

Article

Uranium Mineralogical and Chemical Features of the Na-Metasomatic Type Uranium Deposit in the Longshoushan Metallogenic Belt, Northwestern China

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Abstract: The Longshoushan Metallogenic Belt (northwestern China) is known for its world-class Jinchuan Ni-Cu sulfide (Pt) deposit and is also an important uranium metallogenic belt. The Jiling uranium deposit in this belt is a typical Na-metasomatic uranium deposit, which rarely occurs in China. Mineralization in the Jiling uranium deposit is hosted in granitoids that have suffered a Na-metasomatic alteration. There are three kinds of uranium minerals, including uraninite, pitchblende, and coffinite in the Jiling uranium deposit. Pitchblende is the predominant uranium mineral. Integrating the mineralogy and geochemistry of uranium minerals, and in situ electron microprobe analyzer (EMPA) U-Th-Pb chemical dating, we aimed to unravel the age and nature of the mineralization, to decipher the characteristics of the hydrothermal alteration and the U mineralization process. Based on the microtextural features and compositional variations, primary uraninite was altered to uraninite A and B, and fresh pitchblende was altered to pitchblende A and B. The best-preserved uraninite crystals displayed a euhedral-shape with high Pb and low SiO₂, CaO, FeO, and Al₂O₃ contents, and was interpreted as primary uraninite. The EMPA U-Th-Pb chemical ages revealed that uraninite may have formed at 435.9 ± 3.3 Ma. High ThO₂ + ΣREE₂O₃ + Y₂O₃ contents illustrated that the best preserved uraninite crystallized at a high temperature. Altered pitchblende A showed a relatively brighter gray color in backscattered electron (BSE) images and with a lower SiO₂ content than B. Three analysis spots of the fresh pitchblende showed low contents of ΣSiO₂ + CaO, indicating no obvious alteration. EMPA U-Th-Pb chemical dating gave a mean chemical age of 361 Ma. The low Th + ΣREE₂O₃ contents indicated that this pitchblende formed at a relatively low temperature. According to the different characteristics of occurrence and chemical composition, the coffinite in the Jiling uranium deposit can be divided into coffinite A and B, respectively. The compositional variation of the fresh and altered uraninite and pitchblende indicated that both uraninite and pitchblende underwent at least two discrete hydrothermal fluid alterations. The U mineralization was divided into two stages; uraninite was formed at a high temperature and possibly from a magmatic-hydrothermal fluid during ore stage I. Then, pitchblende was formed at a low temperature, during ore stage II. According to the petrographic observations and their chemical compositions, coffinite A and B resulted from the alterations of uraninite and pitchblende, respectively.

Keywords: Na-metasomatism; uranium deposit; uranium mineral; U-Th-Pb chemical dating; hydrothermal alteration; Longshoushan Metallogenic Belt

1. Introduction

The classification of uranium deposits has been discussed for more than 60 years. During this period, many different uranium deposit classifications have been proposed according to the structural history, the stratigraphic relationship of host rock to ore emplacement, the host environment, genetics of uranium deposit, etc. (e.g., [1]). According to the new International Atomic Energy Agency (IAEA) classification scheme of uranium deposits, fifteen types of uranium deposit have been listed [2,3]. The metasomatic type uranium deposit is a critical type among all types of uranium deposit. The metasomatic type uranium deposits are characterized by a low average grade, but constitute the fourth largest reasonably assured resources of the world [4]. The metasomatic uranium deposits include Na-metasomatic uranium deposits, K-metasomatic uranium deposits, and skarn uranium deposits. The resources of Na-metasomatic uranium deposits account for about 60% of the total resources in metasomatic uranium deposits [1,4].

Sodium Metasomatite uranium deposits are confined to areas of tectono-magmatic activity affected by intense Na or Na-Ca metasomatism that produces albitized facies including albitite, aegirinite, alkaline amphibole rocks, and calcic-ferruginous facies along deeply rooted fault systems [1]. The most important Na-metasomatic type uranium deposits occur in the Ukraine and Brazil [5–7].

Na-metasomatic uranium deposits are rare in China. The Longshoushan Metallogenic Belt (LMB) is one of the few areas in China in which Na-metasomatic type uranium deposits occur. Two Na-metasomatic type uranium deposits, Xinshuijing (No. 701 uranium deposit) and Jiling (No. 706 uranium deposit) uranium deposits, have been identified in this belt. Previous studies on the Jiling uranium deposit mainly focused on the petrology, ore-forming fluid, and geochemistry, and only vein-filling and disseminated pitchblende has been identified in the Jiling uranium deposit. The studies on the alteration characteristics of the Jiling uranium deposit are mainly based on field work, microscopic observations, and whole rock geochemistry, there is little research on uranium mineralogy and geochemistry [8–14]. The primary uranium mineralization characterization, the successive metallogenic stages, and ore-forming processes are still poorly understood constraints.

As Th, REEs, and yttrium (Y) in the uraninite are known can be used to reflect the mineralizing process and with high confidence as provenance indicators. Previous studies have shown that there is a positive correlation between the crystallization temperature of uraninite and their Th, REEs (especially the HREEs), and Y contents. The uraninite with high contents of Th + REEs + Y is generally at a high crystallization temperature, and show a “flat” REE pattern [15–19].

In this study, we present petrographic descriptions, textural relations, and chemical compositions of uraninite, pitchblende, and coffinite, determined with electron microprobe analyzer (EMPA) analyses, and calculation of the U-Th-Pb chemical ages for the uranium oxides from the Jiling uranium deposit. These data were used to determine the characteristics of the hydrothermal alteration and the nature of uranium mineralization, to constrain the chronology of the uranium minerals and to identify the uranium mineralization process [15–25].

2. Geological Setting

2.1. The Longshoushan Uranium Metallogenic Belt (LMB)

The LMB is located between the southwest of the North China Craton and south of the Alxa block. It is connected with the Northern Qilian orogenic belt to the south and the Chaoshui Basin to the north. The Altyn-Tagh Fault, a huge left slip strike-slip fault, cuts the western part of the LMB, and the Tarim Craton adjacent to the west part of the LMB (Figure 1B) [9,26–30].

The LMB is an important uranium metallogenic belt in northwest China and belongs to the Qilian-Kunlun uraniferous province [31]. The Hongshiquan intrusive-type uranium deposit is located in the western part of the LMB [32,33]. Two typical Na-metasomatic uranium deposits (Jiling and Xinshuijing uranium deposits) occur in the middle part of the LMB [9,34]. The world-famous Jinchuan Ni-Cu sulfide (Pt) deposit is located in the eastern part of this metallogenic belt [35–37].

The Paleoproterozoic Longshoushan Group in this area represents the oldest strata, a highly deformed terrane that suffered from amphibolite-facies metamorphism. The Longshoushan Group is overlain unconformably by the Mesoproterozoic Dunzigou Group, and then by the Neoproterozoic Hanmushan Group (Figure 1C) [10,38]. Only a few Late Paleozoic strata unconformably overlay the Hanmushan Group. Mesozoic and Cenozoic strata are rarely present in this area. The magmatic activity was intense in this metallogenetic belt with intrusion ages ranging from Paleoproterozoic to Caledonian [33,39,40].

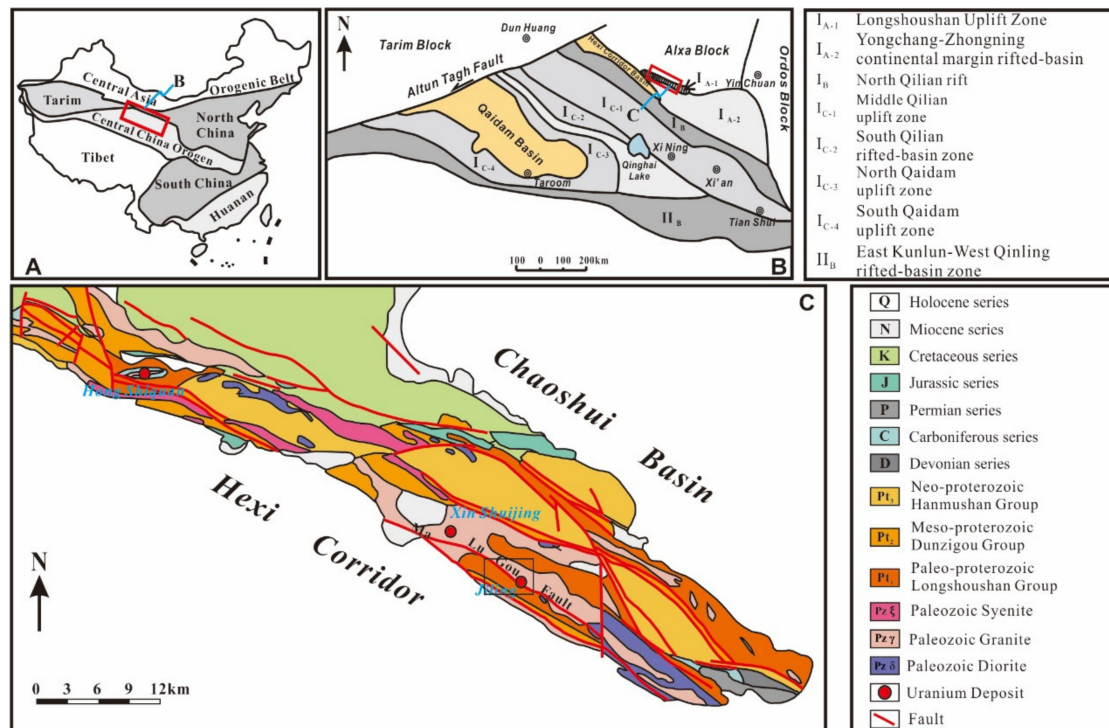


Figure 1. (A) The main geotectonic units of China with the location of the Longshoushan Metallogenetic Belt (LMB). (B) A geological map of northwest China showing the main tectonic units (modified after [41]). (C) A regional geological map of Longshoushan Metallogenetic Belt (LMB), showing the locations of the two sodium metasomatic type deposits (the Jiling and Xinsuijing uranium deposits) and pegmatite uranium deposit (Hongshiquan uranium deposit) (modified after [42]).

2.2. The Jiling Uranium Deposit

The Jiling uranium deposit occurs in the middle part of the LMB and can be classified as a Na-metasomatic uranium deposit [8–10,38]. This deposit is hosted by the Paleozoic Jiling intrusive complex. The NW-trending Jiling complex intrudes into the Proterozoic strata, with a length of 54 km and a width of two to three kilometers, representing an exposed area of 160 km². The Jiling complex is composed of diorite, granite, syenite, and acidic and basic dikes [8,10,14,27,29,30,34,43]. The granitoids in the Jiling complex are mainly composed of medium to coarse-grained gray quartz monzonite and granodiorite (441 ± 14 Ma) [30], medium-coarse grained fleshy red granodiorite and granite (441 ± 15 Ma) [30], fine-grained granite (442 ± 6 Ma) [38], and syenite (427.2 ± 3.6 Ma) [26]. All were dated using the U-Pb isotopic system on zircons by LA-ICP-MS.

The Jiling uranium deposit occurs in the southeastern part of the Jiling intrusive complex, and the ore bodies are typically associated with Na-metasomatic alteration. The NW-trending Malugou Fault zones (F₁₀₁ and F₁₀₂), the main ore-controlling structure, developed to the north of the Paleoproterozoic Longshoushan Group, along nearly EW-trending structures that are the main structures controlling the ore bodies [14,39]. NE-trending and nearly SN-trending post mineralization faults cut both the NW-trending and nearly EW-trending structures (Figure 2A). F₁₀₁ and F₁₀₂ are a pair of parallel structures, with the same occurrence as 220°–230° NW trend and 60°–70° dip angle. The EW-trending

secondary structures and some brittle deformation zones are favorable to uranium mineralization. The F_{105} developed to the south of the Paleoproterozoic Longshoushan Group (Figure 2A), has a 30° – 35° NW trend and 70° – 75° dip angle. The F_{105} is a right strike-slip fault that formed after the mineralization, crosscutting the F_{101} and F_{102} faults and displacing the extension trend of the ore bodies to the northwest (Figure 2B) [14].

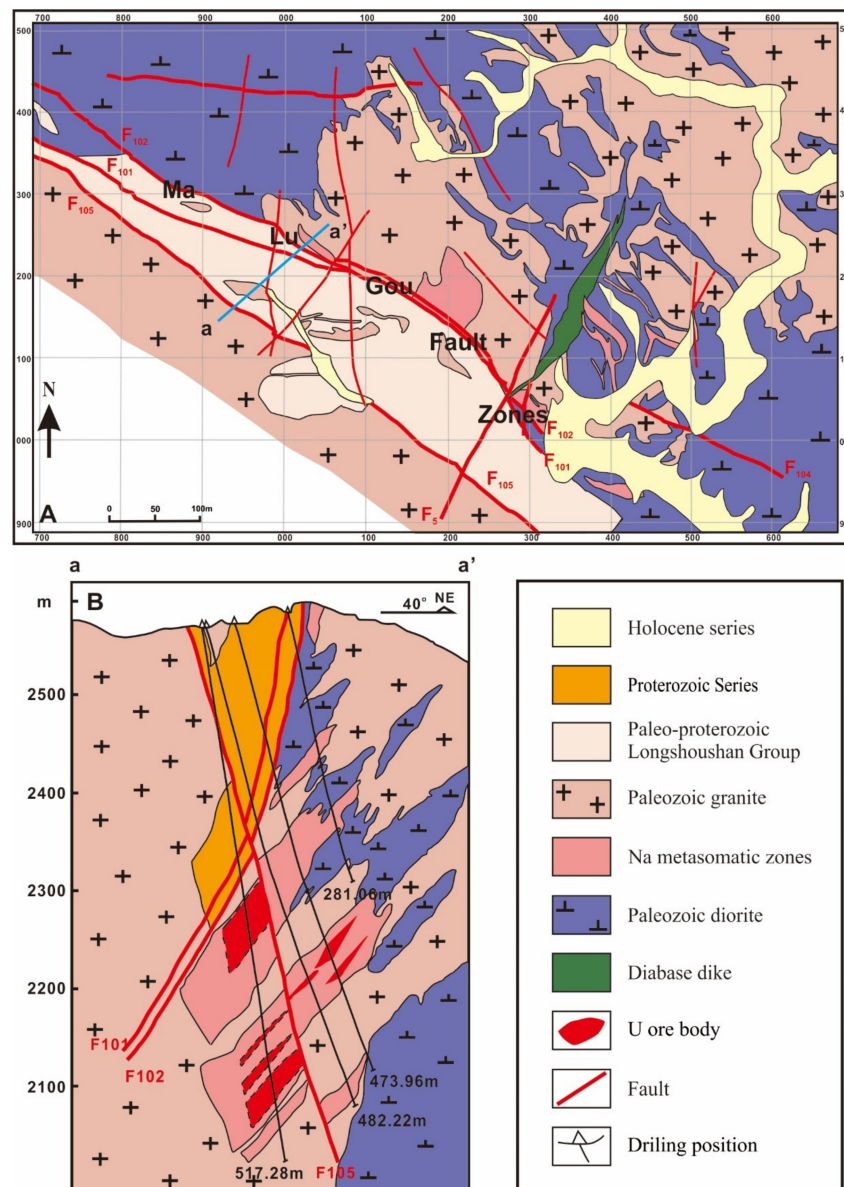


Figure 2. (A) A geological map of the area around the Jiling uranium deposit (modified after [39]). (B) A cross-section of the Jiling uranium deposit (modified after [39]).

In the Jiling uranium deposit, the common type of alteration is represented by albitization developed at the expense of Jiling granites. Na metasomatic zones are generally massive or brecciated rocks strongly controlled by faults. The primary textures of granites are generally preserved but may also be modified during later alterations. The alteration characteristics of the Jiling uranium deposit have been already described [10,14,44]. In this study, we identified three zones (I, II, III) defined by their mineralogical assemblage as developed in Jiling granite (Figure 3). Zone I corresponds to the least altered host granites, part of biotite, feldspars, magnetite, and local allanite were replaced by chlorite and ilmenite. These minerals probably formed later compared to quartz dissolution and albitization,

which have to occur at high temperatures according to the crystallization of Th-REE-rich uraninite as discussed thereafter, with a limited new formation of quartz.

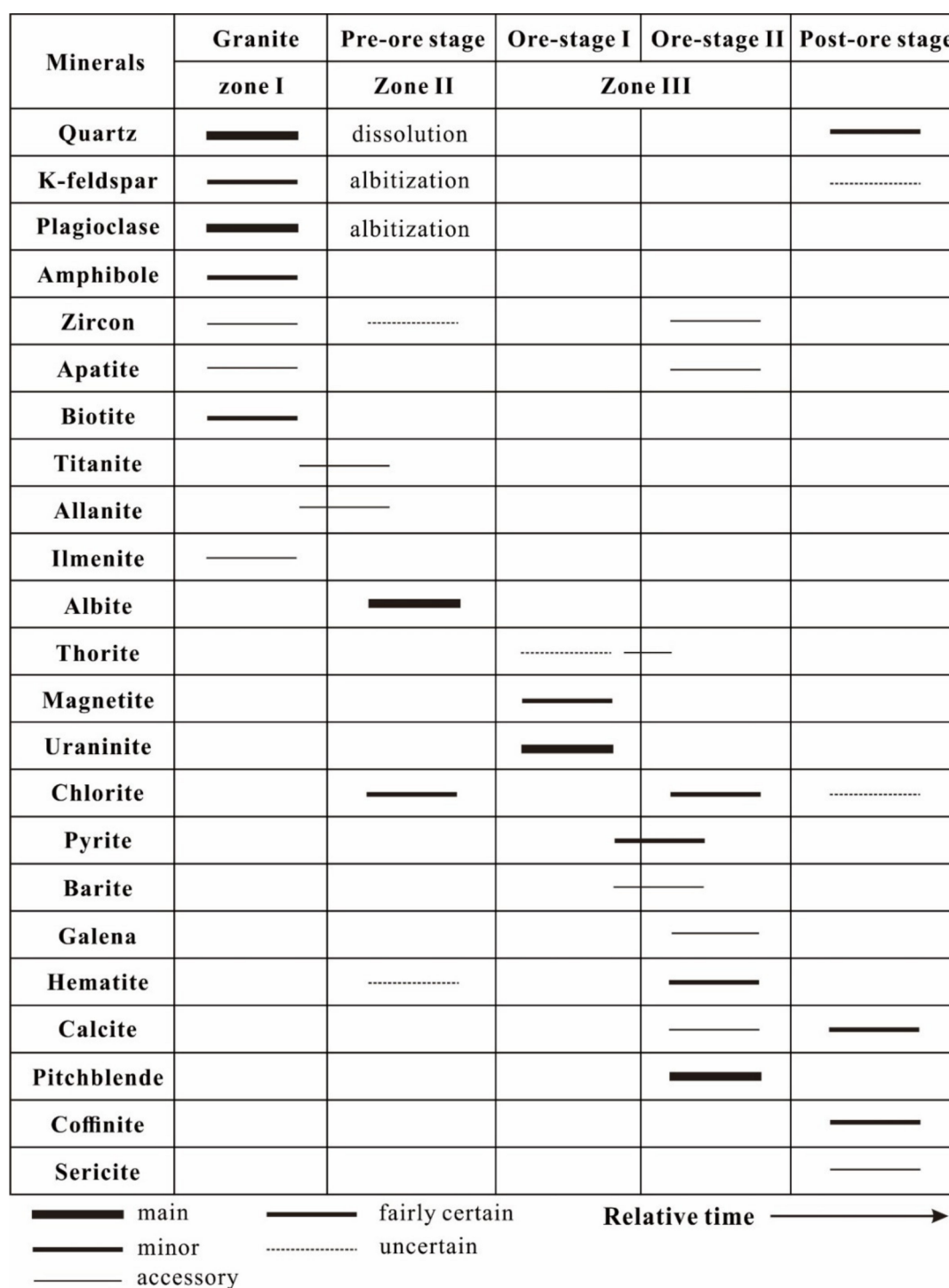


Figure 3. Mineral paragenesis of the Jiling Na metasomatism uranium deposit.

Zone II corresponds to the Na-metasomatic zone, in which quartz is extensively dissolved and the feldspars are replaced by albite leading to the formation of an albitic episyenite. Zone III corresponds to the major uranium mineralized zone, where uraninite crystals are paragenetically associated to magnetite, with a small amount of thorite crystals, in ore stage I at high temperature. Pitchblende crystals are paragenetically associated to pyrite, chlorite, calcite, and galena in ore stage II at lower

temperatures. Coffinite has been identified in this zone, and it occurs as disseminations, veinlets, or crystal aggregates frequently as replacements of uraninite and pitchblende during the post ore stage. The ore bodies are concealed. They have lenticular to irregular-shapes but are almost parallel to the Malugou Fault zones (F_{101} and F_{102}), and they occur in highly fractured and brecciated zones.

3. Analytical Methods

All samples were collected from exploration drill holes performed in the Jiling uranium deposit by the No. 203 Research Institute of Nuclear Industry. The mineralogical study was conducted at the State Key Laboratory of Nuclear Resources and Environment of East China University of Technology (China) using an optical microscope (transmitted and reflected light), a Nova Nano-SEM 450 scanning electron microscope (SEM), and a JEOL JXA 8100 electron microprobe analyzer (EMPA) (Tokyo, Japan). More detailed mappings were obtained using a Nova Nano-SEM 450 scanning electron microscope, backscattered electron (BSE) images were used, to select the targets for EMPA according to variations of grey intensity of uranium minerals [45]. A JEOL JXA 8100 electron microprobe analyzer (EMPA) was used for quantitative analyses.

Major, trace and rare earth elements were obtained by the EMPA and expressed in weight percent oxides. The analytical conditions were 15 KV accelerating voltage, and a 2.0×10^{-8} A beam current with a 2 μm beam diameter for the analysis of uranium minerals. The following standards were used: SiO_2 -garnet, CaO -dolomite, FeO -hematite, Al_2O_3 -biotite, UO_2 , ThO_2 -U-Th-Pb oxide, PbO -galena, Sr -niobate, La_2O_3 -monazite, Ce_2O_3 -monazite, Pr_2O_3 -Pr, Nd_2O_3 -Nd, Sm_2O_3 -Sm, Eu_2O_3 -Eu, Gd_2O_3 -Gd, Tb_2O_3 -Tb, Dy_2O_3 -Dy, Ho_2O_3 -Ho, Er_2O_3 -Er, Tm_2O_3 -Tm, Yb_2O_3 -Yb, Lu_2O_3 -Lu, and Y_2O_3 -Y. Detection limits under the analytical conditions for rare earth elements are presented in Supplementary Materials B.

EMPA U-Th-Pb chemical dating of uraninite was initially proposed by Holmes [46], and has been widely used by various workers over the last decades [18,24,25,47]. This method is based on the assumption that non-radiogenic Pb has not been incorporated in the structure of U-oxides during crystallization, and no Pb loss or reintroduction has occurred after the original crystallization [45].

Based on the supposition that the proportion of radiogenic lead derives only from the thorium and uranium decay within the mineral, the chemical ages can be calculated from the EMP analyses using the following radioactive decay equation [48]:

$$\text{Pb} = \text{U} \cdot (0.99276 \cdot \exp((\lambda_{\text{U}_{238}} \cdot t) - 1) + 0.007196 \cdot \exp((\lambda_{\text{U}_{235}} \cdot t) - 1) + \text{Th} \cdot \exp((\lambda_{\text{Th}_{232}} \cdot t) - 1)$$

where Pb, U, and Th are their contents in atomic% and $\lambda_{\text{U}_{238}}$, $\lambda_{\text{U}_{235}}$, and $\lambda_{\text{Th}_{232}}$ are the decay constraints of $\lambda_{\text{U}_{238}}$ ($1.55125 \times 10^{-10}/\text{year}$), $\lambda_{\text{U}_{235}}$ ($9.8485 \times 10^{-10}/\text{year}$), and $\lambda_{\text{Th}_{232}}$ ($4.9475 \times 10^{-11}/\text{year}$), respectively [49].

The equation is solved using an iteration procedure as follows:

$$\text{PbO} = \text{ThO}_2 \cdot k_0 \cdot (\exp(\lambda_{\text{Th}_{232}} \cdot t) - 1) + \text{UO}_2 \cdot (k_1 \cdot (\exp(\lambda_{\text{U}_{238}} \cdot t) - 1) + k_2 \cdot (\exp(\lambda_{\text{U}_{235}} \cdot t) - 1)$$

The contents of k_0 , k_1 , and k_2 are 0.848485, 0.816367, and 0.0059475, respectively.

4. Petrography and Mineral Assemblage of Uranium Mineralization

Three kinds of uranium minerals have been found in the Jiling uranium deposit, including uraninite, pitchblende, and coffinite. These three uranium minerals have different mineralogical and paragenetic characteristics.

4.1. Uraninite

Uraninite usually occurs as single-cubic crystals, which are partly replaced by pitchblende or coffinite (Figure 4A–D). Based on the uraninite petrographical features and composition variation, most of the uraninite grains underwent different types of alterations. Except for the best preserved uraninite (BP uraninite) crystals, which show insignificant alteration, the altered uraninite grains are divided into two types (altered uraninite A and B).

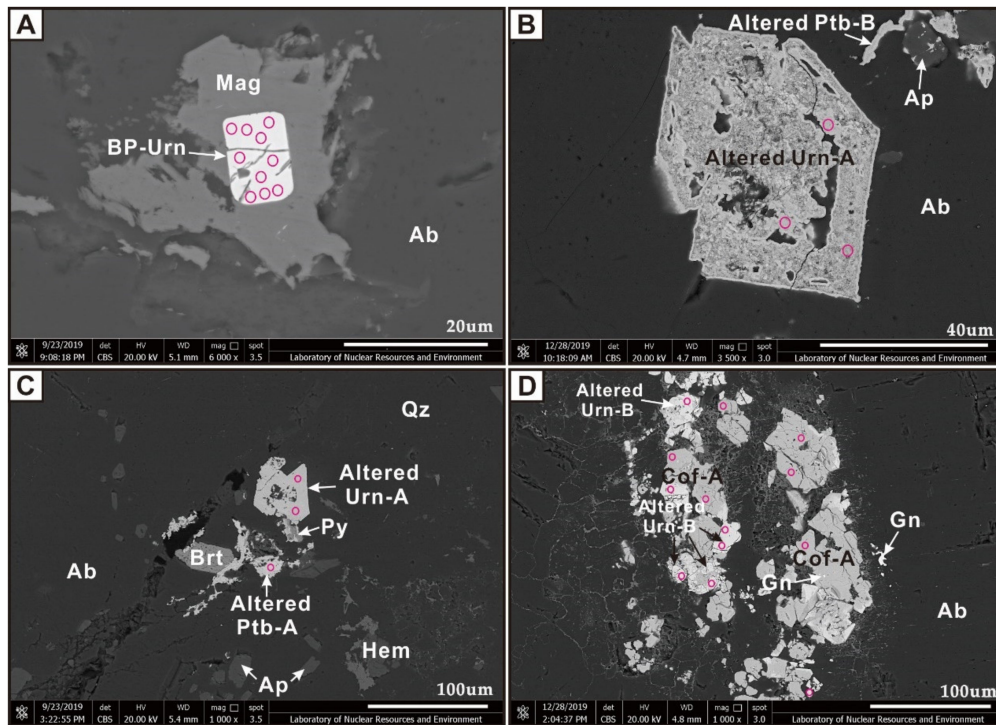


Figure 4. Backscattered electron (BSE) images of the best preserved uraninite (BP uraninite) crystal and altered uraninite A and B in the Jiling uranium deposit. (A) The BP uraninite crystal coexisting with magnetite and associated with albite. (B) Altered uraninite A associated with albite, altered pitchblende B and apatite are nearby (C) Altered uraninite A associated with albite and pyrite, altered pitchblende A, barite, hematite, and apatite are nearby. (D) Altered uraninite B preserved in the core or at the margin of coffinite grains (coffinite A), and coexisting with galena. Ab—albite; Ap—apatite; Brt—barite; Cof—coffinite; Gn—galena; Hem—hematite; Mag—magnetite; Ptb—pitchblende; and Urn—uraninite. Red circles indicate the location of electron microprobe analyzer (EMPA) datapoints.

The BP uraninite crystals are rare and exhibit typically euhedral cubic crystals, $6\ \mu\text{m} \times 10\ \mu\text{m}$ in size (Figure 4A). Most of these uraninite grains occur as inclusions in magnetite; itself included in albite crystals. These uraninite crystals are preserved from alteration likely due to their smaller size and inclusion in magnetite.

Altered uraninite A grains usually occur as euhedral to subhedral single crystals. They have a larger size (30 to $70\ \mu\text{m}$ large) with a diverse range of morphology, including irregular, cubic, and rhombus. They are included in albite and partly replaced by pitchblende (Figure 4B,C). They are heterogeneous and present some cavities (Figure 4B). Apatite, pyrite, and barite can also be observed in the vicinity of altered uraninite A (Figure 4B,C).

Altered uraninite B grains usually occur either as single-crystals in the core or at the edge of coffinite aggregates (Figure 4D). Altered uraninite B probably represents relics of the primary uraninite crystals during a later alteration stage. The galena can also be found as small disseminated crystals nearby altered uraninite B.

4.2. Pitchblende

Pitchblende usually occurs along fractures or as inter-mineral veinlet infilling (tens of microns wide) and as disseminated grains (reaching up to 0.15 mm large), with different mineral associations.

Pitchblende often displays micro-fractures along which the mineral was subjected to different degrees of alteration. Two types of altered pitchblende were distinguished according to the different intensity of gray in BSE images and the different chemical composition described thereafter. Altered pitchblende A showed a brighter gray color in BSE images and with lower SiO₂ content than B. Although these two types of altered pitchblende can be divided, they have similar occurrence features.

Pitchblende occurs as: (1) disseminated along the space between albite, co-precipitated with calcite, and infilling in some microfractures of apatite (Figure 5A); (2) disseminated along the fracture of albite (Figure 5B); (3) infilling along microfractures of albite, and coating around pyrite and albite crystals (Figure 5C,D); (4) calcite followed by pitchblende along microfractures in apatite, and as a colloidal pitchblende cement around apatite, calcite, and baryte; (Figure 5E); and (5) infilling around early apatite and titanium oxide crystals (Figure 5F).

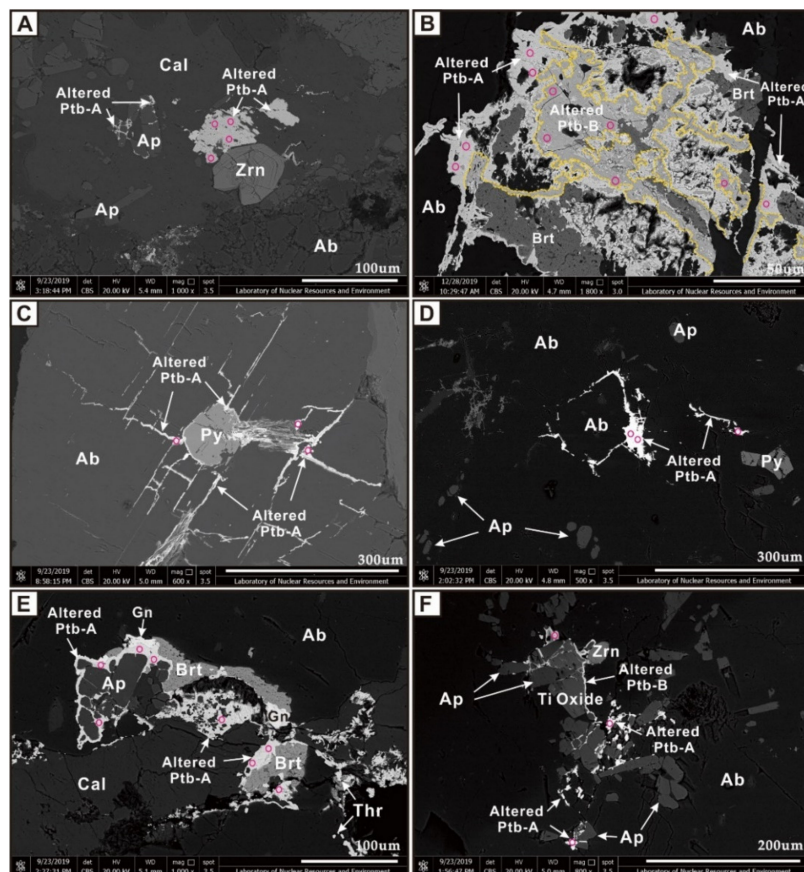


Figure 5. Backscattered electron (BSE) images of altered pitchblende A and altered pitchblende B in the Jiling uranium deposit. (A) Altered pitchblende A disseminated in calcite, adjacent to zircon and infilling microfractures within apatite crystal. (B) Large altered pitchblende (consisting of altered pitchblende A and B) disseminated in the albite crystals and cemented in the barite. (C) Altered pitchblende A infilling microfractures within albite crystal, and rimming a pyrite crystal. (D) Altered pitchblende A rimming an albite crystal and along microfractures, apatite and pyrite crystals are nearby. (E) Altered pitchblende A as a rim around barite, apatite and calcite crystal coexisting with galena and thorite. (F) Altered pitchblende A and B rims around apatite and titanium oxide in albite. Ab—albite; Ap—apatite; Brt—barite; Cal—calcite; Gn—galena; Thr—thorite; Ptb—pitchblende; Py—pyrite; Ti Oxide—titanium oxide; Zrn—zircon. Red circles indicate the location of EMPA datapoints.

4.3. Coffinite

According to the morphological features, two different types of coffinite can be found in the Jiling deposit. Coffinite A occurs as independent crystals irregularly disseminated in the host rocks (Figure 6A) or crystal aggregates filling fractures (Figure 6B). Most of the coffinite A crystals exhibit euhedral or subhedral shapes with a size varying from a few microns to tens of micrometers. Coffinite B occurs as colloidal cement around some gangue minerals or infilling in microfractures of albite (Figure 6C,D).

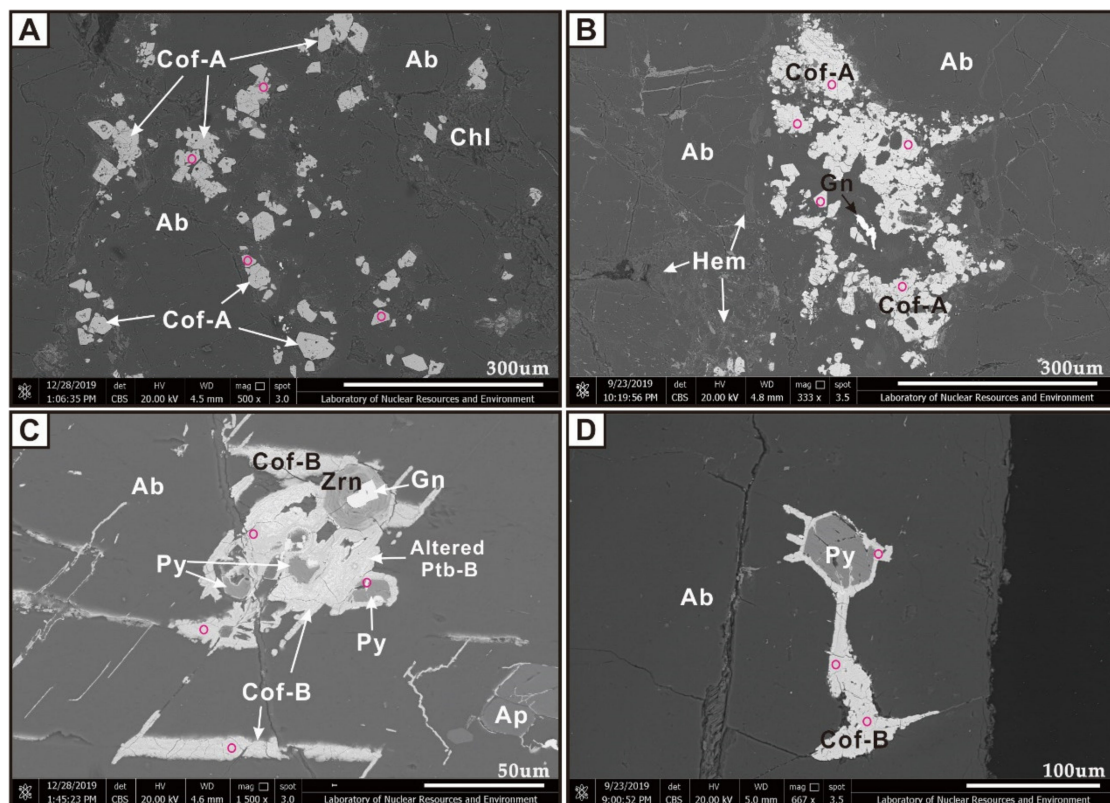


Figure 6. Backscattered electron (BSE) images of coffinite A and coffinite B in the Jiling uranium deposit. (A) Coffinite A occurs as independent mineral grains in the albite and coexisting with chlorite. (B) Coffinite A crystal aggregates filling fractures in albite with galena, hematite dissemination in albite in its vicinity. (C) Coffinite B and altered pitchblende B around zircon and pyrite crystals and as veinlet infilling, galena in the core of a zircon crystal. (D) Coffinite B filling microfractures of albite and rimming a pyrite crystal. Ab—albite; Ap—apatite; Brt—barite; Cof—coffinite; Chl—chlorite; Gn—galena; Hem—hematite; Ptb—pitchblende; Py—pyrite; Zrn—zircon. Red circles indicate the location of EMPA datapoints.

As observed in the BSE images, coffinite A replaced uraninite C during a late alteration episode. Some residual domains of uraninite B occur in the core or at the rim of coffinite A aggregates (Figure 4D). Coffinite A usually coexists with galena, hematite, chlorite, and uraninite B. Coffinite B was generally deposited around the zircon, pyrite, apatite, and galena. Some residual pitchblende B was also identified within the coffinite B. Pyrite and zircon crystals are cemented by pitchblende, with coffinite B replacing pitchblende during a late alteration stage, and a new formation of galena. Traces of pitchblende B were observed on the surface of coffinite B (Figure 6C).

5. Results

The major and minor element chemical compositions of uraninite, pitchblende, and coffinite in the Jiling uranium deposit are presented in Table 1 and Supplementary Materials A.

Table 1. Composition of uraninite, pitchblende, and coffinite in the Jiling uranium deposit (oxide concentrations are in wt.%, with min, max, and median value).

Sample		SiO ₂	CaO	UO ₂	PbO	ThO ₂	SrO	FeO	Al ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃
BP Uraninite A (n = 10)	Min	n.d.	0.05	72.07	4.58	6.51	n.d.	1.23	n.d.	0.13	0.74	0.03	0.80
	Max	0.79	0.23	78.08	4.96	12.59	0.04	2.06	n.d.	0.13	1.34	0.46	1.29
	Median	0.17	0.12	76.82	4.77	9.81	0.02	1.62	n.d.	0.13	1.08	0.16	0.93
	std. Dev	0.21	0.05	2.21	0.10	1.89	0.02	0.23	n.d.	n.d.	0.20	0.12	0.13
Altered Uraninite A (n = 18)	Min	0.47	3.24	79.69	0.04	n.d.	n.d.	0.81	0.03	0.10	0.42	0.02	0.11
	Max	2.02	5.69	89.96	1.18	1.28	0.21	1.51	0.13	0.24	1.00	0.43	0.48
	Median	1.42	4.40	84.77	0.16	0.39	0.03	1.14	0.06	0.13	0.70	0.20	0.25
	std. Dev	0.38	0.71	2.84	0.25	0.40	0.06	0.18	0.03	0.05	0.15	0.09	0.10
Altered Uraninite B (n = 19)	Min	2.97	2.37	75.71	0.05	1.33	0.06	1.13	0.03	0.20	1.33	0.00	0.13
	Max	5.34	4.11	84.37	0.13	4.35	0.16	2.06	0.24	0.62	2.35	0.58	0.29
	Median	3.55	2.95	81.03	0.07	3.28	0.11	1.55	0.12	0.42	1.80	0.23	0.23
	std. Dev	0.55	0.53	2.17	0.02	0.72	0.03	0.29	0.05	0.13	0.30	0.13	0.04
Fresh Pitchblende (n = 3)	Min	0.18	1.04	84.85	4.19	0.75	n.d.	0.19	0.04	n.d.	0.32	0.12	0.21
	Max	0.37	1.20	86.91	4.28	0.83	n.d.	0.98	0.09	n.d.	0.64	0.28	0.25
	Median	0.31	1.09	85.93	4.26	0.82	n.d.	0.92	0.06	n.d.	0.47	0.22	0.23
	std. Dev	0.08	0.07	0.84	0.04	0.03	n.d.	0.36	0.03	n.d.	0.13	0.07	0.02
Altered Pitchblende A (n = 20)	Min	0.55	3.65	80.73	0.04	0.04	0.04	0.82	0.02	0.10	0.37	0.11	0.16
	Max	1.62	5.94	88.80	0.45	1.31	0.14	1.48	0.16	0.24	0.72	0.37	0.46
	Median	1.06	4.64	84.21	0.26	0.14	0.09	1.18	0.05	0.15	0.62	0.20	0.20
	std. Dev	0.29	0.68	2.65	0.09	0.50	0.04	0.19	0.04	0.05	0.10	0.07	0.10
Altered Pitchblende B (n = 20)	Min	2.74	3.33	69.90	0.03	0.71	0.01	0.92	0.05	0.11	0.44	0.11	0.14
	Max	3.60	6.37	81.40	6.93	1.36	0.26	2.03	0.47	0.28	1.10	0.39	0.43
	Median	3.25	5.64	76.05	0.09	0.92	0.14	1.03	0.17	0.18	0.67	0.15	0.28
	std. Dev	0.18	0.83	2.76	1.49	0.13	0.07	0.24	0.08	0.06	0.15	0.08	0.08
Coffinite A (n = 39)	Min	10.01	2.01	49.64	0.03	2.31	0.05	0.29	0.18	0.14	1.36	0.11	0.28
	Max	17.11	3.91	66.35	0.20	8.97	0.07	1.06	0.58	0.51	2.72	0.65	1.56
	Median	14.58	2.64	58.73	0.07	4.55	0.06	0.53	0.37	0.26	1.89	0.38	0.88
	std. Dev	1.44	0.38	4.14	0.05	1.42	0.01	0.18	0.10	0.10	0.30	0.14	0.29
Coffinite B (n = 29)	Min	10.31	1.87	58.45	0.01	0.03	0.06	0.15	0.38	0.15	1.44	0.26	0.49
	Max	20.30	3.24	71.22	1.98	0.11	0.11	1.09	1.05	0.36	2.60	0.61	1.61
	Median	15.00	2.45	63.03	0.07	0.04	0.06	0.33	0.65	0.23	1.97	0.42	1.15
	std. Dev	1.71	0.36	2.66	0.54	0.03	0.02	0.28	0.20	0.05	0.27	0.10	0.27

Table 1. Cont.

Sample		Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃	Total	ΣREE ₂ O ₃
BP Uraninite A (n = 10)	Min	0.23	n.d.	0.31	n.d.	0.20	0.21	0.21	n.d.	0.16	0.21	0.95	96.84	3.01
	Max	0.74	n.d.	0.87	n.d.	1.35	0.49	0.43	n.d.	0.63	0.30	2.51	99.39	6.32
	Median	0.40	n.d.	0.49	n.d.	0.56	0.27	0.28	n.d.	0.31	0.26	1.71	98.51	3.73
	std. Dev	0.15	n.d.	0.18	n.d.	0.35	0.10	0.09	n.d.	0.19	0.04	0.48	0.96	1.09
Altered Uraninite A (n = 18)	Min	0.11	n.d.	0.11	n.d.	0.21	n.d.	n.d.	0.22	0.16	0.22	0.12	90.08	0.94
	Max	0.24	n.d.	0.21	n.d.	0.56	n.d.	n.d.	0.22	0.21	0.22	0.44	98.68	2.00
	Median	0.15	n.d.	0.16	n.d.	0.37	n.d.	n.d.	0.22	0.18	0.22	0.19	94.03	1.34
	std. Dev	0.05	n.d.	0.03	n.d.	0.12	n.d.	n.d.	n.d.	0.02	n.d.	0.10	2.42	0.33
Altered Uraninite B (n = 19)	Min	n.d.	n.d.	0.13	n.d.	0.17	n.d.	n.d.	n.d.	0.16	0.23	n.d.	91.88	2.13
	Max	n.d.	n.d.	0.35	n.d.	0.20	n.d.	n.d.	n.d.	0.23	0.38	n.d.	97.77	3.33
	Median	n.d.	n.d.	0.18	n.d.	0.19	n.d.	n.d.	n.d.	0.20	0.28	n.d.	95.18	2.91
	std. Dev	n.d.	n.d.	0.08	n.d.	0.02	n.d.	n.d.	n.d.	0.03	0.06	n.d.	1.66	0.39
Fresh Pitchblende (n = 3)	Min	0.21	n.d.	0.13	n.d.	0.20	n.d.	0.24	n.d.	0.28	n.d.	0.13	94.13	1.31
	Max	0.21	n.d.	0.31	n.d.	0.20	n.d.	0.32	n.d.	0.28	n.d.	0.13	94.96	1.53
	Median	0.21	n.d.	0.17	n.d.	0.20	n.d.	0.28	n.d.	0.28	n.d.	0.13	94.62	1.51
	std. Dev	n.d.	n.d.	0.08	n.d.	n.d.	n.d.	0.04	n.d.	0.00	n.d.	n.d.	0.34	0.10
Altered Pitchblende A (n = 20)	Min	0.14	n.d.	0.16	n.d.	0.17	0.24	0.24	n.d.	n.d.	n.d.	0.10	90.38	0.42
	Max	0.23	n.d.	0.31	n.d.	0.47	0.24	0.24	n.d.	n.d.	n.d.	0.28	97.07	2.21
	Median	0.15	n.d.	0.17	n.d.	0.26	0.24	0.24	n.d.	n.d.	n.d.	0.15	93.16	1.26
	std. Dev	0.04	n.d.	0.05	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	2.22	0.42
Altered Pitchblende B (n = 20)	Min	0.11	n.d.	0.12	n.d.	0.19	0.19	0.21	0.22	0.17	0.14	0.08	85.88	1.10
	Max	0.28	n.d.	0.23	n.d.	0.35	0.19	0.23	0.24	0.17	0.33	0.28	94.37	2.46
	Median	0.21	n.d.	0.15	n.d.	0.27	0.19	0.22	0.23	0.17	0.24	0.15	88.79	1.43
	std. Dev	0.05	n.d.	0.04	n.d.	0.06	n.d.	0.01	0.01	n.d.	0.07	0.04	2.06	0.33
Coffinite A (n = 39)	Min	0.11	n.d.	0.12	n.d.	0.19	n.d.	0.21	0.22	0.18	0.25	0.42	78.41	2.79
	Max	0.33	n.d.	0.68	n.d.	0.48	n.d.	0.50	0.33	0.64	0.33	1.73	93.90	5.62
	Median	0.21	n.d.	0.32	n.d.	0.33	n.d.	0.29	0.26	0.37	0.27	0.77	86.63	4.73
	std. Dev	0.06	n.d.	0.14	n.d.	0.09	n.d.	0.07	0.04	0.12	0.03	0.28	3.88	0.74
Coffinite B (n = 29)	Min	0.13	n.d.	0.14	n.d.	0.18	n.d.	0.22	0.23	0.18	0.29	0.27	85.32	2.89
	Max	0.51	n.d.	0.67	n.d.	0.49	n.d.	0.51	0.28	0.69	0.29	1.74	93.66	6.39
	Median	0.21	n.d.	0.40	n.d.	0.29	n.d.	0.27	0.25	0.39	0.29	1.18	88.38	5.23
	std. Dev	0.08	n.d.	0.14	n.d.	0.10	n.d.	0.09	0.02	0.15	n.d.	0.44	1.83	1.02

Note: n.d. = not detected; Std. Dev = Standard Deviation.

5.1. Composition of Uraninite

The chemical composition of the BP uraninite crystals in the Jiling uranium deposit was relatively constant. The analytical totals ($n = 10$) ranged from 97.08 wt.% to 99.69 wt.% indicating significant oxidation and/or hydration of the mineral. The UO_2 contents ranged from 72.07 wt.% to 78.08 wt.% with a median value of 76.82 wt.%. The PbO contents were relatively homogeneous with values ranging from 4.58 wt.% to 4.96 wt.% with a median value of 4.77 wt.%. The ThO_2 , Y_2O_3 , and total REE_2O_3 contents were elevated and more variable: 6.51 wt.% to 12.59 wt.% ThO_2 , with a median value of 9.81 wt.%; 0.95 wt.% to 2.51 wt.% Y_2O_3 with a median value of 1.71 wt.%; and 3.01 wt.% to 6.32 wt.% total REE_2O_3 with a median value of 3.73 wt.% (Table 1). The contents of FeO, SiO_2 , and CaO in uraninite A were low, and the Al_2O_3 content was below the detection limit.

In comparison to the BP uraninite crystals, altered uraninite A ($n = 18$) and B ($n = 19$) had lower ThO_2 , PbO, and total REE_2O_3 contents, and higher SiO_2 and CaO contents. The Al_2O_3 contents in altered uraninite A and B were slightly higher than the detection limit. In comparison to the altered uraninite A, altered uraninite B had higher SiO_2 , ThO_2 , and total REE_2O_3 , and lower CaO, UO_2 , PbO, and Y_2O_3 contents (Table 1).

5.2. Composition of Pitchblende

As described above, two types of altered pitchblende were distinguished in the Jiling uranium deposit. Only three analysis spots of fresh pitchblende were obtained during the EMP analyses.

The three fresh pitchblende analyses displayed very limited variations of UO_2 (84.85 wt.%, 85.93 wt.%, and 86.91 wt.%), PbO (4.19 wt.%, 4.26 wt.%, and 4.28 wt.%), and ThO_2 (0.75 wt.%, 0.82 wt.%, and 0.83 wt.%) contents. They also showed very low SiO_2 (0.18 wt.%, 0.31 wt.%, and 0.37 wt.%), FeO (0.19 wt.%, 0.92 wt.%, and 0.98 wt.%), ThO_2 (0.75 wt.%, 0.82 wt.%, and 0.83 wt.%), and Y_2O_3 (below the detection limit or 0.13 wt.%) contents, and moderately high contents of CaO (1.04 wt.%, 1.09 wt.%, and 1.20 wt.%) and total REE_2O_3 (1.31 wt.%, 1.51 wt.%, and 1.53 wt.%).

The altered pitchblende A ($n = 20$) and B ($n = 20$) displayed low analytical totals (90.38 wt.% to 97.07 wt.% with a median value of 93.16 wt.%, and 85.88 wt.% to 94.37 wt.% with a median value of 88.79 wt.%, respectively), indicating strong oxidation and/or hydration. Altered pitchblende A and B also had higher contents of SiO_2 (0.55 to 1.62 wt.% with a median value of 1.06 wt.%; and 2.74 to 3.60 wt.% with a median value of 3.25 wt.%, respectively), CaO (3.65 to 5.94 wt.% with a median value of 4.64 wt.%; and 3.33 to 6.37 wt.% with a median value of 5.64 wt.%, respectively), and lower PbO (0.03 wt.% to 0.45 wt.% with a median value of 0.24 wt.%; and 0.03 to 0.44 wt.% with a median value of 0.09 wt.%, respectively) contents than the fresh pitchblende. Altered pitchblende A showed elevated UO_2 and PbO, and lower contents of SiO_2 , CaO, Al_2O_3 , and ThO_2 than the altered pitchblende B.

5.3. Composition of Coffinite

As described above, two types of coffinite were distinguished in the Jiling uranium deposit. The analytical totals of coffinite A ($n = 39$) and B ($n = 29$) are very low (78.41 wt.% to 93.90 wt.%, with a median value of 86.63 wt.%; and 85.32 wt.% to 93.66 wt.% with a median value of 88.38 wt.%, respectively) indicating a strong oxidation and hydration of this mineral [25].

The concentrations of UO_2 and SiO_2 of these two types of coffinite grains were highly variable, ranging from 49.64 wt.% to 66.35 wt.% with a median value of 58.73 wt.%, 10.01 wt.% to 17.11 wt.% with a median value of 14.58 wt.%; and 58.45 wt.% to 71.22 wt.% with a median value of 63.03 wt.%, and 10.31 wt.% to 20.30 wt.% with a median value of 15.00 wt.% for coffinite A and B, respectively. These variations reflect the strong metamictisation of this mineral associated with the relative migration of these elements leading to non-stoichiometric compositions. In comparison to coffinite A, coffinite B had slightly higher UO_2 contents and obvious lower ThO_2 contents, but their CaO and total REE_2O_3 contents remained relatively constant.

6. Discussion

6.1. Geochemical Evolution of Uranium Mineralization

Several minor and trace elements can be incorporated into uranium oxide lattice at the time of its crystallization, like Th, REEs, and Ca [50]. Furthermore, uraninite is extremely sensitive to alteration and can exchange elements or recrystallize easily during later hydrothermal to supergene alteration events [23,45,51]. This may lead to more or less intense modifications of the composition of the primary uranium oxides. Heterogeneity in the composition of uranium oxides caused by later hydrothermal fluid alteration is common in natural environments [23,45]. In a deposit that was subjected to multiple events of hydrothermal activity and supergene alterations, the characteristics of the hydrothermal or meteoric fluids can be deduced from the chemical variations of uraninite composition (e.g., [24]).

Compared to the BP uraninite crystals, the altered uraninite A and B typically exhibited low contents of $\Sigma\text{ThO}_2 + \text{UO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{PbO}$ and high contents of $\Sigma\text{CaO} + \text{SiO}_2$ (Figure 7A). Low contents of $\Sigma\text{CaO} + \text{SiO}_2$ in BP uraninite suggested that these elements were not significantly incorporated into the crystal structure of uraninite during its crystallization and that the crystals have not been significantly altered. There was a negative correlation between these three types of uraninite groups in the plot of $\Sigma\text{ThO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3$ vs. UO_2 (Figure 7B).

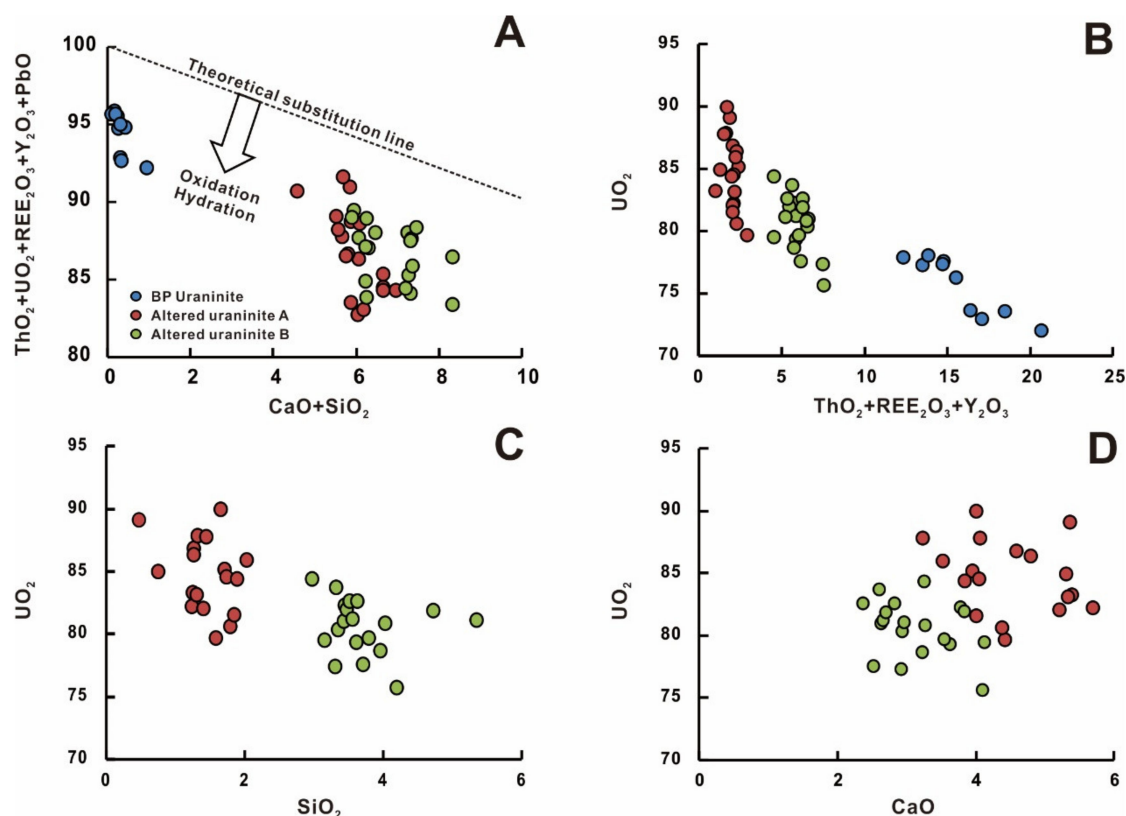


Figure 7. Binary diagrams of different major and minor elements in uraninite (in weight percent). (A) $\text{ThO}_2 + \text{UO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{PbO}$ vs. $\text{CaO} + \text{SiO}_2$ shows that uraninite was subjected to significant hydrothermal alteration. (B) UO_2 vs. $\text{ThO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3$; BP uraninite and altered uraninite A and B were divided into three groups, which shows that fresh uraninite was subjected different degree of hydrothermal alteration. (C) UO_2 vs. SiO_2 shows that there was a compositional gap between altered uraninite A and B. (D) UO_2 vs. CaO shows that altered uraninite A had a slightly higher CaO content than altered uraninite B.

These correlations support that these elements lost the form of the altered uraninite A and B during the hydrothermal alteration and the altered uraninite A underwent more intense alteration than the altered uraninite B. The SiO_2 compositional gap and different contents of CaO between the altered uraninite A and B (Figure 7C,D) indicated that the primary uraninite may have experienced at least two events of hydrothermal fluid alteration. One was more enriched in silica (altered uraninite B) and one was more enriched in calcium (altered uraninite A).

The three fresh pitchblende analyses also had low SiO_2 and CaO contents, and relatively high and constant PbO contents. Based on the textures and compositions, most of the pitchblende in the Jiling uranium deposit also underwent post mineralization hydrothermal alteration with two types. Compared to fresh pitchblende, altered pitchblende A and B had slightly lower contents of $\Sigma\text{ThO}_2 + \text{UO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{PbO}$ and clearly higher contents of $\Sigma\text{CaO} + \text{SiO}_2$ (Figure 8A). Altered pitchblende B had lower $\Sigma\text{ThO}_2 + \text{UO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{PbO}$, UO_2 and higher $\Sigma\text{CaO} + \text{SiO}_2$, $\Sigma\text{ThO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3$ contents than altered pitchblende A (Figure 8A,B), suggesting that altered pitchblende B has undergone more intense alteration than altered pitchblende A.

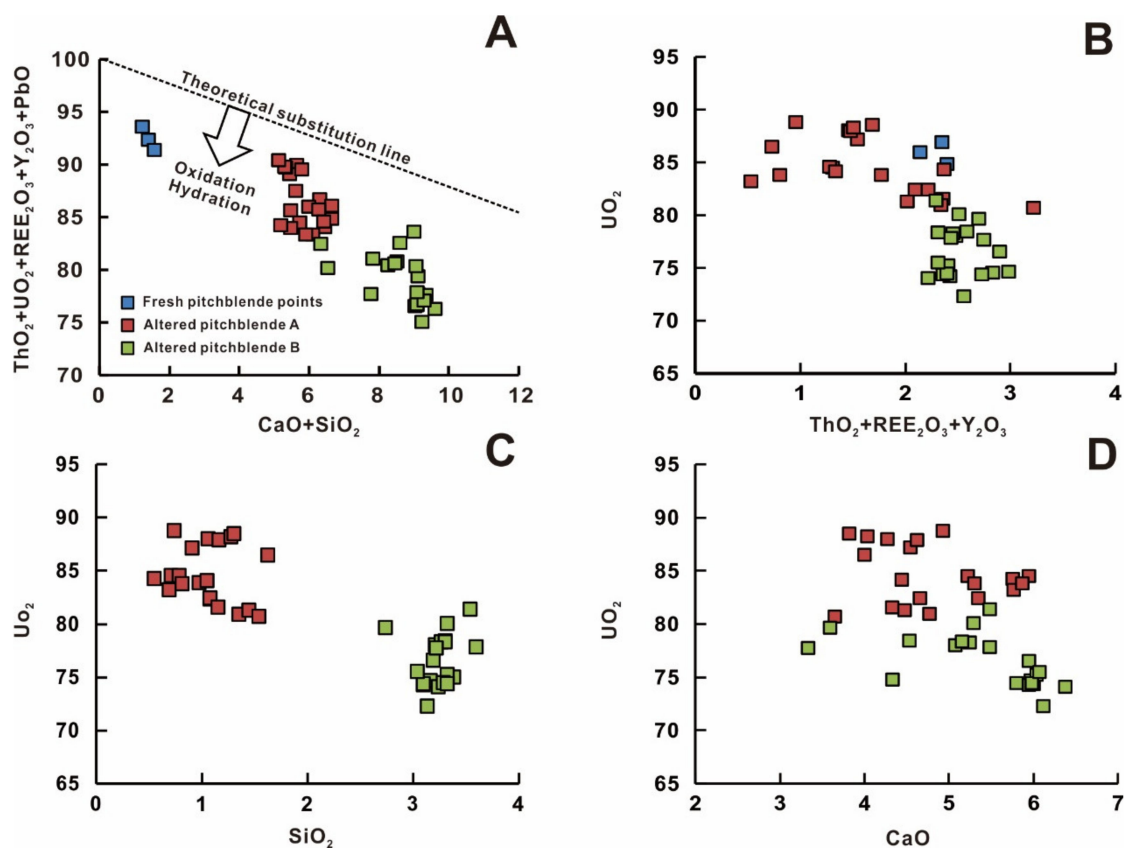


Figure 8. Binary diagrams for different major and minor elements in pitchblende (in weight percent). (A) $\text{ThO}_2 + \text{UO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{PbO}$ vs. $\text{CaO} + \text{SiO}_2$ shows the pitchblende was subjected to hydrothermal alteration with CaO and SiO_2 enrichment. (B) UO_2 vs. $\text{ThO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3$ shows that $\text{ThO}_2 + \text{REE}_2\text{O}_3 + \text{Y}_2\text{O}_3$ contents did not change significantly during the alteration. (C) UO_2 vs. SiO_2 shows that there is a compositional gap between altered pitchblendes A and B. (D) UO_2 vs. CaO shows that altered pitchblendes A and B have the same range content of CaO , and altered pitchblende A has higher UO_2 contents than B.

The difference of SiO₂ contents and the almost same range of CaO contents between altered pitchblende A and B (Figure 8C,D), suggested that pitchblende in the Jiling uranium deposit also experienced at least two separate events of hydrothermal fluid alteration. The hydrothermal fluid that modified altered pitchblende B had a higher SiO₂ content than the fluid that modified altered pitchblende A, but about the same CaO content.

In a closed system, the radioactive decay of U and Th leads to the production of radiogenic Pb, and, thus, should lead to a negative correlation between the PbO and UO₂ + ThO₂ contents in uraninite. However, Pb and U should have a positive correlation in the uraninite formed at the same time, as shown in the study of Kempe [45]. In this study, PbO and UO₂ + ThO₂ also showed a positive correlation in the BP uraninite crystals (Figure 9a). The low contents of Σ SiO₂ + CaO in both BP uraninite and fresh pitchblende, and the homogeneity of the chemical ages suggested that these minerals do not seem to have suffered significant Pb loss.

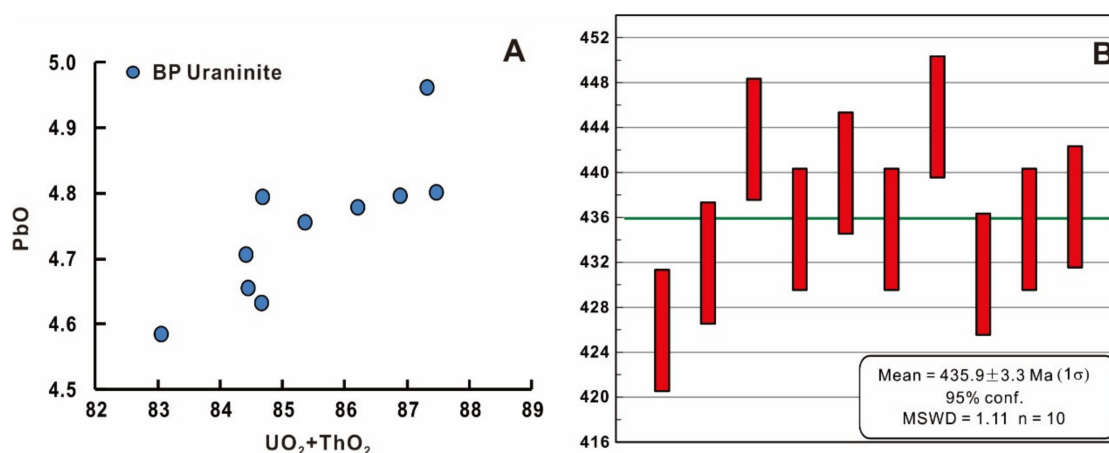


Figure 9. (A) PbO vs. UO₂+ThO₂ shows a positive correlation between the PbO and UO₂+ThO₂ in BP uraninite. (B) Uraninite chemical dating in the weighted average diagram.

The altered uraninite and pitchblende had much lower PbO contents than the best-preserved uraninite and fresh pitchblende, illustrating the Pb loss during the post mineralization alteration. Several mechanisms have been postulated to illustrate the Pb loss in uraninite/pitchblende. The major ideas that have been discussed include (1) U and Pb-loss by coffinitization; (2) U and Pb-loss by leaching; and (3) Pb-loss by diffusion, or recrystallization [52]. The pristine uraninite and pitchblende suffered two episodes of alteration, one with a Ca-rich fluid and one with a Si-rich fluid leading to the two types of altered uraninite and pitchblende. Coffinitization of these minerals resulted from further interaction with Si-rich fluids (e.g., [52]).

6.2. U-Th-Pb Chemical Dating of Uraninite and Pitchblende

Estimation of the crystallization age of uraninite from chemical dating are given in Table 2, with a 1σ uncertainty. As described above, the BP uraninite crystals showed extremely low Si and Ca contents, high and relatively homogeneous Pb contents, illustrating that BP uraninite crystal did not suffer significant alteration since its crystallization. The U-Th-Pb chemical ages obtained from these uraninite ranged from 426 Ma to 445 Ma (Table 2), with a weighted mean age of 435.9 ± 3.3 Ma (n = 10, MSWD = 1.1) (Figure 9b).

Three analyses from the freshest pitchblende displayed low SiO₂ and CaO contents, indicating that these three analyses may have retained the original chemistry of the primary pitchblende. The corresponding U-Th-Pb chemical ages were: 358 Ma, 357 Ma, and 368 Ma, with an average age of 361 Ma.

Table 2. Major element concentrations and calculated age of fresh uraninite and pitchblende from the Jiling uranium deposit.

BP Uraninite								
Sample	SiO ₂	CaO	UO ₂	PbO	ThO ₂	FeO	U/Th	Age
11-1.9-1	0.17	0.14	77.91	4.71	6.51	2.06	11.70	426.00
11-1.9-2	0.16	0.11	77.35	4.80	9.54	1.54	7.92	432.00
11-1.9-3	0.14	0.05	78.08	4.96	9.25	1.50	8.25	443.00
11-1.9-4	0.01	0.23	77.61	4.80	7.07	1.99	10.73	435.00
11-1.9-5	0.00	0.11	72.07	4.63	12.59	1.81	5.60	440.00
11-1.9-6	0.79	0.16	72.98	4.58	10.07	1.23	7.09	435.00
11-1.9-7	0.31	0.12	73.66	4.78	12.55	1.60	5.74	445.00
11-1.9-8	0.12	0.08	77.39	4.80	10.08	1.71	7.51	431.00
11-1.9-9	0.21	0.10	76.29	4.76	9.07	1.55	8.23	435.00
11-1.9-10	0.19	0.16	73.67	4.66	10.77	1.64	6.69	437.00
Mean	0.21	0.13	75.70	4.75	9.75	1.66	7.94	435.90
Std. Dev	0.21	0.05	2.21	0.10	1.89	0.23	1.87	5.39
Fresh Pitchblende Data Points								
10-1.11-2	0.18	1.04	86.91	4.28	0.82	0.19	104.14	358.00
10-1.11-8	0.31	1.09	85.93	4.19	0.83	0.92	101.24	357.00
10-1.11-9	0.37	1.20	84.85	4.26	0.75	0.98	110.62	368.00
Mean	0.29	1.11	85.90	4.24	0.80	0.69	105.33	361.00
Std. Dev	0.08	0.07	0.84	0.04	0.03	0.36	3.92	4.97

6.3. Origin of Uranium Mineralization

The ionic radius of Th, Y, and REE were close to that of U⁴⁺ in eightfold coordination [53]. These elements can be easily incorporated into the structure of uraninite and pitchblende during their deposition. The parameters controlling the incorporation of these elements into the uraninite and pitchblende lattice were essentially the temperature of crystallization and the availability of these elements in the fluids or the silicate melt. In general, low-temperature hydrothermal uraninite or pitchblende was essentially free of Th, whereas those formed at high temperatures were characterized by variable Th + REE + Y concentrations [15,19,24,25,54]. The BP uraninite crystals showed high REEs, Y₂O₃, and ThO₂ contents. This indicated crystallization at high temperatures, such as during magmatic, magmatic-hydrothermal, and metamorphic processes [19,24,45]. Later deposited pitchblende had lower REEs, Y₂O₃, and ThO₂ contents indicating a deposition at a lower temperature than uraninite in the Jiling uranium deposit [19,25].

The REE patterns are an efficient tool for constraining geological models and can reflect the condition of deposit genesis [15,17,55]. The size of the uranium mineral grains of the Jiling uranium deposit were too small to be analyzed by LA-ICP-MS, so REE analyses by EMPA were tentatively used to define the general shape of the REE patterns. The irregularities of uranium mineral REE patterns (chondrite normalized from Sun and McDonough [56]), presented as Supplementary Materials B, resulted from the low accuracy of EMPA analyses, for REE with the lowest abundance, which were below the detection limit. The BP uraninite globally exhibited high REE contents with weak fractionation between the LREE and HREE [15]. As the Eu content was too low to be detected, it was impossible to determine the Eu anomaly. The REE patterns of BP uraninite were similar to uraninite from magmatic uranium deposits, possibly with still higher REE concentrations [15].

Uraninite occurs mainly in high fractionated peraluminous leucogranite and related pegmatites, such as the granites host hydrothermal-vein-type uranium deposit in South China [57,58], high-Ca metaluminous granites, low-Ca peraluminous granites, peralkaline granites, and in weakly peraluminous anatectic pegmatoids resulting from a low degree of partial melting of metasedimentary rocks [59,60]. However, the fresh host-granitoids in the Jiling uranium deposit were metaluminous to peraluminous without magmatic uraninite [30]. The chemical ages of the BP uraninite varied

from 426 Ma to 445 Ma as discussed above, which is similar to the age range of crystallization of the granitoid intrusions in the area around the Jiling uranium deposit (from 427 to 441 Ma, U-Pb isotopic system on zircons by LA-ICP-MS) [30]. These age similarities together with the elevated REE, Th, and Y contents in the uraninite, and the weak fractionation of the whole REE patterns (Supplementary Materials B) are all in favor of a crystallization of the uraninite in the Jiling uranium deposit from magmatic-hydrothermal fluid.

6.4. Uranium Mineralization Process

During the Paleozoic, during the transition from a compressional to an extensional tectonic regime, an upwelling asthenospheric mantle heated up the lithospheric, and induced the generation of mafic and felsic magmas [30]. Granitoids and syenite were formed with different ratios of mixing between the felsic and mafic magmas. Granitoid emplacement ages range from 442 to 435 Ma [30], and the syenite at 427 Ma [29]. During the late-magmatic stage, a magmatic-hydrothermal fluid exsolved from the crystallizing magmas percolated along the Malugou fault zones and developed extensive Na-metasomatic alteration zones in the Jiling granitoids.

During Na-metasomatism, early deformation occurred under a ductile regime, at temperatures higher than 450–500°C, as evidenced by the granoblastic recrystallization of albite [5,61]. Quartz dissolution, albitization of K-feldspar and anorthite, led to enrichments in Na, U, and Th, and depletion in Si, K, and Ca in the Na-metasomatized granitoid [42,62]. The Jiling granitoid had 1.08 to 11.80 ppm U and Th/U ratios of 2.56 to 10.63 (Table 3), respectively, with data from Wang et al. [30] and Zhao [63]. Compared to the bulk earth ratio (Th/U = 3.9 ± 0.1), the relatively high Th/U ratios of many of the samples (Figure 10) from the Jiling granitoid indicate that these rocks lost significant U content during magmatic-hydrothermal fluid exsolution to crystallize uraninite in the metasomatic zones.

Table 3. The U, Th contents and the ratios of Th/U of the Jiling granitoids.

Sample	U	Th	Th/U
LSS12-02 *	7.80	21.50	2.76
LSS12-03 *	3.48	21.50	6.18
GS-16-28	4.22	30.30	7.18
GS-16-32	2.61	13.70	5.25
GS-16-50	1.75	12.15	6.94
ZKN9-2-2	3.90	17.60	4.51
LSS12-10 *	7.23	58.90	8.15
LSS-26 *	9.47	27.70	2.93
GS-16-34	1.08	7.49	6.94
GS-16-31	1.67	8.09	4.84
GS-16-45	3.15	20.40	6.48
GS-16-46	3.62	28.80	7.96
GS-16-29	2.62	14.65	5.59
D13-086 *	7.90	40.13	5.08
04LTW01 *	11.80	30.20	2.56
LSS12-05 *	11.30	42.60	3.77
GS-16-36	2.39	25.40	10.63
Min	1.08	7.49	2.56
Max	11.80	58.90	10.63
Mean	5.06	24.77	5.75

Note: samples with * are from Zhao [63]; those without * are from Wang et al. [30].

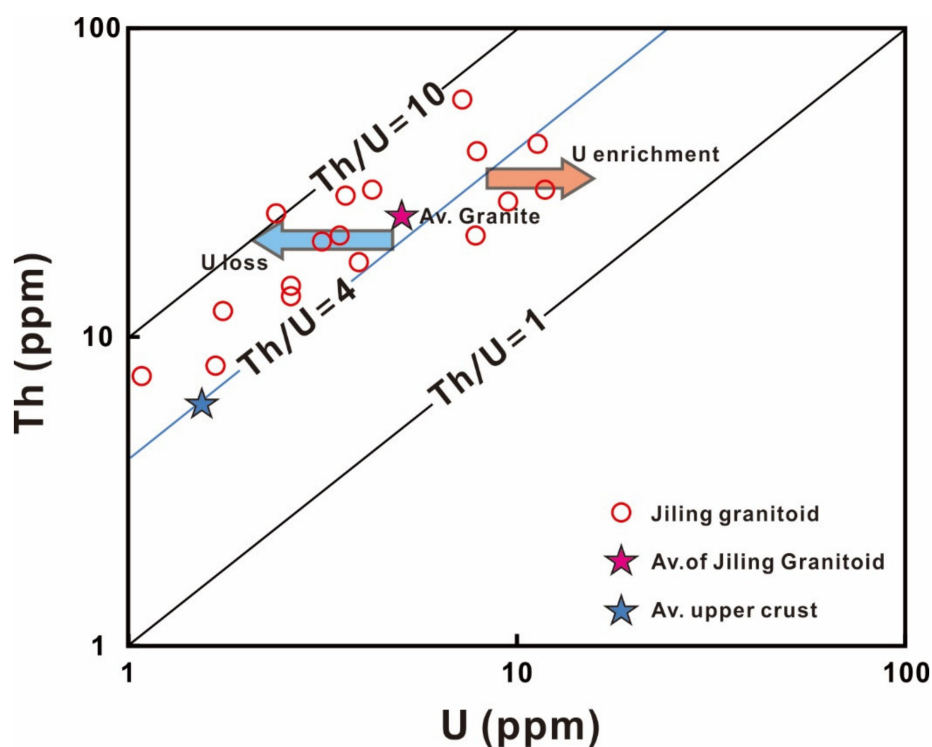


Figure 10. Th vs. U diagram of the Jiling granitoids showing their U and Th enrichment relative to the average upper crust and average granite. Most samples exhibited U depletion compared to the average crust ratio of 3.9.

6.5. Hydrothermal Alteration of Primary Uraninite

After the formation of uraninite in ore stage I, the later hydrothermal activity led to second stage of mineralization in the Jiling uranium deposit. According to the previous studies on the fluid inclusion of calcite, which formed simultaneously with pitchblende [13,44], during ore stage II, the relatively lower temperature meteoric water percolated along the Malugou Fault zones and its secondary structures. Uranium was extracted from U-rich accessory minerals and uraninite formed in ore stage I through the fluid-rock interaction. Then, the extensive hematitization of albitite and the appearance of pink calcite indicate the oxidation of Fe^{2+} in magnetite and/or biotite (e.g., [44]), and suggest that the oxidation of Fe^{2+} may be responsible for the reduction of the carbonate uranyl complex transported by the ore fluids in the ore stage II.

Coffinite is a common mineral in some types of uranium deposits and is mostly deposited at low-temperatures and under reducing conditions. Coffinite can (a) form as a result of changing redox, aSiO_2 , pH, temperature, or pressure conditions, which induce coffinite precipitation [64,65]; (b) result from the alteration of previously crystallized uranium oxides through the uptake of silica under reducing conditions [66].

According to the presence of residual uraninite and altered pitchblende B found in the rim or core of coffinite A and B, respectively (Figures 4D and 6C), and the high Th and REE contents of coffinite A, and the low Th content of coffinite B, we can conclude that coffinite A essentially resulted from the alteration of Th-rich uraninite and coffinite B from low Th pitchblende. The interpretation of the origin of coffinite A is further supported by the fact that high Th contents in coffinite from the Witwatersrand quartz pebble conglomerates, has been interpreted as resulting from an interaction between a Si-rich fluid and detrital Th-bearing uraninites [67].

The different types of coffinites have REE pattern fractionation that is similar to BP uraninite (Supplementary Materials B), confirming that they derive from the alteration of BP uraninite. Combined coffinite B was formed from pitchblende during a later alteration, indicating that the pitchblende

and coffinite may also derive from the remobilization of the primary uraninite in the Jiling uranium deposit. Compared to the altered uraninite A and altered pitchblende A, which formed under hydrothermal alteration enriched in Ca, the altered uraninite B and altered pitchblende B, which formed under hydrothermal alteration enriched in Si, have relatively higher LREE content. And the coffinite formed by the interaction between a Si-rich fluid and BP uraninite, pitchblende shows high LREE too. This may be due to that the Si-rich fluid have relatively high content of LREE, because of the LREE can dissolve and mobile during fluid-rock interaction at low temperature [68,69].

6.6. Comparison with Other Na-Metasomatic Uranium Deposit

Uranium deposits related to Na-metasomatism are widespread around the world [5,70–73]. The most typical and famous uranium deposits associated with Na-metasomatism are from central Ukraine [1,5]. Compared to other Na-metasomatic deposits, such as those from the deposits of central Ukraine. The Jiling uranium deposit present the following specific characteristics:

- (a) The Jiling uranium deposit is hosted only in the Jiling intrusive granitoidic complex, whereas uranium mineralization in Central Ukraine also can be hosted in iron formations, this may be because the iron formation can provide a reduction condition for U precipitation in the ore-forming fluids in Central Ukraine. The iron formation also makes a difference in the mineralogy;
- (b) Due to the extensive U sources there is a thermal plume in the central part of the Ukrainian Shield, the uranium mineralization is spread over a belt of about 150 km in central Ukraine. Due to the limitations of magmatic activity, the uranium mineralization occurrences extend only over several tens kilometers in the Jiling area;
- (c) Due to banded iron formations, the metasomatic alteration episodes are more complex in the Central Ukraine uranium deposits. The Na-metasomatic episode, which is largely predominant in the Jiling deposit, is followed in the Ukraine by an important Ca-metasomatic episode with a new formation of Ca-rich pyroxene and garnet, only represented by minor amounts of carbonates in Jiling, and a late K-potassic event with a new formation of biotite, absent in Jiling [5];
- (d) In central Ukraine and many other deposits there is a time gap between granite emplacement and ore deposit formation; granites were emplaced at 2050 Ma and the mineralization was formed at 1800 Ma, whereas in Jiling, the granitoids and the uranium mineralization were formed around 430 Ma. There was no significant time gap between the first uranium mineralization and host granite emplacement. This is a complicated issue that is affected by many factors, such as different metallogenic geological backgrounds, different metallogenic evolution processes, and different properties of ore-forming fluids between these two places [5];
- (e) Due to the different ore-forming temperatures and host-rock geochemical characteristics between these two places, the uranium minerals predominantly consists of dominantly brannerite, with lesser amounts of low Th-uraninite, U-ferropseudobrookite, and pitchblende in central Ukraine. However, in the Jiling uranium deposit, high Th-REE-Y-uraninite, pitchblende, and coffinite are the main minerals; U-Ti minerals are absent;
- (f) The ore fluids in the Ukraine correspond to waters of surficial or basinal origin, whereas, in the Jiling uranium deposit ore fluids for the primary mineralization are of magmatic origin.

7. Conclusions

Integrating new petrographical/mineralogical observations, mineral chemistry, U-Th-Pb chemical dating, and the results of previous studies in the Jiling area, the following conclusions were obtained:

- (1) Three kinds of uranium minerals, high Th-REE-Y-uraninite, pitchblende, and coffinite, are present in the Jiling uranium deposit, and a great deal of the uraninite and pitchblende were subjected to different degrees of hydrothermal alteration. The pitchblende was the predominant uranium mineral among these three uranium minerals.

- (2) The similarity of the chemical age of the primary uraninite in the Jiling deposit at 435.9 ± 3.3 Ma, with that of the enclosing intrusions, and the high Th and REEY contents of primary uraninite suggest its crystallization at a high temperature from a magmatic-hydrothermal fluid. The primary uraninite was subjected to at least two alteration events to form altered uraninite A, mainly enriched in calcium, and B, mainly enriched in silica, and coffinite A.
- (3) Limited data on the chemical age of fresh pitchblende, suggested a formation age at about 361 Ma. The low Th and REEY contents of fresh pitchblende both suggested its crystallization at a low temperature and possibly from a meteoric-dominated ore fluid. According to the different chemical composition of fresh and altered pitchblende, the fresh pitchblende was also subjected to at least two alteration events to form altered pitchblende A and B, where B had more silica, but with a similar amount of calcium to A.
- (4) In summary, after the Jiling pluton and syenite emplacement, Na-metasomatic alteration was developed extensively along the Malugou fault and secondary structures. This Na-metasomatic alteration was associated with the uranium mineralization. Uraninite was formed at high temperature and possibly from a magmatic-hydrothermal fluid during ore stage I. It would be interesting to determine whether intrusions similar to the Jiling granitoid exist in the area, as they could represent interesting targets for further exploration. Pitchblende was formed at a low temperature, possibly of meteoric origin, essentially from the remobilization of the primary uraninite mineralization during ore stage II. Uraninite and pitchblende were finally partly altered into two types of coffinite during a late alteration episode.
- (5) The relatively high content of LREE in the uranium minerals formed by hydrothermal alteration enriched in Si, suggested that the Si-rich fluid have relatively high content of LREE.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/4/335/s1>, Supplementary Materials A: Complete data of uranium minerals by EMPA, Supplementary Materials B: The chondrite normalized REE patterns of BP uraninite and coffinite in the Jiling uranium deposit and detection limit of rare earth elements for EMPA.

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