Relationship between the hydrogeochemical environment and sandstone-type uranium mineralization in the Ili basin, China

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A R T I C L E I N F O
Article history:
Received 8 January 2010
Accepted 22 November 2010
Available online 27 November 2010
Editorial handling by R. Fuge

A B S T R A C T
This paper describes the occurrence and distribution of U within groundwater of the Ili basin in Xinjiang, China. Dissolved major ions, dissolved gases, pH, Eh and salinity in groundwater were employed to distinguish different hydrogeochemical environments and associated processes affecting U transport within the aquifer. The results show that dissolution and deposition of U by groundwater are closely related to reactions with organic C and minerals such as sulfides, carbonates and silicates along groundwater flow paths. Different chemical reactions predominate and account for changes in the occurrence of U in the rock and water of the oxidized zone, the redox transition zone, and the reduced zone. Knowledge of these associations between U and hydrogeochemical environments could enhance the understanding of relationships of groundwater circulation and U mineralization and could have implications for prospecting for sandstone-type U deposits.

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1. Introduction

Sandstone-type U deposits constitute about 18% of world U resources and are one of the main U mineralization types in the USA, Australia, Niger, South Africa, and central Asia (IAEA, 1996; Hobday and Galloway, 1999; World Nuclear Association, 2009). The U ore in these deposits accumulated within medium to coarse-grained sandstone beds in localized reduced environments, typically in curved zones known as roll-fronts. The convex orientation of roll-fronts points in the direction of regional groundwater flow, implying that groundwater interactions with aquifer minerals played an important role in the formation of the deposits (Rubin, 1970; Goldhaber and Reynolds, 1979; Spirakis, 1996; McKay and Miezitis, 2001; Klauck, 2009).

In recent decades, extensive studies have been conducted regarding the genesis of sedimentary U deposits, the role of groundwater flow, and the relationships of hydrogeochemical processes to U mineralization (Miesch et al., 1960; Goldhaber and Reynolds, 1977; Langmuir, 1983; Hobday and Galloway, 1999; Min et al., 2005; Solodov et al., 2006). These studies have indicated that primary U ore minerals in sandstone-type U deposits are uraninite (UO₂) and pitchblende (U₂O₃; nominally U₃O₈), which are stable under reducing, acidic conditions. However, these minerals can be oxidized and dissolved in neutral-weakly alkaline HCO₃ water. As oxidation progresses, the stoichiometric ratio of O to U in the ore minerals increases from 2 to 3 according to the general formula (Uₓ⁺ₓ−ₓ , Uₖ⁺ₓ−ₓ ) O₂ₓ−ₓ , where x = 0–1. In the presence of oxidizing groundwater, pitchblende gradually becomes hydrated to hydropriephthlite (Uₓ⁺ₓ−ₓ , Uₖ⁺ₓ−ₓ ) O₂ₓ−ₓ nH₂O, which is readily soluble in water. Because U⁴⁺ readily forms aqueous complexes with HCO₃ and CO₂⁻ , the total concentration of dissolved U can be enhanced in the HCO₃⁻ waters by the formation of UO₂(CO₃)₂⁻ and UO₂(CO₃)₃⁻.

Sandstone-type U mineralization in the Ili basin in Xinjiang, China, has been investigated recently in an attempt to understand the U mineralization mechanism and metallocgenic models. This paper describes the regional hydrogeochemical environments and their relationships to U dissolution, transport and accumulation in the basin. Regional hydrogeochemical data, including major ions, dissolved gases, pH, Eh and salinity of groundwater, were systematically collected to identify the hydrogeochemical environments and water–rock interactions associated with U transport and deposition. Insights from this study may be helpful to predict the mobilization and deposition of U and to improve hydrogeochemical exploration approaches for sandstone-type U deposits.

2. Study area

2.1. Geology

The Ili basin covers 40,000 km² and is located in northwestern Xinjiang, China (Fig. 1). It is a meso-Cenozoic intermontane basin that developed on the Precambrian shield. The basement is
composed of Precambrian crystalline rocks and overlying Paleozoic folded strata. The latter is mainly composed of Carboniferous–Permian volcanic rock, sedimentary rock and Hercynian granite. The U content of the Hercynian granite is relatively high with an average value of 7.7 mg/kg, and it is one of the main U sources in the basin. The overlying strata are variegated clastic rock of the middle-upper Triassic Xiaoquangou group (T2 xq), grey to black colored coal-bearing clastic rock of the lower-middle Jurassic Shuixigou group (J1 _sh) and red colored clastic rock of Cretaceous–Tertiary ages (Wang et al., 2003).

Tectonically, the basin is situated in the west section of Tianshan structural belt. The sublatitudinal fault at the southern margin of the basin and the NW-trending fault at the northern margin control not only the borders of the basin in the south and north, respectively, but also the formation and evolution of the basin. Structurally, the basin is divided into a fold zone in the north, a depression zone in the center, and a slope zone in the south. The Mesozoic–Cenozoic strata in the southern slope zone occur as a monoclone with a gentle dipping angle which is a favorable structural unit for the formation of the sandstone-type U deposit.

In the study area, the U ores are downgradient from the source rocks (southern mountainous area). The main ores, Ores A–C as well as several other prospects are distributed zonally and trend nearly west–east in the area (Fig. 1). Uranium ores and mineralization are mainly produced in the Lower–Middle Jurassic Shuixigou group. The Shuixigou strata, which formed as an alluvial fan–fan delta system, consist of shale–sand–shale–coal sequences that can be divided into the Badaowan, Sangonghe and Xishanyao formations, from bottom to top. Based on the change of sedimentary rhythm, previous researchers have divided the Shuixigou group strata into eight sedimentary cycles (Fig. 2). Sandstone-type U ore bodies controlled by the interlayer oxidized zone have been found in cycles I–IV (the Badaowan formation), cycle V (the lower part of the Xishanyao formation) and cycle VII (the upper part of the Xishanyao formation). Shuixigou strata range in thickness from 0 to 510 m (average 300 m) and crop out along river valleys in the study area. The lithology is sandy conglomerate, pebble sandstone, sandstone, siltstone, shale and coal of various thicknesses being grey, grey green and grey black in color; it universally contains charcoal, carbonized plant debris, muscovite and pyrite. The muscovite and charcoal contents increase with decreased particle size. Coal seams are the most obvious strata of Shuixigou group. There are 12 coal seams identified as M1–M12 from bottom to top. Among them M5, M8 and M10 are the most extensive and can be regarded as regional marker beds. Eight sedimentary cycles are divided by the coal seam marker beds (Liu, 2004).

2.2. Hydrogeology

The groundwater in the study area is mainly recharged by meteoric precipitation and surface water. It can be divided into Quaternary phreatic (unconfined) water, Jurassic interlayer porous confined water, and fractured bedrock fissure water in the mountainous area. The Jurassic sandstone and conglomerate aquifer formations are the main hosts for U ore deposits; their aquifuge is composed of shale, while the aquifer is composed of sandstone and conglomerate. Groundwater recharge takes place in the southwestern mountainous area, where the average weathered depth is 2–6 m and well-developed fissures in the granite enhance rainfall infiltration (Xia Yuliang, Liu Hanbing, Lin Jingrong, Fan Guang, 2001, unpublished data). Generally groundwater flows from the south to the north in the basin. Along a flow path from the southern high mountain areas to the northern low mountain-hill regions, the chemical compositions of groundwater can be characterized as three hydrochemical types: (1) HCO3−Ca, (2) HCO3−Ca Na or HCO3−SO4−Na Ca, and (3) SO4−HCO3−Ca Na or SO4−Cl−Na Ca (Wang, 1993). The first type of groundwater occurs in the mountainous areas, the second type occurs in the transition zone between the mountainous area and plain, and the third type occurs in the reduced zone at depth (Fig. 3). In the southern mountain area, the groundwater is low salinity HCO3-type, which contributes to the leaching of U from granitic bedrock. The pH of this groundwater ranges from 7.8 to 8.5.

2.3. The formation of the interlayer oxidized zone

Sandstone-type U deposits are present in the so-called interlayer oxidized zone that evolved over millions of years by infiltration of O2-containing water through confined sandstone aquifers (Liu and Yan, 1991). During the late Jurassic, an extensive oxidized zone started to form within the unconfined surficial aquifer together with a small interlayer oxidized zone within the confined sandstone aquifer (Fig. 2). During the Cretaceous, the interlayer oxidized zone expanded extensively. During the Tertiary, the interlayer oxidized zone continued to advance and grow locally. At present, the oxidation continues mainly within part of the interlayer oxidized zone that had formed during the Tertiary.

The width of the interlayer oxidized zone is closely related to the size of recharge window (Tan, 2002) (Fig. 3). On the whole, the areas with a wider recharge window receive more precipitation and their interlayer oxidized zones grow more widely. The widest window coincided with the location of Ore B, where oxidation in several layers in the Shuixigou group has extended furthest into
the basin. In the region west of the location of Ore A, the width of the interlayer oxidized zone is relatively narrow because this area had the smallest recharge window.

3. Materials and methods

A total of 130 sets of groundwater samples were collected from 42 boreholes with depths of 60–230 m in the area. Most boreholes penetrated the Shuixigou strata and, therefore, passed through the different interlayer oxidized zones (cycles I–VII). All groundwater samples were collected by use of a submersible peristaltic pump. In some boreholes, groundwater samples were taken at different depths by using double-packer techniques. Measurement of water temperature, pH, Eh, dissolved O2 and the depth to water were completed in situ with submersible electrodes. Samples for conventional chemical and U analyses were filtered through a 0.45-μm
filter, and preserved with HNO₃. The samples were kept in sealed polyethylene bottles on ice until analyzed in the laboratory.

Chemical analysis of groundwater was performed according to the following methods: Ca²⁺ and Mg²⁺ by atomic absorption spectrophotometry, K⁺ and Na⁺ by atomic emission spectrophotometry, Cl⁻/C0₄ and SO₂⁻/C0₄ by ion chromatography, Fe²⁺, Fe³⁺ and dissolved U in water by spectrophotometry (with the wavelength precision ±1 nm). All chemical analyses were conducted by Xinjiang Center of Physics–Chemistry, China.

Data were compiled and statistically processed to explore (1) the relationship of U in groundwater to the hydrogeochemical parameters and (2) the associated distributions of U mineralization and U transport in different hydrogeochemical environments along groundwater flow paths.

4. Results and discussion

4.1. The hydrogeochemical zoning of interlayer oxidized zone

Evolving hydrogeochemical conditions are important for the localized development of sandstone-type U mineralization. The essence of sandstone-type U mineralization is a geochemical process whereby U(IV) precipitates from solution within porous aquifer rock. Precipitation results because of acidification and reduction of HCO₃-type, O₂-containing, and U-containing water within a redox transition zone that acts as a geochemical barrier to U(VI) migration.

The integrated hydrogeochemical parameters and the corresponding conceptual model for U transport and deposition (Table 1 and Fig. 4) are identified with a typical distribution of hydrogeochemical types in Shuixigou group cycle V (Fig. 5). As indicated by Table 1, Figs. 4 and 5, from the recharge area to the inside basin, hydrochemical types of groundwater in Shuixigou group aquifer evolve from low salinity HCO₃-type to HCO₃/Cl type; salinity increases gradually; dissolved O₂ and Eh value decrease gradually; pH tends to change from weakly alkaline to neutral and to weakly acidic; and H₂S has a tendency to increase. Thus, hydrochemical zonation has occurred along the groundwater flow path. Based on the change of these hydrogeochemical parameters, hydrogeochemical environment of aquifers in the Shuixigou group has been divided into three zones: (1) oxidized zone (strong oxidized zone, neutral weak oxidized zone), (2) redox transition zone, and (3) reduced zone. The hydrogeochemical characteristics of each zone are discussed below.

4.2. The hydrogeochemical characteristics of the oxidized zone

The hydrogeochemical characteristics of the oxidized zone of aquifer-forming units in Shuixigou group can be described as neutral-weakly alkaline HCO₃–Ca-type water with dissolved O₂ ranging from 3.02 to 15.6 mg/L, Eh ranging from 253 to 804 mv, and pH ranging from 7.06 to 8.6. These characteristics are very similar to the hydrogeochemical characteristics of subsurface and surface water in the south mountainous area (HCO₃–Ca/Na-type, dissolved O₂ between 7.2 and 12.6 mg/L; pH between 7.1 and 8.8; Eh above 400 mv), suggesting that groundwater in the oxidized zone inherited its O₂ and major geochemical characteristics from the upgradient source.

Fig. 4. Hydrogeochemical zoning in Shuixigou group aquifer rock formations.
of complexation with abundant HCO$_3^-$ and OH$^-$. Complex OH$^-$ drive pH from alkaline to neutral values. Because of complexation with abundant HCO$_3^-$ and CO$_3^{2-}$, the predominant forms of dissolved U are UO$_2$(CO$_3$)$_{4}^{2-}$ and UO$_2$(CO$_3$)$_{5}^{2-}$.

Additionally, the Shuixigou group hosts a series of coal-bearing deposits in which the native sandstone and shale are rich in pyrite. During the early stages of formation of the oxidized zone, oxidation of pyrite could release H$_2$SO$_4$. Thus, along the margins of the oxidized zone in these units, the groundwater is acidic with SO$_4^{2-}$ as a major anion. Although the precipitation of U on the surface of the pyrite at mildly acidic pH has been reported to inhibit pyrite oxidation (Riba et al., 2008), eventually, after many cycles of recharge, the pyrite in aquifers ultimately becomes completely oxidized and replaced by Fe oxyhydroxides. Thereafter, the groundwater within the acidic oxidized zone maintains the oxidized, neutral and weakly alkaline characteristics of the upgradient water.

In the early development of the oxidation zone, pitchblende is more easily dissolved and oxidized than sulfide. Shi (1990) reported that when 92–100% of the pitchblende has been hydrated, only 22–23% of the pyrite has been oxidized. In the late development of the oxidation zone, the sulfide has been oxidized; the amount of SO$_4^{2-}$ decreases; acid water is neutralized by carbonates and aluminosilicate minerals; pH rebounds; and the oxidized zone water becomes weakly acidic to weakly alkaline HCO$_3$-water.

4.2.1. Strongly oxidized zone

The strongly oxidized zone develops in the core of the oxidized groundwater flow path and is characterized by a faded yellow, grey-yellow color of weathered rocks. Typomorphic element-Fe has been oxidized to Fe(III) forming oxyhydroxides. Reducing substances like charcoal and sulfide have been inhibited; meanwhile, U has been oxidized and leached from the rock. The groundwater is neutral-weakly alkaline and O$_2$-containing HCO$_3$-water. The leached U is mobile and continually carried by groundwater downgradient. The residual Th/U in the rock is relatively high because U is easily leached and Th is not (Sun and Liu, 2004).

4.2.2. Neutral weakly oxidized zone

The neutral to weak oxidized zone is located near the margins of the oxidized zone. The pH is 7.1–8.6. Dissolved O$_2$ is 2.2–5.5 mg/L, Fe(II) is 0.15 mg/L. Eh is 172–429 mv. Water type is HCO$_3$. HCO$_3$-SO$_4$. Uranium content in water is between $0.4 \times 10^{-6}$ and $10.0 \times 10^{-6}$ mg/L; dissolved species are UO$_2$(CO$_3$)$_{4}^{2-}$ and UO$_2$(CO$_3$)$_{5}^{2-}$. The U content of groundwater in this zone is slightly higher than that in the strongly oxidized zone because of gradual concentration of U along groundwater flowpaths under the weaker oxidization conditions. Accordingly, Th/U in rock decreases (Sun and Liu, 2004).

4.3. The hydrogeochemical characteristics of the redox transition zone

In the interlayer oxidized zone, the redox transition zone lies between the oxidized zone and the reduced zone. The width of the redox transition zone is generally from tens to hundreds of meters in Shuixigou aquifer formations in the study area. The U-bearing water from the oxidized zone infiltrates to the redox transition zone in which reducing substance content increases rapidly, thus U(VI) is reduced and uraninite and pitchblende are precipitated (Shi, 1990).

In the redox transition zone of the Shuixigou aquifer formations, the chemical type of the groundwater is HCO$_3$-SO$_4$. Salinity is slightly higher than that in the oxidized zone, ranging from 0.18 to 2.2 g/L. The pH is 6.1–7.5 and turns from weakly alkaline in the oxidized zone to neutral then to weakly acidic. Iron(II)/Fe(III) increases to values between 3 and 5. Dissolved O$_2$ decreases from more than 10 mg/L to values between 0.9 and 5.4 mg/L. Eh decreases to values between −228 and −3 mv. Hydrogen sulfide starts to accumulate with concentrations between 0.01 and 1.36 mg/L. The Th/U in rock in the redox transition zone is far less than that in other zones (Sun and Liu, 2004). The characteristics of this redox transition are shown in Figs. 6 and 7.

Shuixigou aquifer formations are rich in organic matter that can consume most of the O$_2$ in water through microbial decomposition. Remaining dissolved O$_2$ can be consumed by reducing substances (charcoal and pyrite) when the groundwater arrives at the redox transition zone. Sulfate reduction leads to the increase in H$_2$S concentrations. In such O$_2$-depleted and negative Eh conditions, U becomes reduced and can be precipitated as pitchblende or uraninite in accordance with the following reaction.

$$\text{UO}_2(\text{CO}_3)_2^{2-} + \text{H}_2\text{S} \rightarrow \text{UO}_2 + \text{S}^0 + 2\text{HCO}_3^−$$

4.4. The hydrogeochemical characteristics of the reduced zone

The reduced zone is also called the primary zone. After infiltration through the oxidized zone and the redox transition zone, all the dissolved O$_2$ has been consumed. Within the reduced zone, dissolved SO$_4^{2-}$ in the groundwater reacts with organic materials and is reduced to sulfide, generating HCO$_3$ that promotes the precipitation of CaCO$_3$ as indicated by the overall reaction:

$$\text{CH}_4 + \text{SO}_4^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{H}_2\text{S}$$

Rock that is rich in C and pyrite maintains its grey color in the reduced zone. The anoxic groundwater is enriched in dissolved CH$_4$, H$_2$, and H$_2$S, which indicate strongly reduced conditions. The water is neutral-weakly alkaline with a pH of 7.0–8.0. The salinity of groundwater in the reduced zone increases compared with that in the oxidized zone and redox transition zone. The water type is SO$_4$-Cl or SO$_4$-HCl, decreased concentrations of SO$_4^{2-}$ and HCO$_3^-$ are consistent with SO$_4^{2-}$ reduction and methanogenesis. In this zone, the Eh value of groundwater is negative; and it is generally lower than −100 mv. Uranium concentrations are less than $1.0 \times 10^{-6}$ mg/L and are lower than those in groundwater of the oxidized or transition zone environments. Thorium/U values in rock is the highest (Sun and Liu, 2004). Uranium is immobile.
The analysis above indicates that U occurrence and transport in groundwater are the result of water/rock interaction in different hydrogeochemical environments. Soluble and mobile U(VI) species prevail in the most oxidizing environment, whereas insoluble and immobile U(IV) species are predominant in the most reducing environment. Uranium in groundwater tends to precipitate and accumulate in the transitional reducing environment. Discrepancy of hydrogeochemical environments also leads to different mineral components with different colors in each zone in the surrounding rock (Pérez del Villar et al., 2002). Although U(IV) minerals are most abundant, the corresponding aqueous complexes of U(IV) are found in low concentrations due to their low solubility (Garralon et al., 2007).

5. Conclusions

In the study area, U mineralization and transport in the interlayer oxidized zone can be explained in terms of three hydrogeochemical zones: (1) the oxidized zone, (2) the redox transition zone, and (3) the reduced zone. Each has different rock colors and associated hydrogeochemical characteristics represented by major ions, dissolved gases, pH, Eh, salinity, and U content in groundwater. Uranium in groundwater is dissolved and transported as U(VI) in the oxidized zone; it is precipitated and accumulated as U(IV) in the redox transition zone. In the strongly oxidized zone, UO$_2$ in rock begins to oxidize and evolve to hydropitchblende ($U^{2+}$, $U^{4+}$)$_2$O$_2$$\cdot$nH$_2$O that is soluble in water. In the neutral to weak oxidized zone, the main U species are oxidized carbonate complexes ($UO_2(CO_3)^{3-}$) and $UO_2(CO_3)^{2-}$). In the redox transition zone, U is reduced to relatively insoluble U(IV), which precipitates as uraninite or pitchblende. Thus, the hydrogeochemical environment has an important influence on U speciation and behavior in groundwater. As hydrogeochemical zoning is a common phenomenon especially in large scale groundwater systems, the results may have significance for U mineralization studies in other sandstone-type U deposit areas.
Acknowledgements

The authors thank the laboratory of Xinjiang Center of Physics-Chemistry, China for the analysis of water samples. Special thanks to Dr. Chuck Cravotta for his contribution to both technical and language revision. We gratefully acknowledge comments and helpful information from Dr. Mary P. Anderson, Dr. Ron Fuge and three anonymous reviewers.

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