produced $\delta^{34}$S values from -19.1 to +20.3‰ (mean = +7.3‰). Framboidal pyrite ($n = 5$) with $^{34}$S depletion ranges from -19.1 to -8.0‰ (mean = -13.4‰), whereas the euhedral and cement pyrite ($n = 9$), together with the pyrite occurring along cleavage planes in biotite ($n = 1$) show higher values from +7.9 to +20.3‰ (mean = +17.7‰).

The $\delta^{34}$S values of ore-stage pyrite ($n = 29$) range from -56.9 to -3.8‰ (mean = -34.1‰). Ore-stage framboild pyrite ($n = 12$) ranges from -31.2 to -3.8‰ (mean = -16.4‰), whereas ore-stage euhedral and cement pyrite ($n = 17$) have lower values from -56.9 to -34.3‰ (mean = -46.7‰).

Uranium mineralization

Uranium minerals are closely related to pyrite and Fe-Ti oxides (Fig. 9), mainly distributed: (1) in the interstices of microcrystallites of the closely arranged pyrite framboilds (Figs. 9a-9c), (2)
around the Fe-Ti oxides, euhedral pyrite or pyrite cement generally replacing the Fe-Ti oxides (Figs. 9d-9h), and (3) along cleavage planes in biotite filled with pyrite (Fig. 9i).

Discussion

Alteration of Fe-bearing minerals

The alteration among Fe-bearing minerals can be divided into: (1) alteration from Fe$^{2+}$-bearing to Fe$^{2+}$-bearing minerals, (2) oxidation from Fe$^{2+}$-bearing to Fe$^{3+}$-bearing minerals, and (3) reduction from Fe$^{3+}$-bearing to Fe$^{2+}$-bearing minerals. The multiple alteration processes not only represent the changes of redox environment, but also indicate the multi-stage mobilization and fixation of U (e.g., Reynolds and Goldhaber 1978; Reynolds et al. 1986; Bonetti et al. 2015; Jiao et al. 2018b; Zhang et al. 2019a).

The alteration from Fe$^{2+}$-bearing to Fe$^{2+}$-bearing minerals generally involves: (1) biotite chloritization, and (2) the formation of pyrite whose Fe sources may be biotite, chlorite, Fe-Ti oxides and dissolved Fe$^{2+}$ carried by the descending meteoric water. The alteration of biotite is closely related to the physico-chemical properties of pore fluids (Boles and Johnson 1983; Claeys and Mount 1991). Biotite can be replaced pseudomorphically by chlorite with a greenish tint (Fig. 6e), which may indicate the conditions of low K$^+$/H$^+$ ratios relative to (Fe$^{2+}$ + Mg$^{2+}$)/H$^+$ ratios (Veblen and Ferry 1983; Morad 1986; Morad and Aldahan 1986).

The euhedral pyrite was formed along cleavage planes in biotite, thus indicating high rates of iron leaching and low rates of Fe$^{2+}$ supply during the dissolution of biotite (Morad 1986; Fig. 6a; Table S5: Biotite, GY-11). Additionally, the lower iron content in chlorite (Table S5: Chlorite, GY-
5) associated with pyrite permits the interpretation that the released iron was utilized in the formation of pyrite (Fig. 6g). Previous studies have demonstrated that the substitution of Mg\(^{2+}\) for Fe\(^{2+}\) after the precipitation of chlorite results in a low Fe/(Fe + Mg) ratio in chlorite under conditions of high Mg\(^{2+}\) activities. Pyrite is formed in an anoxic-sulfidic environment due to the released Fe\(^{2+}\) (White et al. 1985; Aldahan and Morad 1986). Thermodynamic calculations performed by Bonnetti et al. (2015) suggested that ilmenite is almost insoluble in the H\(_2\)S-free system over a broad range of pH conditions (approximately from 5 to 11), whereas Fe-Ti oxide grains (predominantly ilmenite) will be altered to Ti-oxide minerals and release Fe\(^{2+}\) in the presence of H\(_2\)S-rich fluids during diagenesis, which is involved in the following reaction (Reynolds and Goldhaber 1978; Bonnetti et al. 2015):

\[
\text{FeTiO}_3 + 2\text{H}_2\text{S} \rightarrow \text{TiO}_2 + \text{FeS}_2 + \text{H}_2\text{O} + \text{H}_2 \quad (1)
\]

The alteration of ilmenite is usually accompanied by the production of relatively large micropores generally filled with pyrite (Fig. 6h). Additionally, due to Fe-Ti oxides containing minor U (Table S5), the U will also be leached out during alteration, and precipitate as U-bearing minerals around the Fe-Ti oxides (Figs. 9g and 9h).

Epigenetic U mineralization is generally considered as a continuous process driven by the translation of the redox front (Bonnetti et al. 2020). There will definitely be a part of dissolved Fe\(^{2+}\) not incorporated into Fe\(^{3+}\)-bearing minerals, thereby providing iron source for ore-stage pyrite. The whole process is supported by the mineralized grey sandstones having the highest pyrite contents and the red sandstones with the lowest (Table S6). In addition, the dissolved U from
oxidized sandstones will precipitate as coffinite and uraninite around the pyrite in grey sandstones (Fig. 9). This process will be further discussed in the next section.

The alteration from Fe$^{2+}$-bearing to Fe$^{3+}$-bearing minerals usually results in the precipitation of goethite and/or hematite from pyrite oxidation mainly involving chemical, biological and electrochemical reactions (Lowson 1982; Evangelou and Zhang 1995). Because the activity of ferro-oxidizing bacteria is greatly reduced with a pH of over 4.5 (Kuznetsov et al. 1963; Rackley 1972), pyrite oxidation is dominated by abiotic chemical reactions in sandstones of the lower member of the Zhiluo Formation (Fig. 3c; pH >7). The process can be illustrated by following reactions (Evangelou and Zhang 1995):

\[
\begin{align*}
\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{Fe}^{2+} + \text{1/4O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + 1/2\text{H}_2\text{O} \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ \\
\text{FeS}_2 + 7\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} & \rightarrow 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \\
\text{Fe(OH)}_3(\text{s}) & \rightarrow \text{FeOOH} + \text{H}_2\text{O} \\
2\text{FeOOH} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}
\end{align*}
\]

Factors such as pH, O$_2$ content, morphology and specific surface of pyrite, as well as hydrological conditions, determine the rate of oxidation (Moses et al. 1987; Nicholson et al. 1990; Evangelou and Zhang 1995), and the final product is dependent on the magnitude of the rate of oxidation. Goethite is the early product (in the reaction 6; Figs. 6k and 6l), and the build-up of goethite around the edge of a particle will decrease rate of pyrite oxidation because of the limitation of oxygen.
diffusion through the armoring effect (Nicholson et al. 1990; Heidari et al. 2017; Mahoney et al. 2019). However, it is the metastable step under arid climate conditions, and goethite can be transformed to hematite by dehydration reaction (in the reaction 7; Fig. 6j; e.g., Walker 1967), thus giving the sandstone reddish color. Therefore, the large-scale distribution of hematite in the altered sandstone with shallow burial (< 800 m) indicates the semi-arid to arid climate, which may also facilitate the dissolution of U (Hobday and Galloway 1999; Bonnetti et al. 2020). Uranium trapped by Fe-Ti oxides, CD and clay minerals together with the primary U originating from intermediate-acid magmatic rocks (U-rich granites; e.g., Zhang et al. 2016) of the Yinshan orogenic belt lying to the north of the basin provide significant sources for the U mineralization in the Dongsheng deposit (Jiao et al. 2006, 2015), as the regional U geochemical background in barren grey sandstones (U_{\text{mean}} = 12.05 ppm) is much higher than the average in the upper continental crust (U_{\text{mean}} = 2.8 ppm; Cuney 2010). Additionally, in outcrops, the pyrite in reduced sandstones was oxidized to goethite, leading to a wide distribution of yellow sandstones due to the relatively weak oxidizing capability of modern weathering (lower S_{\text{total}}/S^{2-} ratio but higher U, TOC and pyrite contents in yellow sandstones than those in red sandstones; Fig. 3; Tables S3 and S6). Meanwhile, the U-bearing minerals in mineralized grey sandstones were oxidized, and the dissolved U flowed down the sandstones with the groundwater, and was re-adsorbed on organic materials (e.g., the CD in the Zhiluo Formation or the coal seams in the Yan’an Formation) nearby (Figs. 1c-1e; Zhang et al. 2019a).

The reduction (Fe^{3+}-bearing to Fe^{2+}-bearing minerals) mainly involves the formation of
authigenic chlorite from hematite. According to pollen analyses, the Hetao graben along the north margin of the basin was formed at least since Late Paleocene (Fu et al. 1994), thus cutting off the sources of U and leading to the termination of large-scale U mineralization (Zheng et al. 2006; Miao et al. 2010; Li et al. 2016). Subsequently, the decrease of oxygenated groundwater led to large amounts of ascending hydrocarbons from the Paleozoic and the early Mesozoic strata, which created a reducing environment (Zhao et al. 1996). Infiltration of hydrocarbons in red sandstones resulted in the reduction of hematite into chlorite (e.g., Zhang et al. 2019), which was evidenced by red calcareous nodules within green sandstones (Figs. 1b-1d and 2b), the similar contents of U and pyrite between red and green sandstones (Tables S3 and S6), and the hematite surrounded by chlorite (Fig. 6f).

**Genesis of the Dongsheng uranium deposit**

Different from the well-established model of roll front-type U deposits (Granger and Warren 1969; Warren 1971, 1972; Reynolds and Goldhaber 1983; Cuney 2009; Bonnetti et al. 2015; Hough et al. 2019), tabular orebodies occur at a regional density-stabilized oxidation-reduction interface (Northrop et al. 1990; Sanford 1990, 1992, 1994; Hansley and Spirakis 1992; Turner et al. 1993; Abzalov 2012). In this occurrence, oxidizing fluids were derived from oxygenated U-bearing meteoric water, whereas reducing fluids were closely associated with organic matter composed of inherent organic materials (such as plant fragments in the Cottonwood Wash U-V tabular deposits, USA; Meunier et al. 1987) in sandstones, and extrinsic humic acid-bearing pore waters (the Grants U region, USA; Turner et al. 1993) from adjacent strata. In the Dongsheng
deposition, due to abundant hydrocarbons in the oil-, gas- or coal-bearing strata underlying the Zhiluo Formation and the inherent CD in the grey sandstone (Jiao et al. 2015; Zhang et al. 2019a), the numerical modeling of fluid flow reported by Xue et al. (2010) indicated that the mixing of descending meteoric fluids and ascending hydrocarbons are responsible for U mineralization. Additionally, the combination of a stable tectonic period followed by regional uplift and an alternating climate from humid to arid is most favorable for ore deposition (Harshman and Adams 1980; Jiao et al. 2015; Bonnetti et al. 2020).

Based on the development of the Ordos Basin and its sedimentary sequences, the sulfur involved in the formation of ore-stage pyrite in the Zhiluo Formation hosting the Dongsheng deposit may be derived from: (1) dissolved sulfate ions from Ordovician marine evaporites, (2) H$_2$S/HS$^{-}$ in extrinsic hydrocarbons, or (3) oxidation of pre-ore pyrite, whose sulfur mainly results from the weathering of volcanic and metamorphic rocks in source area (e.g., Jiao et al. 2015). Because the sandstones of the Zhiluo Formation overlie the Ordovician evaporites by > 2000 m (Li et al. 1984; Yang et al. 2004), there is a sufficient distance for the upward-migrating fluids containing dissolved SO$_4^{2-}$ could be completely consumed by microbial reduction or purely chemical processes in the oil- and coal-bearing late Paleozoic to early Mesozoic sediments. Jiao et al. (2018b) has reported that in outcrops, the majority of pyrite occurs within approximately 4 m of the top of coal seams of the Yan’an Formation, and the farther away from the coal seam, the smaller size of and the less numerous of pyrite grains become in sandstones. This suggests that the formation and distribution of this pyrite is intimately related to H$_2$S escaped from coal seams (Jiao et al. 2018b), and the H$_2$S
seems to be completely fixed within 4 m. However, the orebodies are generally more than 20 m away from the boundary between the Zhiluo and the Yan’an Formation (Fig. 2; Peng et al. 2019). Therefore, it is impossible to have enough H$_2$S/HS$^-$ in extrinsic hydrocarbons to produce ore-stage pyrite, which can also be supported by very little pyrite in green sandstones (Table S6). Therefore, the oxidation of pre-ore pyrite becomes a dominant sulfur source for ore-stage pyrite.

Despite the hydrothermal conditions inferred from fluid inclusions in calcite cements (Xiao et al. 2004; Cao et al. 2016; Akhtar et al. 2017), vitrinite reflectance ($R_o < 0.47\%$) of CD in mineralized grey sandstones suggests mineralization took place at temperatures below 65 °C (Zhang et al. 2019b). The lower $\delta^{34}$S of ore-stage euhedral and cement pyrite ($\delta^{34}$S = -56.9 to -34.3‰) than those of ore-stage framboidal pyrite ($\delta^{34}$S = -31.2 to -3.8‰), together with their paragenetic relationship (Fig. S7) indicate that the different pyrite textural generations may form through distinct mechanisms, rather than a biogeochemical cycle (e.g., Bonnetti et al. 2020). We propose that ore-stage framboidos were produced through bacterial sulfate reduction (BSR), and the following formation of ore-stage euhedral and cement pyrite was via abiogenic Ostwald ripening (Fig. 10).

Sulfate ions (SO$_4^{2-}$) derived from pyrite oxidation were reduced to H$_2$S/HS$^-$ by BSR and formed ore-stage framboidal pyrite (Fig. 10; Machel 2001), which is also supported by the positive correlation between S$^2-$ and TOC in grey sandstones (Reynolds et al. 1982; Fig. 3b). In this process, the bacteria confirmed to be in existence in the Dongsheng deposit prefer the lighter $^{32}$S isotope (Bruchert 2004; Seal 2006; Jiang et al. 2012; Gregory and Kohn 2020), thus meaning that the...
biogenic pyrite will have a lower $\delta^{34}\text{S}$ value than subsequent generations. In a closed system for sulfur, the Rayleigh fractionation may be exhibited, leading to a fraction of frambooidal pyrite produced $\delta^{34}\text{S}$ values higher than pre-ore pyrite (Fig. 8), as predicted by Hough et al. (2019).

Additionally, hydrogen ions produced by organic matter degradation during BSR can be removed by destruction of feldspars and carbonate (e.g., Bonetti et al. 2015), which has contributed to the maintained pH at relatively high values (Fig. 3c). The dissolution of feldspars explains the abundance of kaolinite in the mineralized zone and will supply a silica source for the formation of coffinite (Langmuir 1978).

There are also sulfite and thiosulfate ions generated by pyrite oxidation in neutral to basic solutions (Granger and Warren 1969), and the unstable sulfur species will spontaneously undergo decomposition by disproportionation resulting in $^{34}\text{S}$-depleted HS$^-$ and $^{34}\text{S}$-enriched sulfate (Fig. S8; Granger and Warren 1969; Hough et al. 2019). Pyrite framboi is the metastable phase, and existing surfaces of pyrite have been identified to be conducive to precipitation of pyrite of later stages (Sawlowicz 1993). The $^{34}\text{S}$-depleted HS$^-$ produced from dissolved frambooidal crystals was utilized to generate euhedral and cement pyrite (Fig. 10). This process could be revealed through observations in which frambooidal pyrite was being transformed to euhedral or cement pyrite via Ostwald ripening (Fig. S7; e.g., Morse and Casey 1988; Steefel and Cappellen 1990). Because the $^{34}\text{S}$-enriched sulfate is nonreactive in abiogenic process and removed by groundwater, the pyrite formed through Ostwald ripening will always have lower $\delta^{34}\text{S}$ values than pre-existing or earlier-formed pyrite (Fig. 10; Brunner and Bernasconi 2005), which is evidenced by the very low isotopic
values of euhedral and cement pyrite ranging from -56.9 to -34.3‰, lower than any values of frambooidal pyrite. The sulfur isotopes of abiogenically-derived pyrite are dependent on Eh/pH conditions established by the presence of barite and clausthalite coupled with alternating precipitation between pyrite and ferroselite (Figs. S9 and S10; Ohmoto 1972). The process of producing euhedral grains of pyrite with very low $\delta^{34}$S values via Ostwald ripening in the Dongsheng deposit is in contrast to sulfur recycling processes suggested by Hough et al. (2019) for the Wyoming roll front U deposits.

**Implications**

In sandstone-type U deposits, the mobilization, migration and fixation of U are driven by multiple redox events in low-temperature conditions, which can be directly and effectively documented in textures, paragenetic sequence and chemical compositions of various Fe-bearing minerals. Several alteration processes among Fe-bearing minerals not only give sandstones distinct colors (e.g., red, green and yellow), considered as a criterion for ore prospecting, but provide a minor U source for mineralization (e.g., Fe-Ti oxides, Bonnetti et al. 2015), and can be used to effectively assess the sulfur source of pyrite closely associated with U-bearing minerals. Additionally, textural and sulfur isotopic data provide new insights into the genetic mechanism of ore-stage pyrite in the Dongsheng deposit. Both biogenic and abiogenic mechanisms were involved in the generation of ore-stage pyrite. Namely, framboidal pyrite was produced by BSR, using the sulfur derived from oxidation of pre-ore pyrite, whereas Ostwald ripening was responsible for the formation of euhedral and cement pyrite from framboids. Although the redox
mechanism of the Dongsheng deposit is slightly different from that of deposits in Lake Eyre Basin, Australia (BSR overprinted by hydrothermal fluids, Ingham et al. 2014), deposits in Wyoming, USA (pyrite recycling, Hough et al. 2019) and deposit in Erlian Basin, China (biogenic processes, Bonnetti et al. 2020), which may result from different geologic contexts, the role of bacterial metabolic processes was proposed for all these sandstone-type U deposits, and a biogenic mechanism was considered to be the common and/or initial stage of U mineralization. The alteration processes related to Fe and U of the Dongsheng deposit during the mineralization period are also similar to those of other sandstone-type U deposits (e.g., Warren 1971; Rong et al. 2016), except for the superimposed effects of post-ore hydrocarbon-rich fluids (Miao et al. 2010; Peng et al. 2019) and surface weathering (Jiao et al. 2018b). This study also demonstrates that the careful assessment of U in the context of other redox sensitive elements like Fe and S can provide a more complete picture of the formation of U ore deposits, and the transformation model of Fe-bearing minerals proposed for the Dongsheng deposit may be applied to other mineral resources controlled by redox events.

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References cited


Bonnetti, C., Zhou, L.L., Riegler, T., Brugger, J., and Fairclough, M. (2020) Large S isotope and
trace element fractionations in pyrite of uranium roll front systems result from internally-driven biogeochemical cycle. Geochimica et Cosmochimica Acta, 282, 113-132.


sulfide in the origin of the Ray Point uranium district, south Texas. Economic Geology, 78, 1043-1063.


Hill, 252 p.


Figure captions:

Figure 1. (a) Tectonic units of the Ordos Basin showing the location of the Dongsheng U deposit (modified after Deng et al. 2005; Wang et al. 2011); (b) A cross section showing the spatial
distribution between different colored sandstone units and orebodies in the lower member of the Zhiluo Formation; (c) The U-rich sandstones of the Zhiluo Formation in outcrop; (d) A map of the different colored sandstone units in the Zhiluo Formation in outcrop; (e) The spatial distribution of U contents in the sandstone of the Zhiluo Formation in outcrop.

**Figure 2.** Drill holes cross section showing the geochemical zoning in the lower member of the Zhiluo Formation. (A) Oxidized zone: a. red sandstone; b. residual red color in green sandstone; c. green sandstone; (B) Mineralized zone: d. pyrite and carbonaceous debris in mineralized grey sandstone; e. mineralized grey sandstone; (C) Reduced zone: f. mud gravel and carbonaceous debris in barren grey sandstone; g. carbonaceous debris in barren grey sandstone; h. barren grey sandstone. Abbreviations: CD = carbonaceous debris, MG = mud gravel, Py = pyrite.

**Figure 3.** \( \text{Fe}^{3+}/\text{Fe}^{2+} \) vs. \( S_{\text{total}}/S^{2-} \) (a), TOC vs. \( S^{2-} \) (b) and \( \Delta\text{Eh} \) vs. pH (c) diagrams for different colored sandstones.

**Figure 4.** Photographs showing occurrences of Fe-bearing minerals. (a) Limonite occurring as rims around pyrite grains in grey sandstone due to being exposed to air; (b) Hematite and limonite in red sandstone; (c) Disseminated hematite in red sandstone; (d) Pyrite grains were oxidized to limonite in yellow sandstone; (e) Euhedral hematite grains in red sandstone. Abbreviations: CD = carbonaceous debris, Hem = hematite, Lm = limonite, Py = pyrite.

**Figure 5.** Photomicrographs (a, c, i, transmitted light; g, reflected light), back-scattered electron (b, d-f, j-l) and secondary electron (h) images showing occurrences of Fe-bearing minerals. (a) Hematite filling pores, sample RD-2; (b) Hematite grain; (c) Goethite coating K-feldspar, sample
YW-1; (d) Goethite grains; (e) Framboidal pyrite distributed around the carbonaceous debris; (f) Euhedral pyrite; (g) Pyrite cement, sample DSC-08; (h-i) Chlorite coating the clastic particles; (j) Detrital Fe-Ti oxide grains in grey sandstone; (k) Altered Fe-Ti oxide; (l) Detrital biotite in grey sandstone, sample DSC-20. Abbreviations: Bt = biotite, Cal = calcite, CD = carbonaceous debris, Chl = chlorite, Gth = goethite, Hem = hematite, Kfs = K-feldspar, Kln = kaolinite, Py = pyrite, Qz = quartz.

Figure 6. Back-scattered electron images (a-c, f-j, l) and photomicrographs (d-e, transmitted light; k, reflected light) showing paragenetic relationships of different Fe-bearing minerals. (a) Euhedral pyrite along cleavage planes of biotite in grey sandstone; (b) Hematite along cleavage planes of biotite in red sandstone; (c-d) Goethite along cleavage planes of biotite in yellow sandstone; (e) Biotite grains partly altered to chlorite in green sandstone, sample GN-1; (f) Biotite partly altered to chlorite filled with hematite and pyrite; (g) Pyrite distributed in the matrix of chlorite; (h) Pyrite filling in microfractures of altered Fe-Ti oxide; (i) Framboidal pyrite distributed near the Fe-Ti oxide; (j) Framboidal hematite in red sandstone; (k-l) Goethite occurring as rims of pyrite cores. Abbreviations: Bt = biotite; Cal = calcite, Chl = chlorite, Gth = goethite, Hem = hematite, Py = pyrite, Qz = quartz.

Figure 7. Paragenetic sequence of Fe-bearing and U-bearing minerals in the Dongsheng deposit.

Figure 8. Sulfur isotopes of different generations of pyrite. Abbreviations: Pyrite (1) = framboideal pyrite, Pyrite (2) = euhedral + cement pyrite.

Figure 9. Back-scattered electron images showing the relationship between U-bearing and Fe-
bearing minerals. (a-c) Coffinite filling in framboidal pyrite; (d) Uraninite distributed around the
euhedral pyrite grains; (e) Coffinite distributed near the euhedral pyrite; (f) Coffinite formed
around the pyrite cement; (g) Coffinite distributed around the pyrite cement replacing Fe-Ti oxide;
(h) Coffinite precipitates near the Fe-Ti oxide; (i) Pyrite replaced by coffinite along cleavage
planes in biotite. Abbreviations: Bt = biotite, Cal = calcite, CD = carbonaceous debris, Py = pyrite,
Qz = quartz, Urn = uraninite.

Figure 10. Genetic model for different generations of ore-stage pyrite in the Dongsheng U deposit.
Abbreviations: BSR = bacterial sulfate reduction, CD = carbonaceous debris, CP = clastic particles,
C-Py = cement pyrite, E-Py = euhedral pyrite, F-Py = framboidal pyrite, SRB = sulfate-reducing
bacteria.
Figure 1
Figure 7

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- Abundant
- Minor
- Local

1. Framboidal pyrite
2. Euhedral + Cement pyrite
Figure 10

Hydrologic gradient

SO\textsuperscript{2-} disproportionation

\[ \text{F-P} \quad \text{Ostwald ripening} \]

\[ \text{F-Py} \]

\[ \delta^{34}\text{S: } -19.1 \text{ to } -8.0\% \]

\[ \text{E-Py} \quad \text{C-Py} \quad \text{CP} \]

\[ \delta^{34}\text{S: } +7.9 \text{ to } +20.3\% \]

Pre-ore stage

Ore stage

Ore stage

\[ \text{BSR} \]

\[ \delta^{34}\text{S: } -31.2 \text{ to } -3.8\% \]

\[ \delta^{34}\text{S: } -56.9 \text{ to } -34.3\% \]