

Ore Geology Reviews

Conditions for uranium biomineralization during the formation of the Zoovch Ovoo roll-front-type uranium deposit in East Gobi Basin, Mongolia --Manuscript Draft--

Manuscript Number:	OR GEO-D-21-00186R1
Article Type:	Research paper
Keywords:	roll-front, uranium, bioreduction, organic matter, sulfur isotopes, East Gobi Basin, Mongolia
Corresponding Author:	Dimitrios Rallakis CREGU: Centre de Recherches sur la Geologie des Matieres Premieres Minerales et Energetiques Vandoeuvre-lès-Nancy, Grand Est FRANCE
First Author:	Dimitrios Rallakis
Order of Authors:	Dimitrios Rallakis Raymond Michels Michel Cathelineau Olivier Parize Marc Brouand
Abstract:	The Zoovch Ovoo uranium rollfront-type deposit is hosted in the Sainshand Formation, a Late Cretaceous siliciclastic reservoir, which constitutes the upper part of the post-rift infilling of the Mesozoic East Gobi Basin in SE Mongolia. The Sainshand Formation consists of unconsolidated medium-grained sand, silt and clay intervals deposited in fluvial-lacustrine settings. The uranium deposit is confined within a 60-80 m thick siliciclastic sequence inside aquifer-driven systems. The overall system experienced shallow burial and was never subjected to temperatures higher than 40°C. This study proposes a comprehensive metallogenic model for this uranium deposit. Sedimentological and mineralogical observations from drill core samples to the microscopic scale (optical and Scanning Electron Microscopy) together with in situ geochemistry of late-formed phases (Laser Ablation–Inductively Coupled Plasma Mass Spectrometry, Electron Probe Microanalysis, Fourier Transform–Infrared Spectroscopy) were considered for the reconstruction of the main stages of U trapping. In the mineralized zone, the uranium ore is expressed as Ca–enriched uraninite (UO₂) and less commonly as Ca–enriched phospho-coffinite (U, P)SiO₄. Trapping mechanisms include i) complexation (i.e. uranyl-carboxyl complexes), ii) adsorption on organic or clay particles) and iii) reduction by pyrite and by bacterial activity to amorphous uraninite. In all cases, the organic matter plays either the role of trap for uranium or nutrient for bacteria that can trap uranium through their metabolism. The shallow burial diagenesis conditions do not allow direct reduction of U(VI) by organic carbon. The δ³⁴S values of the iron disulfide are very diverse, fluctuating in extreme cases between -50 to +50‰, with an average δ³⁴S value for framboidal pyrite at 2‰, and -20‰ for euhedral pyrite. The positive and negative values reflect close versus open fractionation systems, while bacterial sulphate reduction (BSR) is active during the whole diagenetic history of the deposit as an essential source of reduced sulfur. Therefore, using detrital organic matter as a carbon source, microorganisms play a significant role in uranium trapping, either as a direct reducing agent for uranium or pyrite formation, which will trap uranium redox driven epigenetic processes.
Suggested Reviewers:	Jean-Dominique Meunier meunier@cerege.fr Andy Wilde wildegeoscience@gmail.com Olivier Kreuzer pkreuzer@gmail.com Alex Otto

	alex.otto@csiro.au
	Philippe Boulvais philippe.boulvais@univ-rennes1.fr
	Christophe Bonnetti christoph.bonnetti@gmail.com
Opposed Reviewers:	

Dimitrios Rallakis
CREGU, GeoRessources, University of Lorraine-CNRS
dimitrios.rallakis@univ-lorraine.fr

Chief Editor
Journal of Ore Geology Reviews
Nancy, 25th February 2021

Sir,

Please find enclosed with this letter a paper entitled "*Conditions for uranium biomineralization during the formation of the Zoovch Ovoo roll-front type uranium deposit in East Gobi Basin, Mongolia*" by Dimitrios Rallakis, Raymond Michels, Michel Cathelineau, Marc Brouand & Olivier Parize, we would like to submit for publication in Journal of Ore Geology Reviews.

This paper focuses on the construction of the metallogenic model of a roll-front type U-deposit formed in unconsolidated series of continental formations in the East Gobi Basin (Mongolia), affected by shallow burial and by continuous fluid circulation since sedimentation.

Organic matter is a particular component for the formation of this deposit. We bring forward the role of microorganisms as we demonstrate that direct reduction of U by carbon is not possible in low temperatures. We also explain the cycle of sulfur, highlighting among other sulfides, the different pyrite generations in pre-ore, syn-ore and post-ore times. We show that pyrite morphology is irrelevant in their ^{34}S isotopic signature and trace element content which are controlled by sulfur availability and roll-front waters input, respectively. We compare our findings with other roll-front cases of the world, in most cases having similar results.

All data taken into account, a full paragenetic succession was constructed highlighting changes in fluid-rock interaction conditions, including roll-front activity. The study ends with the presentation of a complete conceptual metallogenic model for the Zoovch Ovoo deposit that combines all findings and proposes interactions among them.

We think that this study should be published in an international journal, and in this respect, we hope that this paper satisfies all the conditions necessary for its evaluation by the Journal of Ore Geology Reviews. We have chosen this journal because our paper deals with the geological aspects of a mineral deposit in particular uranium ore.

For the reviewing, we suggest the following researchers:

- **Jean-Dominique Meunier**, Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement (CEREGE), Aix-en-Provence, France, meunier@cerege.fr
- **Andy Wilde**, Deep Yellow Limited, Subiaco WA 6008, Australia, wildegeoscience@gmail.com
- **Olivier Kreuzer**, Economic Geology Research Centre, school of Earth & Environmental Science, James Cook University, Townsville, QLD 4811, Australia, pkreuzer@gmail.com
- **Alex Otto**, CSIRO Mineral Resources, ARRC, Bentley, WA 6102, Australia, alex.otto@csiro.au
- **Philippe Boulvais**, Geosciences Rennes, France, philippe.boulvais@univ-rennes1.fr

Yours sincerely,
Dimitrios Rallakis

Manuscript Number: ORGEO-D-21-00186

Conditions for uranium biomineralization during the formation of the Zoovch Ovoo roll-front type uranium deposit in East Gobi Basin, Mongolia

Dear Dr Rallakis,

Thank you for submitting your manuscript to Ore Geology Reviews.

I have completed my evaluation of your manuscript. The reviewers recommend reconsideration of your manuscript following major revision. I invite you to resubmit your manuscript after addressing the comments below. Please resubmit your revised manuscript by May 14, 2021.

When revising your manuscript, please consider all issues mentioned in the reviewers' comments carefully: please outline every change made in response to their comments and provide suitable rebuttals for any comments not addressed. Please note that your revised submission may need to be re-reviewed.

To submit your revised manuscript, please log in as an author at <https://www.editorialmanager.com/orgeo/>, and navigate to the "Submissions Needing Revision" folder.

Ore Geology Reviews values your contribution and I look forward to receiving your revised manuscript.

Kind regards,
Huayong Chen
Editor-in-Chief
Ore Geology Reviews

Editor and Reviewer comments:

Thank you for submitting this very comprehensive study of an interesting uranium deposit. Documentation of high concentrations on U in organic material is a significant contribution. The paper is unevenly written - perhaps different authors contributed different sections. Please see the many comments and suggestions for rewording on the attached file from the associate editor. The figures are in good shape.

The term "pyrite habitus" is awkward and not used much in the literature - use pyrite habit so all will understand.

Pitchblende is an obsolete term for uraninite - either state this or why you chose it or change all to uraninite.

Some references are missing, some appear not to be cited, and some are out of alphabetical order in the reference list.

The terms habitus and pitchblende have been modified for habits and uraninite respectively. The references were carefully reviewed as well.

Reviewer 1: The manuscript could eventually be suitable for publication; however, it needs clarity and substantial improvements involving a major reorganisation and rewrite. Clearly

the author is not a primary English speaker and the manuscript suffers from questionable grammar, some bizarre naming (notably the use of "habitus") and numerous typos. I recommend that a colleague more proficient in English is asked to check thoroughly the revised version.

The rather garbled discussion section highlights what I regard as the main deficiency of this manuscript, namely that the evidence in support of bacterial reduction of uranium is at best circumstantial, particularly in view of the fact that the valence state of uranium associated with organic material is unknown.

The evidence for bacterial reduction is not circumstantial since the system never experienced high temperatures (120°C) that are needed for direct U-C reduction. We discuss all other possibilities and we prove by contradiction that bioreduction is the most possible cause. We stress out that since we have not performed EXAFS we do not know if we have bioreduction or adsorption of U on organic matter when U reaches 20 wt% in vitrinite particles, because no visible crystals can be seen under SEM. We use other studies from the roll-fronts in China and Wyoming to point out the role of bacteria and we find many similarities with Zoovch Ovoo.

I dispute the interpretation of late carbonate-hosted framboidal pyrite, but the "evidence" for this seems to be borrowed from another paper (as is quite a lot of interpretation apparently).

Indeed, the late carbonate phases is referring to the anhedral (type IV) dolomite that was initially described in Rallakis et al., 2020 (Sedimentary Geology) and is also presented in the present paper. I wrote a new chapter towards the end of discussion where the reader can follow the evolution of dolomite from type I to type IV. The paragenesis of dolomite in Zoovch Ovoo is very important for the understanding of the geological history of the deposit and since it records uranium mineralization episodes we decided to use it as an index of timing of events.

The term facies appears to have been used somewhat loosely, and I suggest that the author consults some text books for the correct usage.

Maybe in two cases the term was incorrectly used. I have done the necessary modifications.

I suggest reconsidering the use of the word "pitchblende". Many uranium geologists regard this term as obsolete, and instead use uraninite.

I agree with this suggestion and I have switched pitchblende for uraninite in the text and figures.

Figure 5 is unnecessary - most geologists know what common minerals look like under the microscope. Substitute image/s illustrating paragenetic relationships, if available.

I have followed the structure of other articles on uranium ore i.e. from Bonnetti that has also published in Ore Geology Reviews and I think that discussing the general petrography of sands is a good start. Discussing the paragenetic relationships by showing images in this roll-front would probably be too long and too complicated, therefore I suggest that we use the paragenetic table to present all diagenetic phases and U-episodes.

I have not checked the references.

The references were checked and corrected.

SPECIFIC COMMENTS

Section 1. States the aim of the paper in 3 lines which fail to mention use of stable isotopes, bulk geochemistry, RockEval analysis inter alia. Enlarge to give the reader an idea of what they are really going to read about. And perhaps include why you chose to acquire all this expensive data.

I have modified the last paragraph of the introduction to better express the objectives of the paper.

Section 2.1 - Should be shortened to focus only on relatively recent geological history, i.e. that relevant to uranium deposit formation. Basin appears to have been initiated in Jurassic. Start there? Paragraph 1 in particular should be deleted.

I have kept paragraph 1 and modified Figure 1A,B to show where these metallogenic provinces are located. I removed some text from section 2.1.

Figure 1. Location map (ex CIA if I'm not mistaken) is illegible - should be replaced by a simplified version. Geological map is poor and should be redrafted, for example South Zuunbayan Fault appears to have been drawn on top of a dashed line. Sloppy. Patterns used for different units are also poor. It would be helpful to emphasise the location of the deposit - the font size of the deposit label is smaller than most other features on the map. Emphasise the location of the deposit not the sub-basins! The symbol for the U deposit should also appear in the legend. What is the dashed line next to the deposit? An inferred fault? A sub-basin boundary?

I have modified the map following the suggestions of the reviewers. The geographical map includes the four metallogenic provinces of Mongolia based on Dahlkamp. I have moved the line of South Zuunbayan Fault so it does not coincide with the basin boundaries of Zuunbayan sub-basin. I also added colors instead of patterns for the lithologies and I added the color of the Zoovch-Ovoo deposit in the legend. I also indicate where the Khovsgol and Sainshand sub-basins are located in relation to Zuunbayan sub-basin.

Figure 2. Meandric?

Typographical error "meandering"

Line 50. Use of "habitus"? Suggest using a more widely recognised term. Also, use of the term "ore" is discouraged as it has important economic connotations. Better to use "mineralisation" or similar.

I agree for changing the word habitus. It is latin and not commonly used in English. I have switched it for habits as the editor also suggested. The term ore is used in other articles in U studies. It is a useful term when saying e.g. pre-ore or post-ore. I switched U-ores to U-minerals where possible.

Line 132. Detail on Palaeozoic basement is irrelevant and could be deleted. I suggest renaming 2.3 Stratigraphy (why "lithostratigraphy"?) of the East Gobi Basin.

I have changed the name to the one suggested. I think that talking about the Paleozoic basement is important in this study because these rocks might have acted as U-source rocks.

Line 164. Overlayed = overlain

Agreed.

Line 170. Sag-basin story. Really - it's a story? And the hyphen is not required.

Changed to "period".

Line 185 - 188. Sedimentological controls on U deposition better presented in a different section, not one entitled "Sampling".

I have moved the sedimentological control description in section 4.1.

Line 190. I think that the author misunderstands the term "facies". It is not possible to study a sedimentary facies with a thin section. Some clarity is required as to what material is being studied (and why).

I changed facies for minerals.

Line 196. An SEM cannot establish paragenesis. Paragenesis is determined through interpretation of SEM (and optical microscope) imagery.

I rephrased the sentence.

Line 201. Bulk-rock geochemistry is included in a section entitled "Petrography and Crystal-Chemistry". Inappropriate, as is the hyphen between crystal and chemistry.

I rephrased the sentence.

Line 239. RockEval analysis is common in the hydrocarbon industry but probably needs explanation for the likely readership of this paper. At what facility were RockEval measurements made? QA/QC measures?

I have added all information that I have at hand. These analyses were performed in another institute therefore I do not have at hand more QA/QC details.

Section 4.1. Paragraph 1 would be better placed in the earlier section on Local Geology.

I moved the text as suggested.

Line 254. Incorrect use of the term lithofacies. I suspect that the author is referring to lithologies. If not I would suggest that the various "lithofacies" are described and illustrated as a new section 2.4. The modal mineral composition of various lithologies would in any case be clearer to the reader if presented as a table. This whole section is garbled and unclear.

I have added a Figure (A1) in the Appendix where I present by order of abundance the lithologies encountered in Zoovch Ovoo. I changed the term of lithofacies to lithologies.

Line 262. Homolithic and heterolithic. Uncommon terms. Better to use monomict and polymict. Also what does micro-conglomeratic mean?

I have changed homolithic and heterolithic for the proposed terms. A micro-conglomerate is composed of very coarse sand grains in a silty-clayey matrix.

Line 266. Paragraph mixes observation (minerals present) with inference (lack of chemical alteration). Latter should be placed elsewhere (e.g. in a discussion section).

I kept only the sericitization of feldspars and removed the inference.

Line 272. Mentions XRD analysis of clays. Was this done in this study? If so some commentary should appear in the methods section. If not, where is the reference to the source of this information? Clay identification through XRD is a non-trivial exercise.

I have added a figure in the annex (A3), discussed the XRD results and added a paragraph in the methodology chapter.

Line 279. Again mixing observation with inference. And the inference of 4 generations of dolomite is from another work. Move to a discussion section. This section is supposed to detail observations from the current work.

I see the point of reviewer 1 but I think that it is better to briefly show these four dolomite generations and their relationship to the roll-front as well as to point out that there is another publication where they are discussed in detail. They are discussed in more detail in the discussion section.

Line 285. "reservoir zone" - what does this mean in the context of this paper?

The sand-reservoir in Sainshand Formation where U is located.

Line 292. Illustration of "phytoclats, such as root remains" would be helpful.

For phytoclats and root-relics please refer to Rallakis et al. (2019).

Line 316. Evidence need to support this paragenesis. Refer to some of the images included in the manuscript? The interpretation of pyrite in dolomite as late needs justification, as I can't see why these sulphides can't be early and simply encapsulated in later dolomite.

The pyrite generations and their time relationships from (i) to (v) are well explained in Figure 7C, D. I do not include images of marcasite because it occurs very rarely in my dataset. I have modified also Figure 6 accordingly.

The interpretation of dolomite and pyrite would require using more images on this specific relationship which I finally realize that they are not so useful for my later demonstrations, therefore I decided not to talk about them in the manuscript.

Line 327. Needs more discussion on sphalerite generations.

I have more text to discuss the occurrence of sphalerite.

Line 369. Meaning unclear.

I have rephrased the sentences accordingly.

Line 384. The SPP2 is a scintillometer not a Geiger counter! As SPP2 measures a volume of at least 1m² this would seem to have been a futile exercise. To avoid derision delete L381 to 388. Perhaps enlarge on the significance of the Rockeval analysis? One line is hardly sufficient!

I have modified this chapter, adding more text and being more specific about the Rock-Eval analysis. On one hand Rock-Eval confirmed the organic petrography, having Type III and IV kerogens. On the other hand the increasing radioactivity of the hand specimens does not follow the increasing oxygen index, therefore these results were not further discussed in the discussion chapter.

I also modified the name of the instrument accordingly.

Line 401. I don't think the authors meant to say this! An example I suspect of poor English.

In chapter 4.7 we present these eight different cases where U was recognized in association to another mineral or organic phase.

Line 427. Complete speculation. Delete.

I see the point. The sentence was deleted.

Figure 7. F doesn't convince me of a replacive relationship. The arrows seem to point to framboidal pyrite similar to that on the left of the image. Should be Framboids associated with organic matter. H - the label "U decreasing concentration gradient" is puzzling. Some analysis points are required to show this.

In F framboidal pyrite replaced organic matter. Then uranium replaced pyrite. We are witnessing the second process. We know that pyrite replaced organic matter at the first place because we can see the relic of the organic particle (vitrinite). Profiles with decreasing concentration gradients have been published in Rallakis et al., 2019.

Line 429. "As burial diagenesis is too low to envisage the reduction of U(VI) by carbonaceous moieties"?? I assume the authors are referring to temperature?

Yes this was about temperature, I rephrased the sentence.

Line 461. This relates to another publication?

I added more text to explain why I analyzed the REE spectra of uraninite. I have analyzed the REE patterns of uraninite in Zoovch Ovoo in order to compare it to the patterns

described in "Origin of uranium deposits revealed by their rare earth element signature" by Mercadier et al., 2011.

Line 506. "Radiation halos were identified in quartz grains, not in contact with phospho-coffinite cement. Keeping in mind that direct contact is needed between uranium minerals and quartz for alpha particles to penetrate the mineral lattice, this feature is evidence for pitchblende cement deposition around detrital grains followed by dissolution and redistribution." The logic of this statement is unclear and needs further explanation. As it stands it does not provide evidence.

In Meunier et al. (1990) it is stated that radiation halos are formed only if U-minerals are in contact with quartz grains. Today we observe halos in quartz rims and phospho-coffinite that is not in direct contact. Since phospho-coffinite is a late phase we may argue that uraninite was once in direct contact. Then it was redistributed as the roll-front evolved and later phospho-coffinite was deposited in the porosity that became available.

Line 673. "To our knowledge, these U concentrations are the highest reported in the literature (Rallakis et al., 2019)." First of all, "To our knowledge" is not necessary. There is no mention of what these concentrations are. This would help the reader to understand the argument, though I suspect that the argument has been made in the referenced publication and is only repeated here?

I agree that the "to our knowledge" is redundant.

Line 723. "Pyrite is a very efficient uranium reducing agent in Zoovch Ovoo (Rallakis et al., 2019), as shown by the very intimate association of pyrite with organic matter." This makes no sense whatsoever! One might reasonably argue that reducing conditions associated with the organic material (including bacteria perhaps) induced precipitation of pyrite? And this statement also implies that pyrite is more important in causing uranium precipitation than organic matter, which I suspect was not the author's intent.

I have rephrased this sentence to: Pyrite is an efficient uranium reducing agent in Zoovch Ovoo (Rallakis et al., 2019), and is intimately associated with organic matter.

Line 743. sub-oxic. Meaning what?

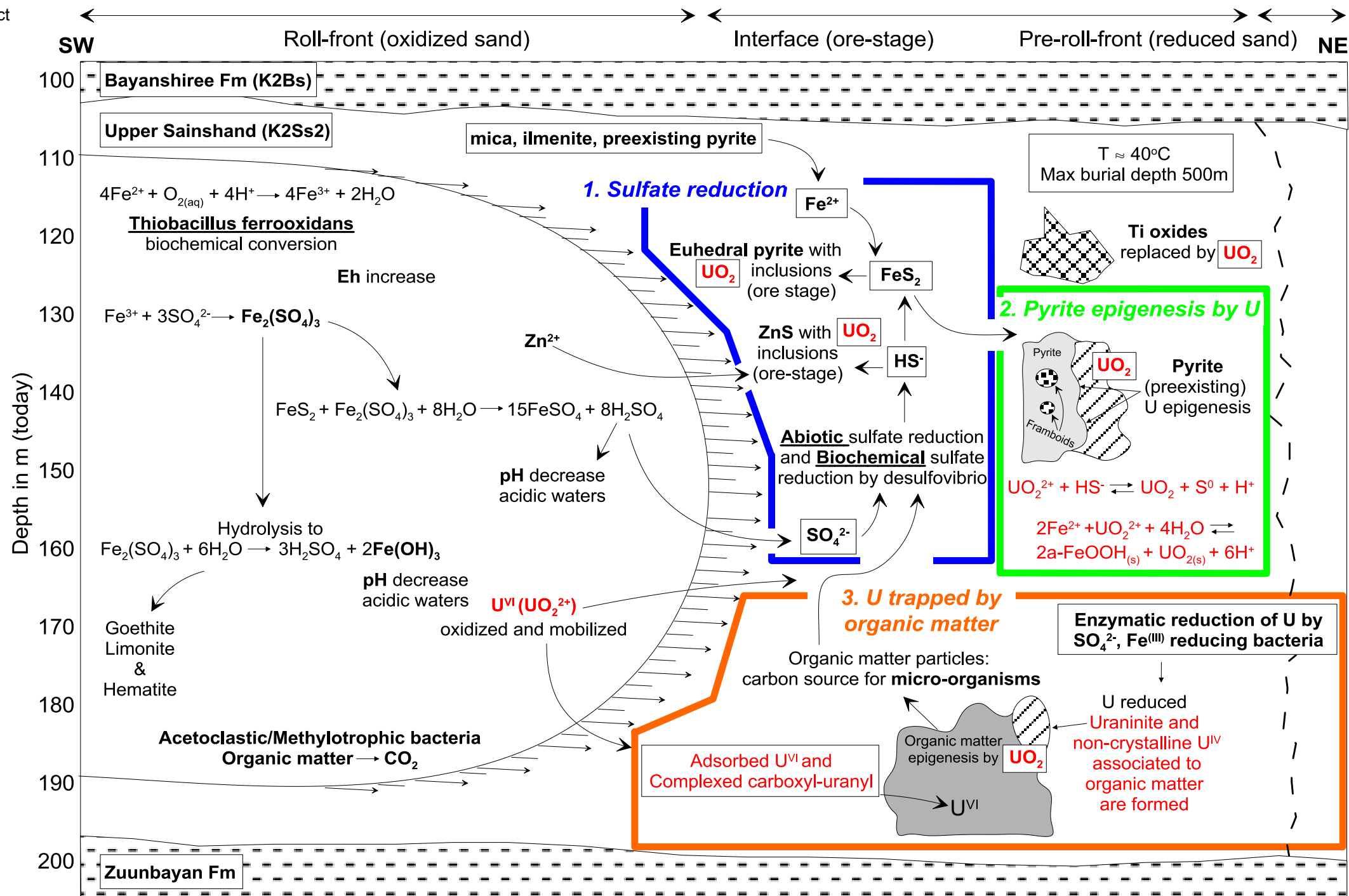
The term suboxic is used here to describe the zone that is ahead the oxidizing zone of the roll-front, where U-ore deposition and ore-stage sulfides precipitate.

Reviewer 2: Well done, thorough study of a complex system. I have made scattered suggestions, most editorial, using the sticky note feature in Acrobat.

Thank you for these corrections. You will find all my answers in your comments in the new revised manuscript.

Highlights

- Uranium occurs at Zoovch Ovoo very intimately associated with organic matter
- (Bio)-oxidation of pyrite liberates intermediate valence sulfur species
- U reduction through biomineralization by bacteria and fungi
- Continuous bacterial activity would increase the uranium concentration
- Significant reducing agents for uranium are micro-organisms and sulfides



Conditions for uranium biomineralization during the formation of the Zoovch Ovoo roll-~~front~~-front-type uranium deposit in East Gobi Basin, Mongolia

Dimitrios Rallakis¹, Raymond Michels¹, Michel Cathelineau¹, Olivier Parize²
and Marc Brouand²

¹Université de Lorraine, CNRS, CREGU, GeoRessources, 54504, Vandoeuvre-lès-
Nancy, France

²ORANO Mining, Le Prisme, 125 Avenue de Paris, 92320, Chatillon, France

Abstract

The Zoovch Ovoo uranium roll-~~front~~-front-type deposit is hosted in the Sainshand Formation, a Late Cretaceous siliciclastic reservoir, which constitutes the upper part of the post-rift infilling of the Mesozoic East Gobi Basin in SE Mongolia. The Sainshand Formation ~~corresponds~~ consists of to unconsolidated medium-grained sand, silt and clay intervals deposited in fluvial-lacustrine settings. The uranium deposit is confined within a 60-80 m thick siliciclastic sequence inside aquifer-driven systems. The overall system experienced shallow burial and was never subjected to temperatures higher than 40[°]C. This study proposes a comprehensive metallogenic model for this uranium deposit. Sedimentological and mineralogical observations from ~~the core~~ drill core samples to the microscopic scale (optical and ~~SEM~~ Scanning Electron Microscopy) together with in situ geochemistry of ~~main~~ newly ~~late-~~ formed phases (Laser Ablation-Inductively Coupled Plasma Mass Spectrometry ~~LA-ICP-MS~~, EPMA Electron Probe Microanalysis, ~~FT-IR~~ Fourier Transform-Infrared Spectroscopy) were considered for the reconstruction of the main stages of U trapping.

In the mineralized zone, the uranium ore is expressed as Ca-enriched uraninite (UO₂) and less commonly as Ca-enriched phospho-coffinite (U, P)SiO₄. Trapping mechanisms include i)

complexation (i.e. uranyl-carboxyl complexes), ii) adsorption on organic or clay particles) and
 iii) reduction by pyrite and by bacterial activity to amorphous uraninite. In all cases, the organic
 matter plays either the role of trap for uranium or nutrient for bacteria that can trap uranium
 through their metabolism. The low-shallow burial diagenesis conditions do not allow direct
 reduction of U(VI) by organic carbon. The $\delta^{34}\text{S}$ values of the iron disulfide are very diverse,
 fluctuating in extreme cases between -50 to +50‰, with an average $\delta^{34}\text{S}$ value for framboidal
 pyrite at 2‰, and -20‰ for euhedral pyrite. The positive and negative values reflect close
versus open fractionation systems, while BSR-bacterial sulphate reduction (BSR) is active
 during the whole diagenetic history of the deposit as an essential source of reduced sulfur.
 Therefore, using detrital organic matter as a carbon source, microorganisms play a significant
 role in uranium trapping, either as a direct reducing agent for uranium or pyrite formation, which
 will trap uranium redox driven epigenetic processes.

Keywords: roll-front, uranium, bioreduction, organic matter, sulfur isotopes, East Gobi
 Basin, Mongolia

1 Introduction

The Central Asia Uraniferous Province (CAUP), one of the most strategic areas in the world
 for uranium reserves, extends from Kazakhstan to the West towards the Transbaikalian region to
 the East (Dahlkamp, 2009; Le Goux et al., 2015; IAEA 2018). Significant roll-front deposits
 exist all over this region, examples include the Chu-sarysu and Syrdarya basins i.e. in
 Kazakhstan in the Chu-sarysu and Syrdarya basins (Aubakirov, 1998; Petrov 1998; Jaireth
 et al., 2008; Munara, 2012; Lach et al., 2015), the Songliao, Ordos and Erlian basins in China
in the Songliao, Ordos and Erlian basins (Huang Xian-Fang et al., 2005; Min et al., 2005; Cai
 et al., 2007; Bonnetti et al., 2015a,b; Cao et al., 2016; Akhtar et al., 2017; Bonnetti et al., 2017;
 Jiao et al., 2018; Zhang et al., 2018; Yue et al., 2019) and the Unegt and Zuunbayan basins
and in Mongolia in the Unegt and Zuunbayan basins (Le Goux et al., 2015; Grizard et al., 2018;
 Boissezon et al., 2020; Rallakis et al., 2019; 2020).

53 Although these roll-front type uranium deposits might appear similar in terms of geochemical
54 signatures and deposit geometry, there are significant differences in their paragenesis, in
55 terms of uranium ore habitus, associated elements and geometry, there are also significant
56 differences in their genetic mechanisms. The pre-ore uranium concentration in the sediments,
57 the amount of detrital organic matter, the nature of uranium reducing agents, microorganisms'
58 role, and uranium-hydrocarbon phases interactions may vary from one deposit to the other.
59 For instance, mineralization in the Chu-Sarysu basin in Kazakhstan occurs in Paleocene
60 continental arkosic sands deposited in fluvial settings, sourced from volcanic rocks (Aubakirov,
61 1998; Petrov, 1998; Munara, 2012). Uranium mineralization is associated with hydrothermal
62 and biogenic pyrite ~~The main facies associated with U mineralization is pyrite of biogenic and~~
63 ~~hydrothermal origin~~ (Lach et al., 2015). Although the proportion of organic matter in the
64 mineralized grey sandstones is low (generally 0.03-0.05% C), Petrov (1998) suggests that this
65 proportion is enough with a minor contribution of iron sulfides to produce large U-deposits in
66 sandstone. Later studies (Jaireth et al., 2008) indicate that the redox conditions were favoured
67 by the upward migration of gases from the oil field (including H₂S) located below the
68 Cretaceous sediments. ~~As in Kazakhstan,~~ U-deposits in sandstones located close to
69 hydrocarbon reservoirs were also identified in the Ordos and Songliao basins in China (Huang
70 Xian-Fang et al., 2005). The formation of uranium deposits in ~~formations low in the organic~~
71 ~~matter organic poor lithologies~~ has been attributed to the input of H₂S, along faults from deep
72 hydrocarbon reservoirs (Reynolds and Goldhaber, 1978). Yet, the role of hydrothermal fluid in
73 the systems is ambiguous and rarely proven, with the rare exception of deposits where fluid
74 inclusions attest to the circulation of hot brines, sometimes with hydrocarbons or gases (Zhu
75 et al., 2012).

76 Some of these deposits were intensively studied in the last decade, and several results point
77 out the contribution of biological activity within the sedimentary reservoirs to explain the U
78 reduction. For ~~instance~~ example, in the Nuheting deposit in the Erlian basin, hydrocarbons and
79 associated gases were invoked as potential reductants (Niu et al., 1995; Zhang and Ding, 1996)

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto

Commented [R1]: Reference added

Commented [R2]: Reference added

Commented [R3]: Added both references

cited in Bonnetti, 2013; ~~and~~ Bonnetti et al., 2015a). The data, however, do not support the hypothesis of hydrocarbons migrations as reducing agents for uranium mineralization. Thus, Bonnetti et al. (2015) indicated that the Nuheting deposit underwent three main stages of mineralization: (i) a synsedimentary/early diagenetic uranium concentration and mineralization, (ii) a late diagenetic *in situ* uranium remobilization and deposition on pyrite and (iii) epigenetic cementation. Another example is the Baxingtuo uranium deposit in the Songliao Basin. It is hosted in the Late Cretaceous Yaojia Formation in medium to fine-grained channel sandstone with abundant type III and IV kerogen detrital organic matter. In rare cases, uranium mineralization was attributed mostly to bacterial processes responsible for uranium reduction (Bonnetti et al., 2017).

The present paper aims to fully characterize the U-minerals ~~ores~~ and their relationships with organic matter and sulfides ~~to set up a paragenetic sequence.~~ Specifically, the petrography of the detrital and diagenetic phases as well as the crystal chemistry of the latter help to build the paragenesis ~~and identify the uranium mineralization episodes. The crystal chemistry of uranium phases reveals the presence of U-minerals, while the trace element content of pyrite seems to be a very effective index to distinguish between pre-ore and syn-ore pyrite generations. The stable isotopes, in particular the *in situ* $\delta^{34}\text{S}$ isotopic analysis of pyrite provide information on the origin of reduced sulfur, while its fractionation signifies the availability of reduced sulfur in the system during the history of the deposit. Organic petrography and Rock-Eval pyrolysis are used for the qualitative assessment of kerogen and its thermal maturity. By The combining the above it is possible to understand the mechanisms responsible for the formation of ore formation uranium mineralization and, while their interplay yielded a geochemical model for the Zoovch Ovoo deposit finally.~~

Commented [R4]: Yes Niu and Zhang and Ding are cited in Bonnetti

104 **2 Geological setting**

105 **2.1 The East Gobi Basin**

106 Mongolia is separated into four metallogenic provinces that host U mineralization, the Gobi-
107 Tamsag where the study area is located, the Khentei-Daur, the North Mongolian and the
108 Mongol-Priargun. These provinces host over forty U mineralization areas that differ in terms of
109 geological setting, mineralization type and age and associated minerals (Figure 1A, B;
110 Dahlkamp, 2009).

Commented [R5]: I used a new map of Mongolia where I draw the 4 metallogenic provinces based on Dahlkamp, 2009.

111 The East Gobi Basin is located in southeastern Mongolia (Figure 1). It includes four morpho-
112 tectonic elements: the Unegt ~~sub-basin, the and~~ Zuunbayan sub-basins ~~as shown on the map~~
113 ~~and, the Sainshand Khovsgol sub-basin and the and Khovsgol Sainshand sub-basins located~~
114 ~~SW and NE of the map, respectively~~ (Johnson, 2004; Prost, 2004). ~~The 700 km-wide by 300~~
115 ~~km-long northeast-southwest trending East Gobi Basin was formed during Mesozoic extension~~
116 ~~It is a northeast-southwest trending continental basin that extends for 700 km in E-W trend and~~
117 ~~300 km in the N-S (Meyerhoff and Meyer, 1987; Prost, 2004), formed by Mesozoic extension~~
118 ~~events (Meyerhoff and Meyer, 1987; Prost, 2004; Johnson and Ritts, 2012). The studied~~
119 ~~dataset originates from the The~~ Zuunbayan sub-basin, ~~which is NE-oriented, covers a surface~~
120 ~~area of 2000 km² and~~ hosts the Zoovch Ovoo uranium deposit (Figure 1C). ~~Although the East~~
121 ~~Gobi Basin's geometry is not very clearly defined, seismic surveys reveal two distinct~~
122 ~~depocenters (Figure 1).~~ The Mesozoic-Cenozoic sedimentary sequence is estimated to
123 approach about 4000 m in thickness. The granitic outcrops in the NE and S parts of the basin
124 are probably the quartz arenite sandstone sources (Prost, 2004). In the Gobi-Tamsag
125 province, U deposits are found within the Upper Cretaceous (Cenomanian) Sainshand
126 Formation from the Zuunbayaan sub-basin. This post-rift sedimentary infill of the East Gobi
127 Basin is composed of medium to coarse-grained sand, deposited in fluvial to flood-dominated
128 delta and lacustrine systems (Cardon et al., 2015; Le Goux et al., 2015).

Commented [R6]: I added this description and indicated their location on the map.

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto, English (United Kingdom)

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto, English (United Kingdom)

Formatted: Font:

Formatted: Font:

2.2 Tectonic history

The East Gobi Basin is a multiphase deformation area (plate interior poly-phase basin) that, according to recent studies and petroleum-exploration seismic profiles, was subjected to four cycles of deformation and subsidence (Prost, 2004; Johnson and Ritts, 2012; Heumann et al., 2014), lasting from Late Paleozoic to Cenozoic:

- Due to the Paleo-Asian Ocean's closure, the Late Permian post-collisional basin produced highly deformed and metamorphosed turbiditic sequences that are unconformably overlain by undeformed non-marine Permo-Triassic fluvial and alluvial sediments (Phase 1).
- ~~The~~ A Late Triassic major sinistral shear zone (East Gobi fault zone), in southern Mongolia that formed major foreland and intramontane basins along with thrust sheets that carried Precambrian and early Paleozoic carbonate klippe over Permian and Triassic units. Early Mesozoic transpressional foreland created by a major sinistral shear zone lasting until Late Triassic and "thrusting" Precambrian and early Paleozoic carbonate klippe (Phase 2).
- The Late Mesozoic rift basin, lasting from the Late Jurassic to Late Cretaceous, is marked by the development of high angle normal faults (Phase 3).
- The Late Cretaceous post-rift succession and the development of a strike-slip basin marked by the regional unconformity and basin inversion. Although the sediments overlying the Late Cretaceous are characterized as a post-rift thermal sag phase, there were probably left-lateral strike-slip faults developing during the Early Cenozoic (Phase 4).

Finally, the Mesozoic sequence is covered by Tertiary-Quaternary fine to coarse-grained alluvial sediments, which form deposits of up to 5 km long and 1-2 km wide. Uplift episodes during the Early Cenozoic are also likely as older units outcrop locally among the Tertiary-Quaternary deposits (Prost, 2004) and are probably linked to the initiation of the ~~The vertical~~

~~movements are probable due to the activity of the~~ Altyn Tagh fault in China and East Gobi
~~Faults~~ during Oligocene-Miocene (Johnson and Ritts, 2012).

2.3 ~~Litho~~Stratigraphy of the East Gobi Basin

The lithostratigraphy of the East Gobi basin is presented in Figure 2. The Paleozoic basement stratigraphy (Devonian-Permian) consists of metamorphosed Paleozoic arc-related volcanics and marine siliciclastics forming the Tavan Tolgoy Unit (Traynor and Sladen, 1995; Lamb and Badarch, 1997; Graham et al., 2001). It is overlain unconformably by a 1000-4000m thick continental sequence from Jurassic to Tertiary (Meyerhoff and Meyer, 1987; Prost, 2004). A hiatus of variable thickness exists between Permian and Middle Jurassic due to repeated episodes of block faulting and multiphase deformation (Johnson, 2004; Itterbeeck et al., 2005).

The Khamar Khovoor Formation was deposited during the Middle and -Upper Jurassic-times and is 750 m thick. The depositional setting at that time was paralic to marginal marine, with a combination of fluvial, lacustrine, deltaic and swamp-organic sedimentation. The fluvial character is expressed by braided rivers depositing sand and the paralic by dominant shale deposits. The Khamar Khovoor Formation forms a hiatus with the overlying Upper Jurassic (Tithonian-Kimmeridgian) Sharlyn Formation that consists of 200 m of well-defined braided fluvial sandstones, conglomerates and to a lesser extent finer sediments, as lacustrine shales (Graham et al., 2001; Prost, 2004). ~~Then a 300-700 m thick sequence consisting mainly of shales interbedded with coarser fractions (dark coloured sandstones, conglomerates, siltstones) and volcanics (red coloured tuffs, basalts) forming the Tsagaan Tsav Formation of Early Cretaceous (Valanginian) age.~~

This was followed by a 300-700 m thick sequence consisting mainly of shales interbedded with coarser fractions (dark coloured sandstones, conglomerates, siltstones) and volcanics (red-coloured tuffs, basalts) forming the Tsagaan Tsav Formation of Early Cretaceous (Valanginian) age. The Tsagaan Tsav Formation is composed of a fining upwards sequence of alluvial fan and braided stream deposits, which is topped by fine material deposited during flooding events (overbank deposits) and lacustrine facies (Graham et al., 2001; Johnson, 2004). The coarser

182 sandstone part of the Tsagaan Tsav Formation is the reservoir unit for the Tsagaan Els and
183 the Zuunbayan oil fields. The Zuunbayan Formation is Hauterivian to Albian and comprises
184 970 m of non-marine poorly compacted sandstones, interbedded with shales and volcanic tuff.
185 The Zuunbayan Formation is divided into three different units: i) the organic-rich basal unit,
186 which contains bituminous shales considered as potential source rock, ii) the central and upper
187 units, which include coals and sandstones with channel geometry along with basaltic flows
188 (Prost, 2004).

189 Within the Zuunbayan sub-basin, the Sainshand Formation hosts the ~~studied-Zoovch Ovoo~~
190 uranium deposit, ~~namely Zoovch Ovoo~~ (Parize, 2013; Le Goux et al., 2015). The Sainshand
191 Formation is of Cenomanian age, and its thickness varies between 100-350 m. The sub-units
192 reflect different lacustrine and alluvial sedimentation cycles, setting up a combination of
193 conglomerate, sand, silt, and clay sediments (Dahlkamp, 2009). The Sainshand Formation is
194 ~~overlayed-overlain~~ by the Late Cretaceous (Santonian-Turonian) Bayanshiree Formation,
195 consisting mainly of reddish to greyish shales with minor ~~input~~ sandstones with channel-
196 shaped geometry (Graham et al., 2001; Johnson, 2004). The thickness of the next two Late
197 Cretaceous lacustrine coarse clastic units, namely the Santonian-Campanian Baruungoyot
198 Formation and the Campanian-Maastrichtian Nemegt Formation, is variable. The Upper
199 Cretaceous post-rift sequence was deposited ~~during-ain a -sag -basin period story~~ (sediment
200 starvation) and was affected ~~(by strike-slip tectonics)-during later in -Cenozoic~~. The series dip
201 significantly along the faulted boundaries, whereas they are sub-horizontal in the ~~core of the~~
202 syncline ~~heart~~. Locally, Tertiary and Quaternary strata are present due to vertical movements
203 of the East Gobi Fault Zone (Johnson and Ritts, 2012; Heumann et al., 2014). They are
204 generally undifferentiated with very fine to coarse sediments that ~~top-up~~ unconformably ~~overlie~~
205 the Late Cretaceous strata (Prost, 2004).

206 In this tectonic framework, the burial history of the regional area of Zoovch Ovoo ~~was based~~
207 ~~on Graham et al. (2001), Prost (2004), Rallakis et al. (2019; 2020) and as well as the~~

geothermal gradient ~~of~~ (4.5°C/100m) were based on Graham et al. (2001), Prost (2004), Rallakis et al. (2019; 2020).

3 Materials and methods

3.1 Uranium ~~location~~ in the Sainshand Formation – Sampling

As the uranium distribution ~~assimilates to roll-front systems~~varies, with the development of redox ~~fronts~~fronts in roll-front systems, samples were recovered from drill-cores along profiles crossing oxidized, active roll-front as well as reduced zones (Figure 3). ~~examples of which are provided in Figure 3.~~ The locations of Profile 1 and 2 in ~~are~~ the roll-front ~~is~~are indicated in Figure 1. In this sedimentological framework, the sand dunes of the lacustrine system serve as uranium reservoirs, and uranium mineralization is confined in between the coarse (sand, conglomerate) and fine (silt, clay) units. The Zoovch Ovoo depocenter is mostly composed of unconsolidated sediments, such as silts and sands. Few consolidated facies are clay matrix-supported, and less commonly dolomite-cemented sandstones (Figure 4). The Sainshand Formation features record depositional conditions ranging from fluvial to flood-dominated delta and lacustrine systems (Dahlkamp, 2009; Parize, 2015; Le Goux et al., 2015).

3.2 Petrography and ~~crystal~~ chemistry

The ~~morphology, nature and composition~~petrographic characteristics of the different types of ~~facies~~minerals were studied in detail on polished thin sections (~30 µm thick), using optical microscopy in transmitted and reflected light modes. The two methodologies used for their ~~sample~~ classification were based on Dott (1964) for petrography and Wentworth (1922) for granulometry.

A PHILIPS XL30 Scanning Electron Microscope (SEM), equipped with an energy dispersive spectrometer using a Si-(Li) semiconductor detector, coupled with a HITACHI S-4800 scanning electron microscope (SEM), to ~~establish~~better observe the mineral paragenesis.

Commented [R7]: This is an accurate sedimentological description of the U-reservoir.

Electron ~~microprobe~~^{probe} microanalyses were carried out using a CAMECA SX100~~CAMECA~~. The calibration was made ~~calibrated~~ using natural and synthetic oxides or alloys (orthoclase, albite, MnTiO₃, wollastonite, hematite and olivine). The analytical conditions were: 10 nA current, accelerating voltage of 15 kV, 10 s counting time for (K, Na, Ca), 20 s for (Al, Fe, Mn) ~~and~~, 40 s for (Mg ~~and~~, U).

Formatted: Font: (Default) Arial

The mineralogical analyses (XRD) were performed on bulk rock powder of carbonate cemented sandstones and on oriented clay extracts using a Bruker D2 Phaser equipped with a LynxEye XE-T detector. The interpretation software package used for the evaluation of the diffractograms was DiffraC.Suite along with EVA.

For the bulk rock geochemistry, the samples were initially dissolved in a microwave oven Milestone MLS 1200 Mega, using a solution of HF-HClO₄-HNO₃-H₂O₂ (Cheburkin and Shotyk, 1996). The concentrations of the major elements (Ca, Fe, K, Mg and Na) were ~~calculated~~ ^{determined} by ~~applying~~ Atomic Absorption Spectroscopy (AAS); ~~whereas the~~ trace elements (As, B, Ba, Co, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Rb, Sr, U, V and Zn) were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

3.3 Stable isotopes analysis

~~The in~~ⁱⁿ situ $\delta^{34}\text{S}$ isotopic analysis was performed on samples containing different pyrite habitus. The analytical instrument used was a ~~Cameca~~^{CAMECA} IMS 1270 ion probe at the Jean Lamour Institute of the School of Mines (Nancy). The results were normalized using an in-house pyrite standard (Spain) and then treated using the formula described in Kitayama et al. (2012). The thin sections were gold coated before mounting. During the analysis, the pyrite crystals were sputtered with a Cs⁺ beam source of 2-3 nA intensity inside a vacuum chamber, with 10 kV acceleration voltage. Each spot analysis was performed under 40 cycles of 5 seconds each.

Formatted: Not Superscript/ Subscript

3.4 Rare earth elements (REE) in uranium minerals and trace elements in pyrite

Rare Earth Elements (REEs) of uranium minerals were analyzed by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at GeoRessources (Nancy). Laser ablation was performed with a 193 nm GeoLas Pro ArF Excimer laser (Microlas®, Göttingen, Germany) equipped with beam homogenization optics by focusing the beam at the sample surface with a constant fluency of 10 J/cm² and constant repetition rate of 5 Hz. Helium was used as a carrier gas to transport the laser-generated aerosols from the ablation cell to the ICP-MS. Ablated material was analyzed by an Agilent 7500c Quadrupole ICP-MS (Agilent®, Santa Clara, California) equipped with an Octopole Reaction System with enhanced sensitivity optional lenses (Cs type, Agilent). The certified glass standards NIST610, NIST612 and NIST614 SRM, were used as reference materials (concentrations from Pearce et al., 1997) for the calibration of the LA-ICP-MS. The protocol for routine analysis of REE in uranium minerals was checked using an in-house reference uraninite standard. Absolute concentrations and detection limits were obtained from the equations developed by Longerich et al. (1996).

The suite of elements analyzed by LA-ICP-MS was La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Detection limits range from a few ppm for Ce to down to 0.5 ppm for heavy rare earth elements. The REE spectra were normalized ~~versus-to~~ the chondrite standard (Masuda et al., 1973; Anders and Grevesse, 1989).

The ~~analyzed-elements~~ elements analyzed by LA-ICP-MS were V, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Pb) in pyrite and Na, Mg, Si, P, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Ba and Pb in U-bearing minerals.

3.5 Organic matter

The macerals were identified using oil immersion microscopy (nomenclature after ICCP, 1963, 1971, 1975, 1998, 2001; Sýkorová et al., 2005; Suárez-Ruiz et al., 2012; Pickel et al., 2017). In core intervals enriched in organic carbon, coal is present as thin laminae within clays or is

dispersed inside carbonate--cemented or un-cemented sands. Mechanical concentrates representing organic matter (40-70 mg), crushed down to 45 µm, of 14 samples namely, 9 sands with coal fragments, 3 organic matter-rich clays and 2 carbonate-cemented sandstones with organic matter were selected for Rock-Eval pyrolysis to determine their main geochemical parameters (Espitalie et al., 1985). The analyses were carried out in the Institute of Earth Sciences in Orléans (ISTO), France.

4 Results

4.1 Nature of the sediments of the Sainshand Formation at the Zuunbayan sub-basin

~~The Zoovch Ovoo depocenter is mostly composed of unconsolidated sediments, such as silts and sands. Few consolidated facies are clay matrix supported, and less commonly dolomite cemented sandstones (Figure 4). The Sainshand Formation features attest of depositional conditions ranging from fluvial to flood-dominated delta and lacustrine systems (Dahlkamp, 2009; Parize, 2015; Le Goux et al., 2015). The studied dataset corresponds to the~~The upper part of the Cenomanian Sainshand Formation was sampled for this study. The ~~lithofacies-lithologies~~ encountered in the Zoovch Ovoo depocenter have a vast granulometric range from silty clays to gravels ~~when considering for~~ the unconsolidated facies and from silty claystones to micro-conglomerates ~~when considering for~~ the cemented facies. Based on 93 samples analyzed by point-counting, the ~~lithofacies-lithologies~~ encountered in Zoovch Ovoo were by order of abundance: a) 47% sands to sandstones with matrix content between 15-75%, b) 32%, sands with less than 15% matrix, c) 10% pyrite--cemented sandstones, d) 5% sandstones cemented by iron oxides, e) 3%, silty clays and f) 3%, carbonate--cemented sandstones (Figure A1). Based on the ICP-MS bulk rock data and the equations from Herron (1988), the lithologies ~~encountered in the Sainshand Formation at Zoovch Ovoo~~ are classified as sub-arkoses, arenites and silty claystones (Figure A1: Clustered bar chart indicating the

Commented [R8]: Added a clustered bar chart for the % distribution of lithofacies in the Appendix as Figure A1.

Formatted: Font: Not Bold

Formatted: Font: Not Bold

lithofacies distribution in Zoovch Ovoo, expressed in percent, as identified by point-counting method on the basis of 97 samples.

Figure A24 in the annex).

Two distinct units are distinguished according to identified in the sedimentological study (Parize et al., 2013). The first lithological unit consists of finely laminated to stratified homolitic monomict to heterolitic polymict silty to sandy-clay, corresponding to varves. The second unit is coarse-grained, sandy to (micro)-conglomeratic, homolitic monomict, with granules of intraclasts originating from the first unit. The coarse sediments correspond to sudden episodes (flood) indicate sudden episodes of sedimentation (floods). Sand dunes are intercalated between the two units that serve as uranium reservoirs, and uranium mineralization is confined in between the coarse (sand, conglomerate) and fine (silt, clay) units.

Detrital quartz, feldspars, biotite, muscovite and very often commonly lithic elements are the main detrital grains or clasts. Feldspar grains are often chemically altered by sericitization. Besides some sericitized feldspars, detrital grains are not chemically altered. Their shapes range from angular to sub-rounded with a maximum grain size of about 1mm (Figure 5). Clay intraclasts up to pebble size are often present in sand layers and detrital rounded dolomite grains. Dolomite is microcrystalline and often associated with siderite (Rallakis et al., 2020).

The sandstones are, for the most part, composed of quartz (40 to 80%), feldspars as K-feldspars (microcline, orthoclase, some % to 25%) and plagioclases (5 to 20%), minor phases (apatite, ilmenite) and a few accessories from of magmatic origin (monazite, zircon, xenotime, rutile, and anatase). The clay/phyllosilicate fraction (biotite, chlorite, muscovite in the coarse-grained fraction) is not abundant and not systematically present. Some tests on the clay mineralogy were conducted by means of X-Ray Diffraction. The analysis was repeated twice, one before (air-dried) and one after ethylene-glycol treatment, since swelling clays were identified (Figure A3 in the annex). It was concluded that the predominant clay fraction is

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Commented [R9]: This sentence was added in response to the first comment of the next section.

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto

Formatted: Default Paragraph Font, Font: (Default) Arial

smectite (recognized by the typical swelling at 14-17 Å followed by kaolinite. In total 6 clay samples were analyzed, revealing the same pattern.

~~The predominant clay fraction is smectite, based on X-Ray diffraction analysis.~~ The consolidated lithologies are only ~~some a few~~ dm thick and correspond to dolomite and pyrite cemented sandstones, the cement accounting for 30% of sandstone volume on average. Four successive generations of dolomite are distinguished (Rallakis et al., 2020): type I (microcrystalline, pre-roll-front), type II (euhedral, pre-roll-front), type III (active roll-front) and type IV (post-roll-front).

Organic matter as detrital coal particles is widespread in all ~~the above-described~~ lithologies. The organic matter can be found as dispersed particles ~~inside the sands~~, silt, and clay or concentrated within sandy laminae (Rallakis et al., 2019). Coal layers are absent ~~inside~~ the reservoir zone, and the organic matter contained in the sediments occurs as detrital particles deposited ~~following along~~ the sedimentary bedding. The coarse, angular and poorly sorted organic particles are linked to medium-sized lithologies (coarse to fine-grained sands). Organic matter particles encountered in fine clay (organic-rich) layers are better preserved ~~and linked to calm depositional conditions under less oxygenated conditions. They are related to calm depositional conditions under less oxygenated conditions and.~~ Well preserved phytoclasts, such as root remains, are often associated with fine-grained organic-rich lithofacies, which could indicate higher plants that grew within the depositional setting (no significant transport).

4.2 Roll front mineralogy and zonation

Uranium mineralization is confined ~~in to~~ sand dunes between the coarse (sand, conglomerate) and fine (silt, clay) units. In the oxidized part of the roll-front, Fe-hydroxides and oxides, namely limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$), goethite ($\text{FeO}(\text{OH})$), and hematite (Fe_2O_3), are present. Entire layers of ~~originally~~ reduced ~~grey~~ claystone can become partially to totally red due to ~~the introduction of~~ iron oxides ~~with the oxidizing roll-front waters~~ (Figure 4).

Formatted: Indent: First line: 0.2"

In the reduced part, euhedral pyrite is the most common authigenic mineral and was recognized in three forms, as framboids, as concentric overgrowth formed around framboids and as euhedral crystals (cubic). In a few cases, the polymorph of FeS₂, marcasite can be identified, developing locally around euhedral pyrite.

Sphalerite is the second most common sulfide after pyrite and was encountered ~~quite often~~ in many mineralized samples. Other sulfides include galena (PbS), greenockite (CdS) and acanthite (Ag₂S). These associated minerals are found rarely, and ~~they are most of the times~~ mainly contained in uranium-rich samples. Furthermore, barite (BaSO₄), gypsum (CaSO₄·2H₂O) and the selenides, namely, clausthalite (PbSe) and stilleite (ZnSe), were recognized in minute quantities. Native selenium is often found associated with organic matter, mainly contained inside cell-walls.

4.3 FeS₂ petrography

A detailed study of the petrographic relationships between FeS₂, detrital elements and other diagenetic mineral phases allowed us to identify several ~~habitus~~ of pyrite: i) isolated framboids within the mineral network, ii) framboids within organic matter particles, iii) concentric overgrowth of framboids, iv) framboids embedded within cubic (euhedral) pyrite, v) series of cubic (euhedral) pyrite, vi) isolated euhedral pyrite, vii) marcasite on isolated euhedral pyrite and viii) framboidal and euhedral pyrite inside ~~a~~-post-uranium dolomite ~~generation~~.

The pyrite ~~habitus-habits~~ allowed us to identify a pyrite paragenetic succession (Figure 6). ~~Seven-Five~~ different FeS₂ (mainly pyrite) were recognized in the following chronological order: formation stages were recognized, namely: i) framboidal pyrite ~~1~~, ii) concentric overgrowth, iii) euhedral pyrite 1 (pre-ore), iv) marcasite and, v) euhedral pyrite 2 (ore-stage) often containing pitchblende-uraninite (UO₂) micro-inclusions, ~~vi, vii, framboidal and cubic pyrite embedded in anhedral (type IV) dolomite cement.~~

The first euhedral pyrite generation, which is formed during a pre-ore stage, ~~presents-shows~~ corrosion features, hence suffered destabilization by circulating fluids (Figure 7A, B). The

Formatted: Subscript

Formatted: Subscript

corrosion is lacking ~~in-from~~ the second euhedral pyrite generation, ore-stage pyrite, which, on the contrary, presents well-developed cubic crystals and may contain uraninite micro-size inclusions (Figure 7C, D). ~~Some pyrite generations appear to be exclusively associated with a post-uranium deposition dolomite cement (type IV dolomite in the paragenesis).~~ Marcasite was identified as pre-ore, precipitating directly after euhedral pyrite generation 1 (pre-ore). ~~Two sphalerite generations were also recognized~~ Sphalerite can contain pitchblende as fracture-filling cement or as spherical micro-inclusions. It definitely postdates the euhedral pyrite that does not contain uranium inclusions but is probably also post-diagenetic with regards to the pyrite that contains uranium inclusions, according to petrographic observations. Sphalerite is also separated in two categories, the Cadmium rich and the Cadmium poor with the Cd concentration in the first being up to 14 wt% and down to 3 wt% in the latter. Both sphalerite types may contain pitchblende inclusions.

Framboidal pyrite is ~~very frequently~~ commonly found inside or at the rim of organic particles, isolated or in groups (polyframboids). ~~Very often~~ Typically, the cell-lumens are used as nucleation sites controlling the morphology of the growing crystal. The degree of epigenetic replacement of organic matter by framboids and their overgrowths (concentric and euhedral pyrite generation 1) vary from a few dispersed framboids to ~~the~~ full replacement. Pyrite has a higher affinity with the maceral collotelline (fused homogenous cell walls without defined cell structure) compared to the maceral telinite (fully or partially fused cell walls) or corpogelinite (discrete homogenous vitrinitic bodies representing the infilling of cell lumens). Even when the internal part of the ~~cell-cell~~ walls is empty, i.e. fusinite, the framboids use it as a nucleation site and grow until they reach the borders of the cell-walls that act as barriers to ~~their~~ further crystal growth. Eventually, when uranium enters the system, the framboids and their overgrowths that have previously replaced organic matter will be gradually replaced by uranium. This epigenetic process is well demonstrated in Figure 7E, F.

4.4 Trace elements ~~of in~~ FeS₂

~~Examples of different forms of pyrite, pyrite associated with U cement, and sphalerite were analyzed for trace elements by LA-ICPMS. The specific geochemical features of the various habitus of pyrite were determined by LA-ICP-MS analysis. In addition to the habitus described above, specific pyrite associated with U cement was distinguished, and few sphalerite occurrences.~~ The concentric pyrite overgrowth could not be analysed as a separate phase from the framboidals due to ~~its small thickness, smaller than the laser beam-analytical limitations of the laser beam.~~

Vanadium and Zn concentrations in all pyrites are usually below 50 ppm and sometimes reach 200 and 100 ppm, respectively. Mo concentrations are more variable, from below detection limit (1 ppm) to up to 3300 ppm.

Copper contents of framboidal pyrite range from 20 ppm up to 1000-3000 ppm. ~~Cu~~-Copper is below 100 ppm for the other pyrite types but can occasionally reach up to 500 ppm. Selenium is usually below the detection limit, but in some instances, both in framboidal pyrite and the other types, it can reach 2000 ppm. Cadmium and Sb are most of the times below 100 ppm. Lead (~~Pb~~) was detected in many different concentrations up to 6600 ppm and may correspond partially to radiogenic Pb. The geochemical plot of Co and Cd plot (Figure 8) distinguishes the different sulfides groups. Pyrite not associated with uranium is depleted in both Co and Cd, irrespective of their morphology. On the contrary, pyrites associated with uranium show an enrichment trend in ~~Co~~-Cd (from a few ppm to 90 ppm) and ~~Cd~~-Co (from a few ppm to 5500 ppm). The euhedral pyrite associated with marcasite contains around 1000-3000 ppm ~~Cd~~-Co and high ~~Co~~-Cd contents in between 100-190 ppm, while marcasite itself has low contents in Cd and Co. Finally, the euhedral pyrite associated with sphalerite has a low ~~Co~~-Cd concentration but up to 10 000 ppm of ~~Cd~~Co, as sphalerite.

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto, English (United Kingdom)

Formatted: Font: (Default) Arial, 11 pt, Font color: Auto, English (United Kingdom)

Commented [R10]: By mistake I wrote Cd instead of Co and vice versa. Same goes for the diagram. Thank you for noticing.

4.5 Isotopic chemistry - $\delta^{34}\text{S}$ of pyrite

The *in-situ* micrometer scale $\delta^{34}\text{S}$ analyses were performed on the various pyrite habits described above (Figure 9). The distribution of all the framboidal pyrite occurrences for $\delta^{34}\text{S}$ (n=22) ranges between -40 and +52‰. The absolute distribution of $\delta^{34}\text{S}$ of all the euhedral/cement pyrite (n=34) ranges from -50 to +34‰. More specifically, Uranium-uranium-associated pyrite (ore-stage pyrite) $\delta^{34}\text{S}$ ranges between -42 and -22‰. Data for framboidal and euhedral pyrites are overlapped over a vast range of values. The distinction between framboidal and euhedral pyrite is more pronounced for the Only extreme values ~~seem specific~~, as the highest (positive) values were obtained in framboids and the lowest (negative) values in euhedral pyrite (Figure 9 ~~Figure 10~~). In general, the framboids tend to be slighter heavier in $\delta^{34}\text{S}$ than euhedral or cement pyrite. This feature is even more ~~pronounced-apparent~~ for framboids associated with organic matter ($\delta^{34}\text{S}$ ranges between +5 to +55‰).

4.6 Organic matter

The macerals identified in the Zoovch Ovoo sands using oil immersion microscopy are presented in Figure 11. Most of the organic matter is, in general, highly altered due to oxidation and weathering, inherited by sedimentation or ~~induced-introduced~~ by the roll-front waters. The kerogen is mainly of type III (vitrinite) and type IV (inertinite). Few occurrences of type II (liptinite) and cutinite could be recognized (Rallakis et al., 2019).

In terms of Rock-Eval analysis (Table 1 and Figure A52), all kerogen samples studied present a very low Hydrogen Index and a linear trend for the Oxygen Index, indicating type III (vitrinite) and IV (inertinite) kerogens. At ~~sample~~ whole-rock scale, since uranium is very often associated with organic matter particles, an attempt was made to correlate the geochemical composition of kerogen with uranium content expressed by radioactivity (counts per second using a ~~Radiagem SPP2 detector~~ Saphymo SPP2-Geiger-Müller counter). Indeed, uranium can significantly modify kerogen's geochemical composition (Rouzaud, 1980; Jaraula et al., 2015; Schulz et al., 2018; Zhang et al., 2019). Alteration processes that affect the organic matter associated to uranium deposits include weathering (surface), meteoric water influx

Formatted: Font: 11 pt

(leaching by oxygenated waters), bacterial alteration and radiolysis (Landais et al., 1987; Forbes et al., 1988; Landais, 1996). As a result, the organic matter in U-deposits shows abnormal values which do not reflect their origin or thermal maturity. In other words, it displays very low HI and progressively higher OI due to radiolysis and probably due to alteration/oxidation processes; i.e. Tmax 420-450°C. However, In Zoovch Ovoo uranium content does not seem to be directly related to the Oxygen Index (Figure A4). However, as the radioactivity measurements were performed at the core scale, they may not represent the uranium concentration in the specific organic particles analyzed by Rock-Eval.

4.7 Petrography of uranium minerals

Uranium crystals were recognized in three forms: i) As independent spheres at the size range of 1 µm, ii) as elongated flakes iii) as large aggregates that resemble epigenetic replacement features of former organic matter particles, pyrite crystals or Fe-Ti oxides (Figure 12). Uranium can be contained in organic matter (OM) from very low (0.5 wt%) to very high concentration grades (about 80 wt%). In the last case, uranium replaces OM while preserving primary maceral textures. Isolated inclusions of uranium oxides are also found inside sphalerite and in one of the euhedral pyrite generations. At a lesser degree, U-oxides were also seen as dispersed inclusions within the clay matrix, deposited in the intergranular porosity pores of dolomite-dolomite-cemented sandstones, within the crystal porosity fractures of feldspar grains and in as epigenetic replacement of pyrite. It also has the potential of U-oxides can also totally replacing-replace Fe-Ti oxides while preserving the former mineral texture.

Based on these observations, it was possible to identify eight different types of uranium occurrences from the studied dataset.

4.8 Geochemistry of uranium

a. The (U+Ca)-Si-P ternary diagram

Analyses of representative of U-phases are plotted in the ternary diagram of P_2O_5 - UO_2 - SiO_2 (Figure 13) as a function of their host phase: U-rich organic matter; U-replaced organic matter;

Commented [R11]: Here I am referring to the morphology/shape of the crystals

489 U-replaced Fe-Ti oxides; U associated to subhedral dolomite cement; U associated with pyrite
490 cement; U associated with anhedral dolomite; U in euhedral (cubic) pyrite; U associated to
491 corroded pyrite cement; U in sphalerite and finally U in a clay matrix.

492 Most of the data are distributed close to the pitchblendeuraninite endmember, with some P
493 enrichment which causes a slight deviation from the stoichiometric formula UO_2 . Other
494 analyses plot close to the phospho-coffinite stoichiometry, yet with slight P deficiency, and are
495 interpreted as Phospho-coffinite. Pure coffinite is absent, and there is no continuous set of data
496 from pitchblendeuraninite to phospho-coffinite, suggesting the absence of an overall
497 pitchblendeuraninite to coffinite transformation. U in clay matrix shows anomalous enrichment
498 in SiO_2 due to analytical interference with phyllosilicates. P_2O_5 content tends to indicate that
499 the composition is similar to the samples plotting below phospho-coffinite composition (non-
500 stoichiometric phospho-coffinite described above).

501 b. The relationships between U and organic matter

502 The organic matter at Zoovch Ovoo is derived from land plants and occurs as detrital particles
503 concentrated into clay layers, clay intraclasts or sandy laminae. Biological features of the
504 particles are preserved depending on their transportation (proximal or distal origin). The
505 thermal maturity of the organic matter is very low (peat to lignite stage). In the studied samples,
506 U is intimately associated with organic matter. Very high concentration (up to 20 wt%) with no
507 expression of uranium minerals was found in macerals (Rallakis et al., 2019) (Figure 14).
508 Organic particles conserving their textural features are in some cases entirely replaced by U-
509 oxides. ~~Although EXAFS data are lacking, the most likely U form is uranyl carboxyl groups.~~

510 Also, UO_2 can entirely replace organic matter particles with partial preservation of organic
511 structure (suggesting epigenesis). As burial diagenesis is too low to envisage the reduction of
512 U(VI) by carbonaceous moieties (maximum temperature in the reservoir < 40°C), the role of
513 micro-organisms for the reduction of U(VI), either directly through their physiological activity or
514 by providing, reduced sulfur could be inferred. Finally, Fe(II) carboxylates were also considered
515 as possible reducing agents (Boyanov et al., 2007).

Formatted: Subscript

b. Geochemistry of uranium – REE patterns

The REE pattern of the uranium minerals hosted in particular type of deposits i.e. roll-front, volcanic related, vein type and others may provide information linked to their genetic mechanism, thus permitting classifications in salinity, temperature and source. This approach became possible by studying and comparing the REE patterns of major uranium deposits worldwide for which the genetic mechanism is already known i.e. roll-front, volcanic-related, unconformity-related, intrusive etc. (Mercadier et al., 2011). The REE content of uraninite (UO₂) in Zoovch Ovoo was studied relative to different occurrences, i.e. (A) UO₂ replacing organic matter, (B) UO₂ associated with pyrite and (C) UO₂ in a clay matrix. The REE content was measured using LA-ICP/MS (Figure A4A5), and the data were normalized relative to chondrite (Anders and Grevesse, 1989). In all cases, the REE concentrations range between 10³-10⁴ that of chondrite. Overall, two REE profiles were distinguished: one LREE enriched for the UO₂-organic matter and UO₂-pyrite and another HREE enriched for the UO₂-organic matter and UO₂-clay matrix. Both types of REE profile show a significant negative anomaly for Eu.

Comparing the average REE concentrations on UO₂ crystals and the bulk rock REE concentration (Figure A53), it appears that the average spectrum acquired on UO₂ is approximately 100 times richer in REE than the bulk rock. Furthermore, the average spectrum of UO₂ shows enrichment in HREE, while bulk rock data show the opposite trend. Both cases show a significant negative Eu anomaly. By comparing our data with Mercadier et al. (2011) it could be concluded that there is a good fit between the REE spectra of Zoovch Ovoo and the roll-fronts of Kazakhstan. The water source in the latter is meteoric, the U-source is monazite and the temperature of formation does not exceed 50°C.

Commented [R12]: In reply to the comment of JMH, I have analyzed the REE patterns of uraninite in Zoovch Ovoo in order to compare it to the patterns described in "Origin of uranium deposits revealed by their rare earth element signature" by Mercadier et al., 2011.

5 Discussion

5.1 Mineral paragenesis in Zoovch Ovoo

The complete sequence of paragenesis from sedimentation through early diagenesis, roll-front formation, to late diagenesis processes ~~at the origin of the whole series of minerals at~~ Zoovch Ovoo is summarized in Figure 15.

Early diagenetic stage

The organic matter observed in Zoovch Ovoo sediments is detrital and comes from two sources, one distal and one proximal, as suggested by the organic particles' preservation status. The low burial temperature conditions lead to the organic matter's low thermal maturity, which reached the lignite stage ($\%R_r \approx 0.4$; Rallakis et al., 2019).

Detrital sediments are neither affected by diagenesis nor by cementation. The dolomite cemented sandstone layers are an exception and their formation is linked to proto-dolomite deposition (Rallakis et al., 2020).

Dolomite types I (microcrystalline) and II (euhedral) were formed during early diagenesis and are associated with siderite. Siderite is the earliest expression of reduced iron implicated in diagenesis, indicating reducing conditions in the absence of a reduced sulfur source. The appearance of the first framboidal pyrite generation is diagnostic of the triggering of bacterial sulfate reduction. The overgrowth of pyrite and dolomite and the formation of the first euhedral pyrite generation and marcasite also belong to the pre-ore stage. Sphalerite 1 occurs after marcasite and witnesses-marks the input of Zn enriched waters.

Effect of roll-front waters

The partial dissolution of the dolomite I and II due to the reactivity with the roll-front waters is responsible for forming secondary porosity and is followed by the formation of subhedral (type III) dolomite (Rallakis et al., 2020). The roll-front also affects the first euhedral pyrite and sphalerite generations, causing their epigenetic replacement by UO_2 . ~~On the~~

~~contrary~~Furthermore, both the second euhedral pyrite and sphalerite generations are co-genetic to the first uranium precipitation episode since they contain ~~pitchblende~~uraninite inclusions (~~pitchblende~~-uraninite 1). The first uranium episode refers to the incipient stages of U precipitation, followed by the second uranium episode, which refers to the massive introduction of U in the system (~~pitchblende~~-uraninite 2). During the second U episode, ~~pitchblende~~uraninite tends to be accumulated as follows:

- i. as uranium oxides at the rims of the organic particles (UO₂): decreasing concentration gradients towards the inner part of the particles are observed, but the full replacement of the organic particle is possible.
- ii. as uniform cement inside the clay matrix, ~~preferably~~-preferentially on parts that were previously ~~pyrite~~-pyrite-cemented.
- iii. in the intergranular porosity between the detrital grains or in the secondary porosity caused by dolomite dissolution.
- iv. and finally, by epigenesis of the first pyrite and sphalerite generations and the pyrite associated with organic matter.

Late diagenetic stage

The late diagenetic stage is characterized by the formation of anhedral (type IV) dolomite, precipitated from formation fluids very lean in REE. The strong negative Eu anomaly of this anhedral dolomite (Fowler and Doig, 1983; Rallakis et al., 2020) and the newly formed framboidal and euhedral pyrite found inside its lattice indicate post-roll-front reducing conditions, most likely during the uplift stage (Rallakis et al., 2019). Furthermore, type IV dolomite cement was confirmed in samples collected from the area outside the roll-front. Anhedral dolomite is therefore disconnected from the roll-front influence. It is also found in coarse to micro-conglomeratic lithologies suggesting a link with high permeability layers, in contrast with dolomite type I and II present in fine-grained sediments.

During late diagenesis, phospho-coffinite and quartz cement (authigenic quartz) formed locally, indicating mobility of Si and P from unknown sources (Figure 13). Mobilization of

phosphorus may be linked to bacterial activity. Indeed, previous studies (Gächter and Meyer, 1993; Hutchens et al., 2006; Bonnetti et al., 2015b) have shown that microorganisms are responsible for the release of P from organic compounds as well as from the dissolution of apatite during BSR, where bacteria use P for their metabolism. Apatite is an accessory mineral that is very often encountered in Zoovch Ovoo.

The direct long-term contact of detrital grains, i.e. quartz, feldspars and micas with pitchblende-uraninite cement, induced radiation damage, is responsible for forming that formed pleochroic halos around these minerals, visible under cathodoluminescence (Figure A4A6). In particular, radiation halos were identified in quartz grains, not in contact with phospho-coffinite cement. Keeping in mind that direct contact is needed between uranium minerals and quartz for alpha particles to penetrate the mineral lattice, this feature is evidence for pitchblende-uraninite cement deposition around detrital grains followed by dissolution and redistribution. Such processes were already described by Meunier et al. (1990a) and are characteristic of roll-front systems.

5.2 Significance of the sulfides ~~habitus and crystal chemistry~~ mineral habits and mineral chemistry

~~While e~~Although euhedral pyrite is interpreted ~~of as~~ abiotic in origin, framboidal pyrite may be related either to abiotic or biotic processes. Experiments on abiotic pyrite formation showed that framboids obtained in the laboratory are unstable and easily converted to euhedral pyrite (Sawlowicz, ~~2012~~2000). On the contrary, biologically derived framboids are stable in the presence of organic matter (~~Mc Lean~~MacLean et al., 2008). Therefore, pyrite occurring as stable framboids observed in sedimentary rocks ~~are is~~ most often interpreted as derived from bacterial activity (Álvarez-Iglesias and Rubio, 2012; Cavalazzi et al., 2014; Bonnetti et al., 2017; Hough et al., 2019). Also, low crystallinity iron sulfide (as mackinawite and greigite) has been detected in association with organic matter particles in our samples (Rallakis et al., 2019), a feature consistent with the activity of microbial sulfate reducers (Watson et al., 2000; Wolthers et al., 2000; Veeramani, 2013). Finally, at Zoovch Ovoo, pyrite is exclusively

concentrated in laminae enriched in organic matter (Figure A5A7), while it is not present in surrounding facies. Hough et al. (2019) suggest that in roll-front systems, such a situation is a sign of pyrite formation in the presence of microorganisms. For all these reasons, we consider pyrite framboids ~~of~~in our samples as derived from sulfate-reducing bacteria (SRB) feeding on the detrital organic matter.

The first euhedral generation (pre-ore) pyrite seems to have formed ~~in the continuity of as continuous overgrowths on~~ framboids (framboidal pyrite 1) and their concentric overgrowths if present (Figure A6A8). This transformation is caused by minimizing the crystal surface energy during growth to become more stable (Sawlowicz, 1993; 2000). The genetic relationship is known because pyrite clusters of embedded framboids were found in the central part of euhedral crystals (~~briefly presented in~~ Figure 8C-F).

Marcasite can sometimes be observed at a paragenetic position between the first (pre-ore) and second (ore stage) euhedral pyrite generations. Therefore, it is the last pre-roll-front iron disulfide. As marcasite forms under a pH of 5 in the roll-front waters (Murowchick and Barnes, 1986; Anthony et al., 2003), it frequently has a specific position within the geometry of roll-fronts (Hough et al., 2019), which may explain its occasional observation in our samples.

All four pre-roll-front iron disulfides are characterized by a depletion in Cd, Co, Ni and to a lesser extent in V, Zn, Mo and Cu, relative to the second euhedral generation formed during the ore-stage (Figure 8). Marcasite is significantly enriched in As compared to all other iron disulfides. According to Savage et al. (2000), Lowers et al. (2007), and Ingham et al. (2014), reduced arsenic (As^{-1}) is incorporated in the iron disulfide lattice by substituting sulfur. Arsenic was probably scavenged due to low sulfur availability during the final iron disulfide formation before the roll-front waters recharge.

The petrographic analysis did not confirm any hydrothermal minerals or alterations. Hence, sphalerite must be attributed to the introduction of the roll-front waters that together with U carry metallic elements such as Ni, V, Co, Cd, Zn, As, Pb and others. Thus, this stage is marked by the ore-stage pyrite (euhedral generation 2) significantly richer in heavy metal elements, in

646 contrast to pre-ore pyrite (framboids and euhedral generation 1) (Figure 8). Two reasons may
647 explain the origin of the trace elements:

- 648 1) the roll-front waters are leaching these elements from host lithologies i.e. a combination
649 of mafic rocks (Co, Ni; Goldschmidt, 1954; Clark et al., 2004), granitic rocks (Mo; Blevin
650 et al., 1996) and organic-rich black shales (As, V; Brumsack, 2006) together with U.
651 Indeed, meta-volcanic and intrusive rocks are outcropping in the vicinity of the Zoovch
652 Ovoo depocenter, which could serve as potential sources (Graham, et al., 2001; Figure
653 1).
654 2) these trace elements are incorporated in ore stage sulfides after ~~been-being~~ leached
655 from pyrite by oxidizing waters during the roll-front displacement. The trace metals
656 would then concentrate in the roll-front waters and be available to crystallize ore stage
657 pyrite in the more reduced part of the roll-front (Descostes et al., 2010; Ingham et al.,
658 2014; Bonnetti et al., 2020).

659 Concerning native Se found with organic matter, Ingham et al. (2014) proposed that in roll-
660 front systems, Se is being scavenged from the dissolution of pre-ore pyrite or ideally from other
661 Se-bearing minerals. Indeed, there are selenides in the Zoovch Ovoo reservoir, such as
662 clausthalite (PbSe) and stilleite (ZnSe), potentially a source for Se.

663 5.3 Interpretation of sulfur isotopes

664 In the Sainshand Formation, detrital sediments (Figure 5) are dominated by quartz, feldspar
665 and micas. ~~Besides Apart from~~ the mineralized laminae enriched in organic matter, no pyrite
666 is detected in the rocks. Therefore, the source and transport of sulfur available for
667 mineralization must be related to the circulation of roll-front waters. Two possible sources may
668 be considered:

- 669 1) Sulfates dissolved from evaporite deposits leached by the circulating waters. Considering
670 that the Sainshand Formation temperature at Zoovch Ovoo never exceeded 40°C (Graham et

Commented [R13]: These references were already listed.

Commented [R14]: Sentence added to show the presence of mafic rocks in the vicinity

Field Code Changed

Formatted: Font: (Default) Arial

Commented [R15]: We have used the paragenetic sequence table (Figure 15) to list the diagenetic phases recognized in the deposit as a function of time. Phases that appear only locally were not indicated as their chronology is more or less uncertain.

Commented [R16]: Here we aim to demonstrate that pyrite is exclusively linked to organic matter, often found in sand laminae, same for uranium mineralization.

al., 2001; Prost, 2004, Rallakis et al., 2019; 2020), reduced sulfur species could be obtained through bacterial activity. Such activity would lead to the formation of framboidal pyrite.

2) Sulfur species derived from the oxidative alteration of pyrite by roll-front waters. Indeed, (bio)-oxidation of pyrite in roll-front systems liberates intermediate valence sulfur species, which will contribute in the formation of pyrite in the roll-front (Granger and Warren, 1969; Rackley, 1972; Hough et al., 2019). In Zoovch Ovoo, the pre-ore pyrite present in the organic-rich laminae (framboidal pyrite 1, euhedral overgrowth and euhedral pyrite 1) would then become a possible initial pool of sulfur.

The $\delta^{34}\text{S}$ ranges from +52‰ to -52‰, which is very large but not unusual in roll fronts worldwide. There are examples of other roll-front deposits (Ingham et al., 2014; Bonnetti et al., 2015b; Lach et al., 2015; Hough et al., 2019; Bonnetti et al., 2020) that demonstrate similar values for the $\delta^{34}\text{S}$ of pyrite as those observed at Zoovch Ovoo (Figure 9). For instance, the deposit from Pepegooona and Pannikan (Lake Eyre Basin-South Australia) ~~with~~has pyrite with a range of $\delta^{34}\text{S}$ from -43.9 to +32.4‰ (Ingham et al., 2014). Another example is Lost Creek and Willow Creek Mine Unit 10 (Wyoming-USA) deposits ~~with-that have~~ $\delta^{34}\text{S}$ from -68.1 to +142.8‰ and from -48.1 to +68.2‰, respectively (Hough et al., 2019). Bonnetti et al. (2020), in their study of the roll-front systems of the Mesozoic, found values between -30.5‰ to +18.8‰.

At first glance, very negative $\delta^{34}\text{S}$ values in pyrite from roll-front deposits are attributed to bacterial activity and more positive to abiotic pyrite precipitation mechanisms (Bonnetti et al., 2020). However, sulfur isotope values in roll-fronts also depend on redistribution mechanisms. Therefore, we plotted our data within the diagram proposed by Hough et al. (2019) in Figure 10 for comparison.

In our study, pyrite shows heavy $\delta^{34}\text{S}$ values (+10 to +52‰). According to literature, evaporites have a $\delta^{34}\text{S}$ range from +20 to +35‰ (Makhnach et al., 2000) and can be considered a potential S source. Yet, pyrite $\delta^{34}\text{S}$ values higher than the mean evaporites composition imply an additional condition to fractionation. Alternately, according to the diagram

of Hough et al. (2019), the highly positive $\delta^{34}\text{S}$ pyrite may also derive from a Rayleigh fractionation in closed isotopic systems. It is therefore suggested that pyrite (Figure 9) showing heavy $\delta^{34}\text{S}$ values (framboidal pyrite 1) may have been fractionated from evaporites-derived sulfate in a semi-closed isotopic system. Pyrite isotopic compositions also show $\delta^{34}\text{S}$ values expanding to lighter isotopic values (+10 to -52‰). According to Hough et al. (2019), this might be linked to more open-system conditions.

These authors also suggest that strong fractionation to negative values may ~~sign~~suggest the effects of precipitation under neutral pH conditions and inheritance of light sulfur isotopes linked to multiple stages of pyrite dissolution/precipitation. Indeed, oxidation of pyrite deposited during previously occurring roll-fronts activity and subsequent sulfur disproportionation reactions may provide reduced sulfur species of light isotopic composition, even though dissolution and transport can both influence the isotopic distribution of sulfur (Seibert, 2017).

Pyrite habitus (euhedral vs framboids) are well separated spatially and isotopically in other study cases (Hough et al., 2019). In the Erlian basin, pre-ore vs ore pyrite is well divided into pre-ore (framboids) vs ore (colomorph + subidiomorphic) pyrite generations with distinct isotopic signatures (Bonnetti et al., 2017). In our case, euhedral and framboids are spatially associated and (present multiple overgrowths) in the same mineralized laminae and have the same large span of isotopic compositions.

The large span of $\delta^{34}\text{S}$ values observed for all pyrite habitus in our samples may be tentatively linked to fluctuating sulfate-containing water recharge periods alternating between open (high sulfate availability, recycling of isotopically light sulfur derived from altered pyrite) and a closed system (low sulfate availability, heavy isotopic enrichment). Both bacterial (framboids) or abiotic (euhedral) pyrite precipitation processes would have been submitted to this hydrological regime to lead to the very intricate pyrite petrography, and isotope geochemistry observed.

~~Yet, framboidal~~Framboidal pyrite 1 is the earliest pyrite generation observed and is followed by euhedral pyrite 1 (pre-ore) and euhedral pyrite 2 (contemporaneous to U ore). Framboidal

pyrite 1 would then be the primary episode of reduced sulfur occurrence (hence controlled by bacterial sulfate reduction - BSR). Euhedral pyrite 1 and 2 (both of abiotic origin) would then derive from the recycling of framboidal pyrite 1 by the roll-front (since no other sulfur source is observed ~~in the facies of Zoovch Ovoo~~). However, pyrite is always located in the close vicinity of organic matter rich laminae, which suggests that whatever the pyrite generation, microbial activity controls the overall fate of reduced sulfur in the system (Figure ~~A5A7~~).

The fate of sphalerite is very similar to euhedral pyrite (sphalerite 1 is pre-ore, sphalerite 2 contains micro-inclusions of ~~pitchblende-uraninite~~). Yet, the origin of Zn is unknown.

5.4 Uranium trapping processes involving pyrite

The petrographic study of sulfides in the Zoovch Ovoo samples revealed widespread U-pyrite association. In many cases, epigenetic replacement of pyrite by uranium oxides is observed (Figure 7). Also, pyrite dissolution features exist (Figure 16). In both instances, they concern pre-ore pyrite (framboidal pyrite 1 and euhedral pyrite 2; Figure 7), suggesting sulfide instability in roll-front waters during uranium precipitation.

Dissolution of pyrite by roll-front waters would lead to Fe(II) liberation and reduced sulfur species (S_0 , HS^- , polysulfides). Fe(II) in solution may be considered as an efficient reducer for uranium (Boyanov, 2007; Du et al., 2011) as reduced sulfur species might be (Hua et al., 2006; Boonchayaanant et al., 2010). However, if dissolution occurs before uranium precipitation, the solute dispersion in the aqueous solution may prevent ~~pitchblende-uraninite~~ growth at the expense of pyrite.

It is more likely that the uranium reduction process may have happened at the contact with solid FeS_2 as explained by Wersin et al. (1994) or Eglizaud et al. (2006). According to these authors, the interaction between pyrite and U(VI) is a two-step process. First, U(VI) is adsorbed on the pyrite surface, and then the redox reaction is initiated. Reduced uranium can be found either sorbed or precipitated as UO_2 (Eglizaud et al., 2006; Bruggeman et al., 2010). Progressive oxidation of Fe(II) and S_2^- by U(VI) at the surface of the pyrite crystals lead from

partial to complete replacement of FeS₂ by UO₂ (Figure 7E-F). This microsite redox chemistry would not preclude syn-ore euhedral pyrite 2 to precipitate with UO₂ (Figure 7C, D) since overall pyrite precipitation is driven by the presence of reduced sulfur provided by thiosulfate disproportionation (Hough et al., 2019) and by BSR, as explained earlier.

Similar observations concern sphalerite: Sphalerite 1 generation occurs before U precipitation in the diagenetic sequence and may show epigenetic replacement by ~~pitchblende~~uraninite. The second ZnS generation is co-genetic ~~to-with~~ U deposition and contains ~~pitchblende~~uraninite microsize inclusions (Figure 12C).

The biogenic iron sulfides, mackinawite and greigite, detected in association ~~to-with~~ organic matter particles (Rallakis et al., 2019), are also able to act as reducers of U(VI) to UO₂ (Hua and Deng, 2008; Veeramani et al., 2013). It is also known that sulfate-reducing bacteria can generate reduced sulfur species such as H₂S and native sulfur (Gruner et al., 1953; Kochenov et al., 1977; Picard et al., 2017). These compounds can induce a reduction of dissolved uranium (Spirakis, 1996).

The sulfur isotopes data obtained on the Zoovch Ovoo pyrites give evidence of the availability of reduced sulfur produced through bacterial sulfate reduction. ~~Indeed, P~~pyrite, sphalerite mackinawite, and greigite are ~~therefore present and~~ strongly associated with organic matter. Petrographic study of the uranium-sulfides relationships evidenced epigenesis and hence reduction of U(VI) by sulfides. Thus, even though sulfides are responsible for U precipitation, the sulfate-reducing bacterial community is the primary control of the precipitated uranium ore pool.

5.5 Uranium trapping processes involving organic matter

Uranium occurs at Zoovch Ovoo very intimately associated with organic matter particles at high concentration without expression of a mineral phase or as UO₂ replacing partially macerals with partial preservation of the original biological woody texture (Figure 14). ~~To our knowledge, these~~ Such U concentrations in wood material are the highest reported in ~~the~~

Field Code Changed

777 literature (Rallakis et al., 2019). Simple adsorption/complexation cannot be ruled out but may
778 not explain such concentrations.

779 U(VI) trapping mechanism in interstitial waters by organic matter was for many decades not
780 very clearly understood when dealing with low-temperature abiotic systems. Nakashima et al.
781 (1984) and Nakashima (1992) and Cumberland et al. (2018) suggested that organic matter
782 can trap uranium by complexation, forming uranyl-carboxyl functional groups. Such a process
783 is possible for immature organic matter, such as peat, which may scavenge uranium by a factor
784 of 10^4 from groundwater containing uranium at ppb levels (Idiz et al., 1986; Owen and Otton,
785 1995). However, this process is not reduction [as U remains under the oxidized state as U(VI)]
786 but adsorption/complexation by carboxylic acids and phenolic groups of the immature organic
787 matter (Warwick et al., 2005; Bryan et al., 2012).

788 Also, Nakashima et al. (1984) and Nakashima (1992) proved that direct reduction of U(VI)
789 by organic matter (in particular by hydrocarbonaceous moieties) is only possible at $T > 120^\circ\text{C}$.
790 Such a process is unlikely to have occurred within the Sainshand formation since the
791 temperature never exceeded 40°C (Graham et al., 2001; Prost, 2004; Rallakis et al., 2019;
792 2020).

793 **5.6 Organic matter and bacteria as redox trap for uranium**

794 The high concentration of U in the organic matter without expression of uranium minerals
795 can be achieved via direct reduction of U(VI) by bacteria, leading to the formation of amorphous
796 U(IV) (Bhattacharyya et al., 2017). The mechanism of U reduction through biomineralization
797 by bacteria and fungi was also studied by Lovley et al. (1991) and by Min et al. (2005) in
798 laboratory experiments and the case of Chinese roll-front systems, respectively. Micro-
799 organisms consortia can play ~~there~~ a significant role in the control of the redox conditions for
800 uranium precipitation as shown by these studies.

801 Biomineralization of uranium occurs then in two steps. First, the complexation of uranium,
802 attributed to the bacterial excreted ligands around their cells as non-crystalline U(IV)

803 (Bhattacharyya et al., 2017), whereas the precipitation that follows is accredited to the redox
804 change, driven by enzymatic reactions (Gadd, 1996; Suzuki and Banfield, 1999; Wilkins et al.,
805 2006). Such a process would lead to organic matter rich in U, presenting no expression of UO_2
806 minerals as observed in our samples (Figure 14). Yet, Meunier et al. (1990b) considered that
807 U was dispersed in the organic matter in similar cases, occurring under its reduced state U(IV),
808 forming very probably tiny-sized U oxide crystals. Such micro-minerals could not be observed
809 at the highest SEM magnification yet cannot be excluded (Figure 14). Bhattacharyya et al.
810 (2017) located U trapped in non-crystalline form, using synchrotron, in similar cases.

811 Uranium can be reduced by sulfate-reducing bacteria (Lovley et al., 1993; Wilkins et al.,
812 2006; Cardenas et al., 2010) and to some extent by the methanogenic strains (Holmes et al.,
813 2018). The chemical reactions and the bacteria species that could occur in such a process are
814 presented in Table 2. In Zoovch Ovoo, bacteria could thrive in the low-temperature
815 environment ($T < 80^\circ\text{C}$), using the abundant coal fragments concentrated in laminae (Rallakis
816 et al., 2019) as nutrients.

817 We might propose that organic matter is essential in trapping uranium through its role as a
818 nutrient for micro-organism communities that control the trapping of uranium either by
819 complexation-adsorption of U(IV) or direct reduction of U(VI). The continuous bacterial activity
820 would progressively lead uranium to concentrate in the organic matter up to 20 weight%,
821 eventually under amorphous U(VI) form. U(VI) may also be reduced by microorganisms into
822 UO_2 , as ~~pitchblende~~uraninite intimately associated with the fine organic structures (i.e. cellular
823 walls geometry). With further organic carbon consumption by bacteria, UO_2 may entirely
824 replace the organic particles (Figure 7; Figure 14).

825 Pyrite is a ~~very~~efficient uranium reducing agent in Zoovch Ovoo (Rallakis et al., 2019), ~~as~~
826 ~~shown by the very intimate association of pyrite with~~and is intimately associated with organic
827 matter. Petrography and sulfur isotopes suggest that reduced sulfur present ~~be is~~is derived from
828 bacterial sulfate-reducing communities. Yet, such communities also need organic carbon as a
829 nutrient. Therefore, the presence of organic matter is essential: 1) to BSR, which induces the

formation of pyrite, a redox trap for U; 2) to microbial communities, which act as a trap for U. In other words, organic matter plays a primary role in the formation of the ore deposit of Zoovch Ovoo since it sustains microbial activity and provides an efficient biogeochemical trap for uranium (Lovley et al., 1991; Detmers et al., 2001; Min et al., 2005; Menor-Salván et al., 2010).~~is thus warrant of the high efficiency of the biogeochemical uranium trap.~~

5.7 The model: biogeochemical roll-front trap of the Zoovch Ovoo uranium deposit

The combination of the various biogeochemical processes described in this paper is summarized within a conceptual roll-front system in Figure 17.

Bio-reduction of sulfur, S-recycling in the roll-front and reduced iron availability

Meteoric waters bearing sulfate and uranium percolate downdip through the permeable sandy horizons of the reservoir. In Zoovch Ovoo's case, sulfate could derive from the dissolution of sulfates (gypsum or celestite formed at the surface during evaporation), as was suggested by the strong positive $\delta^{34}\text{S}$ isotopic values of framboids (Figure 9). Sulfates might also derive from the oxidation of pyrite by dissolved oxygen (Stumm and Lee, 1961) and the activity of micro-organisms like *Thiobacillus ferrooxidans* present in the percolating surface waters (Rackley, 1972). Consequently, Fe(III) precipitates as hydroxides (goethite/limonite) and oxides (hematite) (Schwertmann, 1991).

In the sub-oxic part of the roll-front, dissolution of phyllosilicates (e.g. biotite) and ilmenite, abundant in the Sainshand formation (Figure 5), may release Fe(II). ~~Updip Pyrite-pyrite~~ dissolution may also provide Fe(II) and reduced sulfur species available for the precipitation of euhedral pyrite (Granger and Warren, 1969; Boulegue, 1981; Brunner and Bernasconi, 2005; Hough, 2019). The subsequent pH drop would explain the dolomite dissolution features observed in dolomite types that were formed prior to the introduction of roll-front waters i.e. microcrystalline (type I) and euhedral (type II) dolomite.

In the reduced part of the roll-front, bacteria like the genus *Desulfovibrio* would be present and reduce sulfate (the dominant sulfur source) into sulfides (Rackley, 1972), producing

Commented [R17]: Reference added

intermediate valence species of sulfur (such as S_2^- , HS^- , H_2S , S_0) (Figure 17, sulfate reduction). Reduced iron would then react with the reduced sulfur leading to the formation of framboidal pyrite. The resulting pH increase would allow subhedral (type III) dolomite, ~~typical~~ indicative of roll-front activity, to precipitate if the Mg concentration and carbonate activity in the waters is sufficiently high (Rallakis [et al.](#), 2020).

U reduction process and deposit formation

Bio-reduction of U is an essential process for reducing uranium at near-surface temperatures (Rackley, 1972; Huang, 1978; Lovley et al., 1991). Bacteria would then reduce U(VI) to form non-crystalline U(IV) (Bhattacharyya et al., 2017) and uraninite/coffinite. Thus, organic matter plays a central role in the metallogenic system. It concentrates uranium by adsorption or complexation and is also a source of nutrients to sustain bacterial activity responsible for metal reduction.

Importance of uplift

The relatively shallow aquifers probably underwent a nearly continuous bacterial activity responsible for many chemical features and processes controlling the U and sulfide precipitation. However, the main uranium deposition events occur since the beginning of uplift when enhanced fluid movement sustained roll-front activity.

The rifting phase in East Gobi Basin was ceased at the end of Early Cretaceous. From Cenomanian and on, the sedimentary sequence in Zoovch Ovoo experienced uplift and erosion (estimated at 300 m at maximum), entering the thermal cooling phase (Prost, 2004; Graham et al., 2001). During Tertiary, the Zuunbayan fault system was reactivated with strike-slip movement (Johnson and Ritts, 2012; Heumann et al., 2014) moving the reservoir from 500 to 200 m – present day depth. These local tectonics could be responsible for opening the system, allowing meteoric waters to percolate through Sainshand Formation, carrying dissolved uranium in oxidized state as U(VI) as well as Fe(III), SO_4^{2-} and bacteria. This new water mass was certainly in disequilibrium with dolomite and had a higher oxidation state than the Sainshand aquifer. The disequilibrium is evidenced by the dissolution features of the pre-

Commented [R18]: This whole sub-chapter is new and was added to highlight the importance of uplift and to provide more details about the four dolomite types and their usage in burial history reconstruction. The aquifer waters were since deposition (and continue to be today) saturated in respect to dolomite. This equilibrium was disrupted upon the introduction of roll-front waters when U deposition occurred and was re-established with uplift.

roll-front dolomite cements and the deposition of U minerals in the secondary porosity as well as by the appearance of the subhedral (type III) dolomite. With progressive uplift, parts of the roll-front were cut-off and reducing conditions were locally re-established. In sediments that are not leached by the roll-front waters, the type II dolomite does not show any dissolution features. Consequently, these parts were re-equilibrated with the aquifer waters which were saturated in respect to dolomite. Thus, the remaining uncemented sand layers, particularly the coarser units were percolated by the aquifer waters allowing the anhedral (type IV) dolomite cement to precipitate. In a previous study (Rallakis et al., 2020) the four dolomite petrographic types, as presented in the paragenesis table from type I to IV (Figure 15) and discussed chronologically in this chapter, were used to track the burial history of the reservoir.

To conclude the uplift episodes in Cenozoic displaced and combined the biochemical trap ingredients, allowing progressive enrichment in uranium through time.

Late processes

During the stages of the roll-front activity, ~~pitchblende~~uraninite often experienced coffinitization with phosphorus incorporation leading to phospho-coffinite (U, P(SiO₄)) (Figure 13). Previous studies (Gächter and Meyer, 1993; Hutchens et al., 2006; Bonnetti et al., 2015b) have shown that micro-organisms are responsible for releasing P from organic compounds as well as from the dissolution of apatite during BSR. It remains, however, to determine whether P is coming from organic compounds or from the dissolution of apatite, which is a common accessory mineral in the Zoovch Ovoo sands.

6 Conclusion

The Zoovch Ovoo U-ore deposit was formed in uncemented sands deposited in fluvio-lacustrine settings, where relatively abundant coal particles were concentrated as laminae. This feature is a crucial parameter for the precipitation of sulfides and uranium ores.

908 The mineral sequence proposed in this study highlights multiple episodes of sulfides
909 (essentially pyrite, sphalerite) and uranium deposition (non-crystalline, ~~pitchblende~~uraninite,
910 phospho-coffinite). Sulfides precipitated during pre-, syn- and post-ore stages as reflected by
911 specific contents in trace metals. The δS^{34} compositions changes are, however, not consistent
912 with pyrite morphology or generation. The ~~heavy $\delta^{34}S$ values of pyrite vast range of values~~
913 between +10‰ to +52‰ ~~is are~~ controlled by sulfate inputs, sulfur recycling from sulfides, and
914 bacterial sulfate reduction under conditions of open and closed systems.

915 Regarding the very close association of sulfides with organic matter particles, bacterial
916 activity is suspected as a significant provider of reduced sulfur. ~~The Since the~~ burial
917 temperature of ~~the~~ Sainshand formation never exceeded 40°C. ~~The direct reduction of~~
918 uranium by organic matter ~~is, therefore, could be~~ excluded, ~~considering that temperatures over~~
919 ~~120°C are required for direct reduction~~. Unusually high concentrations of up to 20 wt% of
920 ~~uranium without within organic matter without~~ crystalline expression ~~in organic~~
921 ~~matter(amorphous)~~ suggests that bacteria play an essential direct role in the trapping process.
922 The continuous bacterial activity would increase the uranium concentration until the
923 ~~pitchblende~~uraninite mineral is expressed, accompanied by the destruction of organic carbon,
924 leading to total replacement features resembling epigenesis.

925 Pyrite epigenesis by uranium is also the central ~~trapping~~ mechanism ~~of trapping~~, implying
926 the reduction of U(IV) by solid reduced sulfur (and Fe(II) to some extent). It appears that the
927 significant reducing agents for uranium in the Zoovch Ovoo are micro-organisms and sulfides.
928 Also, bacteria have a major influence on the sulfur cycle, controlling ~~at least~~ a part ~~at least~~.
929 Their intimate association to organic ~~matter-matter~~-rich laminae is explained ~~by the fact that in~~
930 ~~consideration of~~ micro-organisms ~~use using~~ coal particles as a carbon source. Therefore, the
931 Zoovch Ovoo uranium ore deposit may be considered as a (bio)-geochemical trap. It appears
932 that the relatively shallow aquifers probably underwent a nearly continuous bacterial activity
933 which is responsible for many chemical features and processes controlling U and sulfide
934 precipitation. ~~However,~~ major uranium deposition events occurring since the beginning of uplift

Commented [R19]: We do not know the valence state, hence we cannot conclude if we have oxide (reduced) or adsorbed/complexed U (oxidized).

Commented [R20]: I wrote a small paragraph about the source of U and the significance of trace elements in ore-stage sulfides.

(Oligocene-Miocene) triggered enhanced fluid movements, sustaining roll-front activity. The latter displace and combine the bio-(geo)chemical trap ingredients, allowing progressive enrichment in uranium through time.

The exact uranium source is not easy to identify; however, the following formations outcrop in the region and have strong potential to act as such: 1) the granitic, 2) metamorphic and 3) volcanic basement rocks and 4) the volcanic ash/glass that covers Sainshand Formation.

The enrichment of ore-stage sulfides in certain trace elements is a probably a gradual process (Ni, V, Co, Cd, Zn, As, Pb and others). It is linked to the continuous dissolution of pre-ore sulfides in the oxidized zone of the roll-front and the formation (re-precipitation) of ore-stage sulfides at the roll-front interface, in the same sense that the concentration gradient of uranium ore increases as the roll-front evolves.

Deposition of the ore is therefore dependent on circulating fluids carrying U reaching the organic-rich laminae. This hydrologic factor is controlled by the permeability network inherited from sedimentation allowing the input of S, U and micro-organisms by percolating waters. Knowledge of the spatial sedimentary organization of the most transmissive layers and distribution of organic matter are, therefore, two crucial parameters for further prospection.

7 Acknowledgements

This work was performed and funded in the research framework between ORANO Mining and CREGU (*Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques*), in the Laboratory of GeoRessources in Nancy, France (contract number 40077759 of 15/03/2016). We are grateful to COGEOBI's geological team for the hospitality and the equipment provided during the field work as well as for taking care of the shipping of the samples from Mongolia to France. People from the laboratory of GeoRessources, in particular Marie Christine Boiron and Chantal Peiffert, are acknowledged for their contribution to the REE *in situ* analysis. Andreï Lecomte and Olivier Rouer are acknowledged for the crystal

chemistry analyses and the manipulation of the analytical means. A special thanks to Denis Mangin from the Institute of Jean Lamour of the School of Mines in Nancy (France) for the *in situ* analysis of the S isotopes and to Mohammed Boussafir from the Institute of Earth Sciences in Orleans (France) for the Rock-Eval analyses. ~~Finally~~Finally, the authors would like to acknowledge the two anonymous reviewers that played a catalytic role in polishing the present manuscript.

8 References

- AKHTAR, S., YANG, X., PIRAJNO, F. (2017). Sandstone type uranium deposits in the Ordos Basin, Northwest China: A case study and an overview. *Journal of Asian Earth Sciences* 146, 367-382.
- ÁLVAREZ-IGLESIAS, P., & RUBIO, B. (2012). Early diagenesis of organic-matter-rich sediments in a *ría* environment: organic matter sources, pyrites morphology and limitation of pyritization at depth. *Estuarine, Coastal and Shelf Science*, 100, 113-123.
- ANDERS, E., GREVESSE, N. (1989). Abundances of the elements – Meteoritic and solar. *Geochimica et Cosmochimica Acta*, vol. 53, pp. 197-214.
- ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W. NICHOLS, M.C. (2003). Eds., *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, VA 20151-1110, USA. <http://www.handbookofmineralogy.org/>.
- AUBAKIROV, KH.B. (1998). On the deep origin of ore-forming solutions in the uranium deposits in platform sequence of depressions (with Chu-Sarysu Province as an example). *Geology of Kazakhstan* 2(354), pp. 40-47.
- ~~BERNER, R.A. (1984). Sedimentary pyrite formation and update*. *Geochimica et Cosmochimica Acta*, 48, pp. 605-615.~~
- ~~BLEVIN P.L., CHAPPELL B.W. AND ALLEN C.M. (1996). Intrusive metallogenic provinces in eastern Australia based on granite source and composition. *Trans. R. Soc. Edinb. Earth Sci.* 87, 281-290.~~
- BHATTACHARYYA, A., CAMPBELL, K.M., KELLY, S.D., ROEBBERT, Y., WEYER, S., BERNIER-LATMANI, R., BORCH, T. (2017). Biogenic non-crystalline U(IV) revealed as major component in uranium ore deposits. *Nature communications*, 8, doi.10.1038/ncomms15538
- BOISSEZON, H.DE., LEVY, L., JAKYMIW, C., DISTINGUIN, M., GUERIN, F., DESCOSTES, M. (2020). Modeling uranium and ²²⁶Ra mobility during and after an acidic *in situ* recovery test (Dulaan

Formatted: French (France)

Uul, Mongolia). *Journal of Contaminant Hydrology*, 103711, ISSN 0169-7722, <https://doi.org/10.1016/j.jconhyd.2020.103711>.

BONNETTI, C., CUNEY, M., MALARTRE, F., MICHELS, R., LIU, X., PENG, Y. (2015a). The Nuheting Deposit, Erlan Basin, China: Synsedimentary vs Diagenetic Uranium Mineralization. *Ore Geology Reviews*, 69, pp. 118–139. doi.org/10.1016/j.oregeorev.2015.02.010

BONNETTI, C., CUNEY, M., MICHELS, R., TRUCHE, L., MALARTRE, F., LIU, X., YANG, J. (2015b). The Multiple Roles of Sulfate-Reducing Bacteria and Fe-Ti Oxides in the Genesis of the Bayinwula Roll Front-Type Uranium Deposit, Erlan Basin, NE China. *Economic Geology*, V. 110, pp. 1059-1081.

BONNETTI, C., LIU, X., ZHAOBIN, Y., CUNEY, M., MICHELS, R., MALARTRE, F., MERCADIER, J., CAI, J. (2017). Coupled uranium mineralization and bacterial sulphate reduction for the genesis of the Baxingtu sandstone-hosted U deposit, SW Songliao Basin, NE China. *Ore Geology Reviews*, 82, pp. 108-129.

BONNETTI, C., LINGLI, Z., RIEGLER, T., BRUGGER, J., 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*, vol. 282, pp. 113-132. doi.org/10.1016/j.gca.2020.05.019

BOONCHAYAANANT, B., GU, B., ORTIZ, M.E., CRIDDLE, C.S. (2010). Can microbially-generated hydrogen sulfide account for the rates of U(VI) reduction by a sulfate-reducing bacterium?. *Biodegradation*, 21, pp.81-95.

[BOULÈGUE, J. \(1981\). Simultaneous Determination of Sulfide, Polysulfides and Thiosulfate as an Aid to Ore Exploration. *Developments in Economic Geology*, 15, pp. 21-36. doi.org/10.1016/0375-6742\(81\)90053-4](#)

BOYANOV, M., O'LOUGHLIN, E.J., RODEN E.E., FEIN, J.B., KEMMETH, K.M. (2007). Adsorption of Fe(II) and U(VI) to carboxyl-functionalized microspheres: The influence of speciation on uranyl reduction studied by titration and XAFS. *Geochimica et Cosmochimica Acta*, vol. 71, pp. 1898-1912. DOI : [10.1016/j.gca.2007.01.025](https://doi.org/10.1016/j.gca.2007.01.025)

BRYAN, N.D., ABRAHAMSEN, L., EVANS, N., WARWICK, P., BUCKAU, G., WENG, L., VAN RIEMSDIJK W.H. (2012). The effects of humic substances on the transport of radionuclides: recent improvements in the prediction of behaviour and the understanding of mechanisms, *Applied Geochemistry*, 27 (2), pp. 378-389.

BRUGGEMAN, C., MAES, N. (2010). Uptake of Uranium(VI) by Pyrite under Boom Clay Conditions: Influence of Dissolved Organic Carbon. *Environ. Sci. Technol.* 2010, 44, 11, 4210–4216

BRUMSACK H.J. (2006). The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232, 344-361.

BRUNNER B., BERNASCONI S. (2005) A revised isotope fractionation model for dissimilatory sulphate reduction in sulphate reducing bacteria. *Geochim. Cosmochim. Acta* 69, 4759–4771.

~~BLEVIN P.L., CHAPPELL B.W. AND ALLEN C.M. (1996). Intrusive metallogenic provinces in eastern Australia based on granite source and composition. *Trans. R. Soc. Edinb. Earth Sci.* 87, 281-290.~~

CAI, C.F., LI, H.T., QIN M.K., LUO, X.R., WANG, F.Y., OU, G.X. (2007). Biogenic and petroleum-related ore-forming processes in Dongsheng uranium deposit, NW China. *Ore Geology Reviews* 32, 262-274.

CAO, B.F., BAI, G.P., ZHANG, K.X., HE, B. (2016). A comprehensive review of hydrocarbons and genetic model of sandstone-hosted Dongsheng uranium deposit, Ordos Basin, China. *Geofluids*, 16, pp. 624-650.

CARDENAS, E., WU, W.M., BETH LEIGH, M., CARLEY, J., CARROLL, S., GENTRY, T., LUO, J., WATSON, D., GU, B., GIN DER-VOGEL, M., KITANIDIS, K.P., JARDINE, P.M., ZHOU, J., CRIDDLE, C.S., MARSH, T.L., TIEDJE, J.M. (2010). Significant Association between Sulfate-Reducing Bacteria and Uranium-Reducing Microbial Communities as Revealed by a Combined Massively Parallel Sequencing-Indicator Species Approach. *Applied and Environmental Microbiology*, 20, pp. 6778-6786; DOI: 10.1128/AEM.01097-10

CARDON, O., LE GOUX, F., SALABERT, J. (2015). Prospection d'uranium en Mongolie: découverte majeure dans le désert de Gobi [Uranium exploration in Mongolia: important discovery in the Gobi Desert]. *Revue Générale Nucléaire*, vol. 47, pp. 12-19.

CAVALAZZI, B., AGANGI, A., BARBIERI, R., FRANCHI, F., & GASPAROTTO, G. (2014). The formation of low-temperature sedimentary pyrite and its relationship with biologically-induced processes. *Geology of Ore Deposits*, 56(5), 395-408.

CHEBURKIN, A. and SHOTYK, W. (1996). An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius Journal of Analytical Chemistry*, vol. 354, pp. 688-91.

~~CHEN, R.Y., LUO, X.R., CHEN, Z.K., YU, J., YANG, Y. (2006). Restoration of burial history of four periods in Ordos Basin. *Acta Petrolei Sinica* 27, 43-47 (in Chinese with English abstract).~~

CLARK, C., GRGURIC B., SCHMIDT, M.A. (2004). Genetic implications of pyrite chemistry from the Palaeoproterozoic Olary Domain and overlying Neoproterozoic Adelaidean sequences, northeastern South Australia. *Ore Geology Reviews*, 25, pp. 237-257.

CUMBERLAND, S.A., ETSCHMANN, B., BRUGGER, J., DOUGLAS, G., EVANS, K., FISCHER, L., KAPPEN, P., MOREAU, J.W. (2018). Characterization of uranium redox state in organic-rich Eocene sediments. *Chemosphere*, 194, pp. 602-613.

Formatted: English (United States)

1058 ~~CAVALAZZI, B., AGANGI, A., BARBIERI, R., FRANCHI, F., & GASPAROTTO, G. (2014). The formation of~~
 1059 ~~low-temperature sedimentary pyrite and its relationship with biologically induced processes.~~
 1060 ~~Geology of Ore Deposits, 56(5), 395-408.~~

1061 DAHLKAMP, F.J. (2009). Uranium Deposits of the World: Asia, Berlin Heidelberg: Springer-Verlag, 493
 1062 pp.

1063 DESCOSTES, M., SCHLEGEL, M.L., EGLIZAUD, N., DESCAMPS, F., MISERQUE, F., SIMONI, E. (2010).
 1064 Uptake of uranium and trace elements in pyrite (FeS₂) suspensions. Geochimica et
 1065 Cosmochimica Acta, 74, pp. 1551-1562.

1066 DETMERS J., BRÜCHERT V., HABICHT K. S., KUEVER J. (2001). Diversity of sulfur isotope fractionations
 1067 by sulfate-reducing prokaryotes. Applied Environmental Microbiology, 67, pp. 888-894.

1068 DOTT, R. H. JR. (1964). Wacke, greywacke and matrix-What approach to immature sandstone
 1069 classification?. Journal of Sedimentary Petrology, vol. 34, No. 3. pp. 625-632.

1070 DU, X., BOONCHAYAANANT, B., WEI-MIN, W., FENDORF, S., BARGAR, J., CRIDDLE, C.S. (2011).
 1071 Reduction of Uranium(VI) by Soluble Iron(II) Conforms with Thermodynamic Predictions.
 1072 Environmental Science & Technology, American Chemical Society, 45, pp. 4718-4725.

1073 EGLIZAUD, N., MISERQUE, F., SIMONI, E., SCHLEGEL, M.L., DESCOSTES, M. (2006). Uranium (VI)
 1074 interaction with pyrite (FeS₂): chemical and spectroscopic studies. Migration 2005, Avignon,
 1075 France, pp. 651-656. DOI : [10.1524/ract.2006.94.9-11.651](https://doi.org/10.1524/ract.2006.94.9-11.651)

1076 ESPITALIE, J., DEROO, G., MARQUIS, F. (1985). Rock-eval pyrolysis and its applications. Oil Gas Sci.
 1077 Technol. -Rev IFP 40-6, 755-784.

1078 [FORBES, P., LANDAIS, P., BERTRAND, P., BROSSE, E., ESPITALIÉ, J., YAHAYA, M. \(1988\). Chemical](#)
 1079 [transformations of type-III organic matter associated with the Akouta uranium deposit \(Niger\):](#)
 1080 [Geological implications. Chemical Geology, 71, pp. 267-282.](#)

1081 FOWLER, A.D., DOIG, R. (1982). The significance of europium anomalies in the REE spectra of
 1082 granites and pegmatites, Mont Laurier, Quebec. Geochimica et Cosmochimica Acta, 47, pp.
 1083 1131-1137.

1084 GÄCHTER, R., MEYER, J.S. (1993). The role of microorganisms in mobilization and fixation of
 1085 phosphorus in sediments. Hydrobiologia, 253, pp. 103-121.

1086 GADD, G.M. (1996). Influence of microorganisms on the environmental fate of radionuclides.
 1087 Endeavour, 20, pp. 150-156.

1088 GOLDSCHMIDT V. M. (1954). Geochemistry. The Clarendon Press, Oxford, p. 730.

1089 GRAHAM, S.A., HENDRIX, M.S. JOHNSON, C.L., BADAMGARAV, D., BADARCH G., AMORY, J., PORTER,
 1090 M., BARSBOLD, R., WEBB, L.E., and HACKER B.R. (2001). Sedimentary record and tectonic
 1091 implications of Mesozoic rifting in southeast Mongolia. Geological Society of America Bulletin,
 1092 vol. 113, pp. 1560-1579.

Formatted: French (France)

Field Code Changed

1093 GRANGER, H.C.; WARREN, C.G. (1969). Unstable sulfur compounds and the origin of roll-front type
 1094 uranium deposits. *Economic Geology*, 64 (2), pp. 160-171.

1095 ~~GRIZARD, P., SCHMITT, J.M., GOBLET, P. (2018). Hydrogeology of an arid endorheic basin (Tsagaan Els,~~
 1096 ~~Dornogobi, Mongolia): field data and conceptualization, three-dimensional groundwater~~
 1097 ~~modeling, and water budget. *Hydrogeology Journal*, doi.org/10.1007/s10040-018-1868-1~~

1098 GRUNER, J.W., GARDINER, L., SMITH, D.K (1953). Studies relating to the origin and distribution of
 1099 uranium deposits on the Colorado Plateau. Annual Report for July 1, 1952 to March 31. Division
 1100 of Raw Materials, Washington 25, D.C., 58 p.

1101 ~~GRIZARD, P., SCHMITT, J.M., GOBLET, P. (2018). Hydrogeology of an arid endorheic basin (Tsagaan Els,~~
 1102 ~~Dornogobi, Mongolia): field data and conceptualization, three dimensional groundwater~~
 1103 ~~modeling, and water budget. *Hydrogeology Journal*, doi.org/10.1007/s10040-018-1868-1~~

1104 HERRON, M.M. (1988). Geochemical classification of terrigenous sands and shales from core or log
 1105 data: *Journal of Sedimentary Petrology*, v. 58, no.5, pp. 820- 829.

1106 HEUMANN, J.M., JOHNSON, L.C., WEBB, L.E., TAYLOR, P.J., JALBAA, U., MINJIN, C. (2014). Total and
 1107 left-lateral displacement across the East Gobi Fault Zone, southern Mongolia: Implications for
 1108 timing and modes of polyphase intracontinental deformation. *Earth and Planetary Science Letter*
 1109 (392), pp. 1-15.

1110 HOLMES, D.E., ORELANA, R., GILOTEUAX, L., WANG, L.Y., SHRESTHA, P., WILLIAMS, K., LOVLEY, D.R.,
 1111 ROTARU, A.E. (2018). Potential for *Methanosarcina* to Contribute to Uranium Reduction during
 1112 Acetate-Promoted Groundwater Bioremediation. *Microbial Ecology*, 76, pp. 660-667.

1113 HOUGH, G., SWAPP, S., FROST, C., FAYEK, M. (2019). Sulfur Isotopes in Biogenically and Abiogenically
 1114 Derived Uranium Roll-Front Deposits. *Economic Geology*, v. 114, no. 2, pp. 353-373.

1115 HUA, B, XU, H., TERRY, J., DENG, G. (2006). Kinetics of Uranium(VI) Reduction by Hydrogen Sulfide in
 1116 Anoxic Aqueous Systems. *Environmental Science and Technology*, 40, 4666-4671.

1117 HUA, B., DENG, B. (2008). Reductive immobilization of uranium (VI) by amorphous iron sulfide.
 1118 *Environmental Science & Technology*, 42, pp. 8703-8708.

1119 HUANG, W.H. (1978). Geochemical and Sedimentologic Problems of Uranium Deposits of Texas Gulf
 1120 Coastal Plain. vol. 62, 6, pp. 1049-1062.

1121 HUANG, XIAN-FANG., LIU, DE-CHANG., DU, LE-TIAN., ZHAO, YING-JUN. (2005). A new sandstone type
 1122 uranium metallogenetic type—‘structure—oil, gas type’. In: JINGWEN, M., BIERLEIN, F.P. (eds),
 1123 *Mineral Deposit Research: Meeting the Global Challenge. Proceedings of the Eighth Biennial SGA*
 1124 *meeting, Beijing, China, August 2005*, 265–268.

1125 HUTCHENS, E., VALSAMI-JONES, E., HAROUIYA, N., CHAÏRAT, C., OELKERS, E.H., McELDONEY, S. (2006).
 1126 An Experimental Investigation of the Effect of *Bacillus megaterium* on Apatite Dissolution,
 1127 *Geomicrobiology*, 23(3), pp. 177-182.

1128 IDIZ, E.F., CARLISLE, D., KAPLAN, I.R. (1986). Interaction between organic matter and trace metals in a
 1129 uranium rich bog, Kern County, California, U.S.A, *Applied Geochemistry*, 1, 573-590.

1130 INGHAM, E.S., COOK, N.J., CLIFF, J., CIOBANU, C.L., HUDDLESTON, A. (2014). A combined chemical,
 1131 isotopic and microstructural study of pyrite from roll-front uranium deposits, Lake Eyre Basin,
 1132 South Australia. *Geochimica et Cosmochimica Acta*, 125, pp. 440-465.

1133 INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA) and NUCLEAR ENERGY AGENCY (NEA). (2018).
 1134 Uranium 2018: Resources, production and Demand, NEA No. 7413, © OECD 2018, pp. 462.

1135 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY (ICCP), 1963. *International Handbook of Coal*
 1136 *Petrography*, 2nd Edition. CNRS. Academy of Sciences of the USSR, Paris, Moscow.

1137 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY, (ICCP), 1971. *International Handbook of Coal*
 1138 *Petrography*, 1st Supplement to 2nd Edition. CNRS, Paris.

1139 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY, (ICCP), 1975. *International Handbook of Coal*
 1140 *Petrography*, 2nd Supplement to 2nd Edition. CNRS, Paris.

1141 INTERNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY, (ICCP), 1998. The new vitrinite
 1142 classification (ICCP System 1994). *Fuel* 77, 349–358.

1143 INTERNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY, (ICCP), 2001. The new inertinite
 1144 classification (ICCP System 1994). *Fuel* 80, 459–471.

1145 ITTERBEECK, J.V., HORNE, D.J., BULTYNCK, P., VANDENBERGHE, N. (2005). Stratigraphy and
 1146 palaeoenvironment of the dinosaur-bearing Upper Cretaceous Iren Dabasu Formation, Inner
 1147 Mongolia, People's Republic of China, *Cretaceous Research*, Volume 26, Issue 4, August 2005,
 1148 pp. 699-725.

1149 JAIRETH, S., MCKAY, A., LAMBERT, I. (2008). Association of large sandstone uranium deposits with
 1150 hydrocarbons. *Australian Government, Geoscience Australia*, 89, 6 p.

1151 JARAULA, C.M.B., SCHWARK, L., MOREAU, X., PICKEL, W., BAGAS, L., GRICE, K. (2015). Radiolytic
 1152 alteration in the Mugla Rock (Australia) uranium deposit. *Applied Geochemistry*, vol. 52, pp. 97-
 1153 108.

1154 JERZYKIEWICZ, T., RUSSELL, D.A. (1991). Late Mesozoic stratigraphy and vertebrates of the Gobi Basin.
 1155 *Cretaceous Research*, 12, pp. 345-377.

1156 JIAO, Y.Q., WU, L.Q., RONG, H., ZHANG, F., YUE, L., TAO, Z.P., SUN, Y.H. (2018). Geological modeling of
 1157 uranium reservoir: The geological foundation of revealing the metallogenic mechanism and
 1158 solving “Remaining Uranium”. *Earth Science* 43, 3568-3583 (in Chinese with English abstract).

1159 JOHNSON, C.L. (2004). Polyphase evolution of the East Gobi basin: sedimentary and structural records
 1160 of Mesozoic-Cenozoic intraplate deformation in Mongolia. *Basin Research* (16), 79-99.

1161 JOHNSON, C.L. and RITTS, B.D. (2012). Plate interior poly-phase basins. In: BUSBY, C. and AZOR PEREZ,
 1162 A. (2012). *Tectonics of Sedimentary Basins: Recent Advances*. Wiley, Hoboken, ISBN:
 1163 9781444347135, pp. 567-582.

1164 KITAYAMA, Y., THOMASOT, E., O'NEIL, J., WING, B. (2012). Sulfur-and oxygen-isotopes, constraints on
 1165 the sedimentary history of apparent conglomerates from the Nuvvuagittuq Greenstone Belt
 1166 (Nuvanik, Quebec). *Earth and Planetary Science Letters*, 355, pp. 271-282.

1167 KOCHENOV, A.V., KOROLEV, K.G., DUBINCHUK, V.T., MEDVEDEV, Y.L. (1977). Experimental data on
 1168 precipitation of uranium aqueous solution. *Geochemistry International*, 14, pp. 82-87.

1169 ~~KOHN, M.J., RICUPITI, L.R., STAKES, D., ORANGE, D.L. (1998). Sulfur isotope variability in biogenic pyrite:
 1170 Reflections of heterogeneous bacterial colonization?. *American Mineralogist*, 83, pp. 1454-1468.~~

1171 LACH, P., CATHELINEAU, M., BROUAND, M., FIET, N. (2015). In-situ isotopic and chemical study of pyrite
 1172 from Chu-Sarysu (Kazakhstan) roll-front uranium deposit. *Procedia Earth and Planetary Science*,
 1173 13, pp. 207-210. doi.org/10.1016/j.proeps.2015.07.049

1174 LAMB, M.A. and BADARCH, G. (1997): Paleozoic sedimentary basins and volcanic-arc systems of
 1175 southern Mongolia: New stratigraphic and sedimentologic constraints: *International Geology*
 1176 *Review*, v. 39, p. 542-576.

1177 LANDAIS, P., CONNAN, J., DEREPE, J.M., GEORGE, E., MEUNIER, J.D., MONTHIOUX, M., PAGEL, M.,
 1178 PIRONON, J., POTY, B. (1987). Alterations of the organic matter, a clue for uranium ore genesis.
 1179 *Uranium*, 3, 307-342.

1180 LANDAIS, P. (1996). Organic geochemistry of sedimentary uranium ore deposits. *Ore Geol. Reviews*,
 1181 11, pp. 33-51.

1182 LE GOUX, F., BANZAGACH, T.O., DELAUNAY A., NYAMDORJ, B.I., JAKUES, E., KORSHUNOV, A., PARIZE,
 1183 O. and BROUAND, M. (2015). The Major Gobi Uranium Deposits, Upper Cretaceous East Gobi
 1184 Basin, Mongolia: Geodynamical and Mineralogical Key Parameters of Uranium Ore Geology. In:
 1185 *Mineral Resources in a Sustainable World, 13th SGA Biennial Meeting 2015*, vol. 5, 1815-1818.

1186 LONGERICH H.P., JACKSON S.E. and GÜNTHER D. (1996). Laser Ablation Inductively Coupled Plasma,
 1187 Mass Spectrometric Transient Signal Data Acquisition and Analyte Concentration Calculation.
 1188 *Journal of Analytical Atomic Spectrometry*, vol. 11, p. 899-904.

1189 LOVLEY, D.R., PHILLIPS, E.J.P., GORBY, Y. A., LANDA, E.R. (1991). Microbial reduction of uranium.
 1190 *Nature*, 350, pp. 413-416. doi:10.1038/350413a0

1191 LOVLEY, D.R., RODEN, E.E., PHILLIPS, E.J.P., WOODWARD, J.C. (1993). Enzymatic iron and uranium
 1192 reduction by sulfate-reducing bacteria. *Marine and Petroleum Geology*, 113, pp. 41-53.

1193 LOWERS, H.A., BREIT, G.N., FOSTER, A.L., WHITNEY, J., YOUNT, J., UDDIN, M.N., MUNEEM, A. (2007).
 1194 Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. *Geochimica et*
 1195 *Cosmochimica Acta*, 71, pp. 2699-2717.

1196 ~~MACHEL H. G., KROUSE H. R., Sassen R. (1995) Products and distinguishing criteria of bacterial and~~
 1197 ~~thermochemical sulfate reduction. Applied Geochemistry, 10, pp. 373-389.~~
 1198 ~~MACLEAN, L.C.W., TYLISZCZAK, T., GILBERT, P.U.P.A., ZHOU, D., PRAY, T.J., ONSTOTT, T.C., SOUTHAM,~~
 1199 ~~G. (2008). A high-resolution chemical and structural study of framboidal pyrite formed formed~~
 1200 ~~within a low-temperature bacterial biofilm. Geobiology, 6(5), pp. 471-480.~~
 1201 ~~<https://doi.org/10.1111/j.1472-4669.2008.00174.x>~~
 1202 MAKHNACH, A., MIKHAILOV, N., KOLOSOV, I., GULIS, L., SHIMANOVICH, V., DEMENEVA, O. (2000).
 1203 Comparative analysis of sulfur isotope behavior in the basins with evaporites of chloride and
 1204 sulfate types. Sedimentary Geology, 134, pp. 343-360.
 1205 MASUDA A., NAKAMURA N., and TANAKA T. (1973). Fine structure of mutually normalized rare-earth
 1206 patterns of chondrites, Geochimica et Cosmochimica Acta, 37, pp. 239-248.
 1207 MENOR-SALVAN C., TORNOS, F., FERNANDEZ-REMOLAR, D., AMILS, R (2010). Association between
 1208 catastrophic paleovegetation changes during Devonian-Carboniferous boundary and the
 1209 formation of giant massive sulfide deposits. Earth and Planetary Science Letters,
 1210 doi:10.1016/j.epsl.2010.09.020.
 1211 ~~MERCADIER, J., CUNNEY, M., LACH, P., BOIRON, M.C., BONHOURE, J., RICHARD, A., LEISEN, M., KISTER,~~
 1212 ~~P. (2011). Origin of uranium deposits revealed by their rare earth element signature. Terra Nova,~~
 1213 ~~23, No.4, pp.264-268.~~
 1214 MEUNIER, J.D., SELLIER, E., PAGEL, M., (1990a). Radiation damage rims in quartz from uranium bearing
 1215 sandstones. Journal of Sedimentary Petrology, 60, pp. 53-58.
 1216 MEUNIER, J.D., LANDAIS, P., PAGEL, M. (1990b). Experimental evidence of uraninite formation from
 1217 diagenesis of uranium rich organic matter. Geochimica et Cosmochimica Acta, 54, pp. 809-817.
 1218 MEYERHOFF, A.A. and MEYER, R.F. (1987). Geology of heavy crude oil and natural bitumen in the USSR,
 1219 Mongolia, and China. In: MEYER, R. F, ed., Exploration for heavy crude oil and natural bitumen:
 1220 AAPG Studies in Geology 25, pp. 31-101.
 1221 ~~MIN, M., XU, H., CHEN, J., FAYEK, M. (2005). Evidence of uranium biomineralization in sandstone-~~
 1222 ~~hosted roll-front uranium deposits, northwestern China, Ore Geology Reviews, Volume 26,~~
 1223 ~~Issues 3-4, July 2005, pp. 198-206.~~
 1224 MUNARA, A. (2012). Formation des gisements d'uranium de type roll : approche minéralogique et
 1225 géochimique du gisement uranifère de Muyunkum (Bassin de Chu-Sarysu, Kazakhstan). Thèse
 1226 soutenue le 9 Juillet 2012, PhD Univ. H. Poincaré Nancy. 327p.
 1227 MUROWCHICK, J. B., & BARNES, H. L. (1986). Marcasite precipitation from hydrothermal solutions.
 1228 ~~Geochimica et Cosmochimica Acta, 50(12), 2615-2629.~~

Formatted: German (Germany)

Formatted: German (Germany)

Field Code Changed

Formatted: German (Germany)

Formatted: Font: +Body (Calibri)

Formatted: Font: +Body (Calibri)

Formatted: Font: +Body (Calibri)

Formatted: Font: +Body (Calibri), French (France)

Formatted: Font: French (France)

Formatted: French (France)

Formatted: French (France)

1229 NAKASHIMA, S., DISNAR, J.R., PERRUCHOT, A., TRICHET, J. (1984). Experimental study of mechanisms
1230 of fixation and reduction of uranium by sedimentary organic matter under diagenetic or
1231 hydrothermal conditions. *Geochimica et Cosmochimica Acta*, 48, pp. 2321-2329.

1232 NAKASHIMA, S. (1992). Complexation and reduction of uranium by lignite. *Science of the Total*
1233 *Environnement*, 117-118, pp. 425-437.

1234 NIU, L., HUANG, S., YANG, G. (1995). The characteristics of uranium mineralization and genesis of
1235 Nuheting uranium deposit in Erlian Basin, Inner Mongolia. *China Nucl. Sci. Technol. Rep.* 1995-
1236 00 (in Chinese with English abstract).

1237 ~~OHMOTO, H., GOLDBERGER, M.B. (1997). Sulfur and carbon isotopes. In: Barnes, H. L. (Ed.),~~
1238 ~~*Geochemistry of hydrothermal ore deposits*, 3rd edition, Wiley, New York, pp. 517-611.~~

1239 ~~ORR W.L. (1974a). Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation~~
1240 ~~-study of Big Horn Basin Paleozoic oils. *American Association Petroleum Geologists Bulletin* 58,~~
1241 ~~2295-2318.~~

1242 OWEN D.E., OTTON J.K. (1995). Mountain wetlands: efficient uranium filters-potential impacts.
1243 *Ecological Engineering*, 5, pp. 77-93.

1244 PARIZE, O. (2013). Le remplissage de la dépression de Tsagaan Els et les dépôts fluviatiles associés
1245 (Crétacé moyen, Bassin de Zuunbayan). Implication stratigraphiques et sédimentologiques sur
1246 le gisement de Zoovch Ovoo – Synthèse des résultats 2012-2013. Octobre 2013, édition
1247 décembre 2014. Rapport technique AMS-DGS-TEC-SDYRT-0008, (Poster AMS-DGS-TEC-SDY-RT-
1248 0008_PosterZoovchA1_2013).

1249 PARIZE, O. (2015). Le remplissage de la dépression de Tsagaan Els et les dépôts fluviatiles associés
1250 (Crétacé moyen, Bassin de Zuunbayan). Implication stratigraphiques et sédimentologiques sur
1251 le gisement de Zoovch Ovoo – Synthèse des résultats 2012-2013. Octobre 2013, édition
1252 décembre 2014. Rapport technique AMS-DGS-TEC-SDYRT-0008, (Poster AMS-DGS-TEC-SDY-RT-
1253 0008_PosterZoovchA1_2013).

1254 PEARCE N.J.G., PERKINS W.K., WESTGATE J.A., GORTON M.P., JACKSON S.E., NEAL C.R. AND CHENERY
1255 S.P. (1997). A compilation of new and published major and trace element data for NIST SRM 610
1256 and NIST SRM 612 glass reference materials. *Geostandards and Geoanalytical Research*, vol. 21,
1257 pp. 101-114.

1258 PETROV N.N. (1998). Les gisements épigénétiques du Kazakhstan. *Géologie du Kazakhstan*, 2(354): pp.
1259 22-39. (trans. from Russian).

1260 PICARD, A., GARTMAN, A., CLARKE, D.R., GIRGUIS, P.R. (2017). Sulfate-reducing bacteria influence the
1261 nucleation and growth of mackinawite and greigite. *Geochimica et Cosmochimica Acta*.
1262 doi.org/10.1016/j.gca.2017.10.006

PICKEL, W., KUS, J., FLORES, D., KALAITZIDIS, S., CHRISTANIS, K., CARDOTT, B.J., MISZ-KENNAN, M., RODRIGUES, S., HENTSCHEL, A., HAMOR-VIDO, M., CROSDALE, P., WAGNER, N. (2017). Classification of liptinite - ICCP System 1994. *International Journal of Coal Geology*, 169, pp. 40-61.

PROST, G.L. (2004). Tectonics and hydrocarbon systems of the East Gobi basin, Mongolia, *AAPG Bulletin*, vol. 88, No. 4, pp. 483-513.

RACKLEY, R.I. (1972). Environment of Wyoming Tertiary Uranium Deposits. *The American Association of Petroleum Geologists Bulletin*, v. 56. No. 4. Pp. 755-774.

RALLAKIS, D., MICHELS, R., BROUAND, M., PARIZE, O., CATHELINEAU, M. (2019). The Role of Organic Matter on Uranium Precipitation in Zoovch Ovoo, Mongolia. *Minerals* 9(5), 310. DOI: [10.3390/min9050310](https://doi.org/10.3390/min9050310)

RALLAKIS, D., MICHELS, R., BROUAND, M., PARIZE, O., CATHELINEAU, M. (2020). Dolomite cements in Cenomanian continental sand deposits: time evolution and significance (Zoovch Ovoo U-deposit, East Gobi Basin, Mongolia). *Sedimentary Geology*, vol. 405(C), 105688. doi.org/10.1016/j.sedgeo.2020.105688

REYNOLDS, R.L., GOLDBERGER, M.B. (1978). Origin of a South Texas roll-type uranium deposit; I. Alteration of iron-titanium oxide minerals. *Economic Geology*, 73(8): 1677-1689.

ROUZAUD, J.N., OBERLIN, A., TRICHET, J. (1980). Interaction of uranium and organic matter in uriferous sediments. *Physics and Chemistry of the Earth*, vol. 12, pp. 505-516.

SAVAGE, K.S., TINGLE, T.N., O'DAY, P.A., WAYCHUNAS, G.A., BIRD, D.K. (2000). Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California. *Applied Geochemistry*, 15, pp. 1219-1244.

SAWLOWICZ, Z. (1993). Pyrite framboids and their development: a new conceptual mechanism. *Geologische Rundschau*, 82(1), pp. 148-156.

SAWLOWICZ, Z. (2000). Framboids: from their origin to application. *Polska Akademia Nauk – Oddział W Krakowie, Prace Mineralogiczne*, 88, 80 pp.

SCHULZ, H.M., YANG, S., PANOVA, E., BECHTEL, A. (2018). The role of Pleistocene meltwater-controlled uranium leaching in assessing irradiation-induced alteration of organic matter and petroleum potential in the Tremadocian Kaporie Formation (Western Russia), *Geochimica et Cosmochimica Acta*, doi: <https://doi.org/10.1016/j.gca.2018.10.029>

SCHWERTMANN, U. (1991). Solubility and dissolution of iron oxides. *Plant and soil*, 130, pp. 1-25.

SEIBERT, S., DESOURVIERES, C., SKRZYPEK, G., DENG, H., PROMMER, H. (2017). Model-based analysis of $\delta^{34}\text{S}$ signatures to trace sedimentary pyrite oxidation during managed aquifer recharge in a

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font:

Formatted: Normal, Justified, Indent: Left: 0", Hanging: 0.39", Line spacing: 1.5 lines

1296 heterogeneous aquifer. Journal of Hydrology, 548, pp. 368-381.
 1297 <https://doi.org/10.1016/j.jhydrol.2017.02.030>

1298 SPIRAKIS, C. (1996). The role of organic matter in the formation of uranium deposits in sedimentary
 1299 rocks. *Ore Geology Reviews*, 11, pp. 53-69.

1300 STUMM, W., LEE, G.F. (1960). The chemistry of aqueous iron. *Schweizerische Zeitschrift für Hydrologie*,
 1301 22(1), pp. 295-319.

1302 SUÁREZ-RUIZ, I., FLORES, D., MENDONÇA FILHO, J.G., HACKLEY, P.C. (2012). Review and update of the
 1303 applications of organic petrology: Part 1, geological applications. *International Journal of Coal*
 1304 *Geology*, 99, pp. 54-112.

1305 SUZUKI, Y., BANFIELD, J.F. (1999). Geomicrobiology of Uranium, chapter 8. In: Burns, P.C., Finch, R.
 1306 (1999). *URANIUM: Mineralogy, Geochemistry and the Environment*, Reviews in Mineralogy, 38,
 1307 673 p.

1308 SÝKOROVÁ, I., PICKEL, W., CHRISTIANIS, K., WOLF, M., TAYLOR, G.H., FLORES, D., 2005. Classification
 1309 of huminite—ICCP System 1994. *International Journal of Coal Geology* 62, 85–106.

1310 TRAYNOR, J.J. and SLADEN, C. (1995). Tectonic and stratigraphic evolution of the Mongolian People's
 1311 Republic and its influence on hydrocarbon geology and potential: Marine and Petroleum
 1312 Geology, v. 12, p. 35-52.

1313 VEERAMANI, H., SCHEINOST, A.C, MONSEGUE, N., OAFOKU, N.P., KUKKADAPU, R., NEWVILLE, M.,
 1314 LANZIROTTI, A., PRUDEN, A., MURAYAMA, M., HOCELLA, Jr. M.F. (2013). Abiotic Reductive
 1315 Immobilization of U(VI) by Biogenic Mackinawite. *Environmental Science and Technology*, 47, 5,
 1316 2361-2369.

1317 WARWICK, P., EVANS, N., HALL, A., WALKER, G., STEIGLEDER, E. (2005). Stability constants of U(VI) and
 1318 U(IV)-humic acid complexes. *Journal of Radioanalytical and Nuclear Chemistry*, 266(2), pp. 179-
 1319 190.

1320 WATSON, J., CRESSEY, B., ROBERTS, A., ELLWOOD, D., CHARNOCK, J., AND SOPER, A. (2000). Structural
 1321 and magnetic studies on heavy-metal-adsorbing iron sulphide nanoparticles produced by
 1322 sulphate-reducing bacteria. *J. Magn. Magn. Mater.* 214 (1-2), 13–30. doi:10.1016/s0304-
 1323 8853(00)00025-1

1324 WENTWORTH, C.K. 1922. A scale of grade and class terms for clastic sediments. *Journal of Geology*.
 1325 30:377-392. WORDEN, R.H. & BURLEY, S.D. (2003). Sandstone diagenesis: the evolution of sand
 1326 to stone, *Sandstone Diagenesis: Recent and Ancient*. International Association of
 1327 Sedimentologists, 44 pp. ISBN: 978-405-10897-3.

1328 WERSIN, P., HOCELLA, M.F., PERSSON, P., REDDEN, G., LECKIE, J.O., HARRIS, D.W. (1994). Interaction
 1329 between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence of sorption and
 1330 reduction. *Geochimica et Cosmochimica Acta*, 58(13), pp. 2829-2843.

- 1331 WILKINS, M.J., LIVENS, F.R., VAUGHAN, D.J., LLOYD, J.R. (2006). The impact of Fe(III)-reducing bacteria
1332 on uranium mobility. *Biogeochemistry*, 78(2), pp. 125-150.
- 1333 WOLTERS, M., VAN DER GAAST, S. J., AND RICKARD, D. (2003). The structure of disordered
1334 mackinawite. *Am. Mineral.* 88 (11-12), 2007–2015. doi:10.2138/am-2003-11-1245
- 1335 YUE, L., JIAO, Y., WU, L., RONG, H., XIE, H., WANG, Q., YAN, Q. (2019). Selective crystallization and
1336 precipitation of authigenic pyrite during diagenesis reservoir sandbodies in Ordos Basin. *Ore*
1337 *Geology Reviews*, vol. 107, pp. 532-545.
- 1338 ZHANG, R., DING, W. (1996). Discussion on geological characteristics of Nuheting type uranium deposit
1339 and the relation between oil and gas-bearing water and uranium metallogenesis. *Galaxy of*
1340 *Research Achievements of Uranium Geology of China*. Bureau of Geology, CNNC, Beijing, pp.
1341 205–214.
- 1342 ZHANG, F., JIAO, Y.Q., WU, L.Q., RONG, H., WANG, L.H. (2018). Relations of uranium enrichment and
1343 carbonaceous debris within the Daying uranium deposit, northern Ordos Basin. *Journal of Earth*
1344 *Science*, DOI: 10.1007/s12583-017-0952-0.
- 1345 ZHANG, F., JIAO, Y., WU, L., RONG, H., WANG, L., ZHANG, Z. (2019). In-situ analyses of organic matter
1346 maturation heterogeneity of uranium-bearing carbonaceous debris within sandstones: A case
1347 study from the Ordos Basin in China, *Ore Geology Reviews*, doi:
1348 <https://doi.org/10.1016/j.oregeorev.2019.03.021>
- 1349 ZHU, M., WU, R., LIU, X., NIE, F., YU, D. (2012). Geologic Setting of Interformational Braided Channel
1350 Type Sandstone Uranium Deposits in North China, East China Institute of Technology,
1351 29/05/2012 IAEA Conference, PowerPoint Presentation. Available online from:
1352 [https://www.slideshare.net/monatom/05-xiaodong-liu-geologic-setting-of-](https://www.slideshare.net/monatom/05-xiaodong-liu-geologic-setting-of-interformationalbraidedchannel-type-sandstone-uranium-deposits-in-north-china)
1353 [interformationalbraidedchannel-type-sandstone-uranium-deposits-in-north-china](https://www.slideshare.net/monatom/05-xiaodong-liu-geologic-setting-of-interformationalbraidedchannel-type-sandstone-uranium-deposits-in-north-china)
1354 <https://www.britannica.com/place/Mongolia>, Accessed date: 25 February 2021

Formatted: French (France)

1355

1356 FIGURES

1357 **Figure 1:** Location map of Mongolia presenting A) the four metallogenic provinces
1358 hosting U, namely from North to South 1) North Mongolian, 2) Khentai-Daur, 3) Mongol-
1359 Priargun, 4) Gobi-Tamtsag (Dahlkamp, 2009) and; B) of the study area (~~Encyclopædia~~
1360 ~~Britannica~~) and C) a simplified geological map of East Gobi Basin with the morpho-
1361 tectonic elements. The Zoovch Ovoo roll-front U deposit is located in the Zuunbayan
1362 sub-basin in East Hongor Tolgoy and Bayanshiree plateau (map modified from
1363 Graham et al., 2001).

1364 **Figure 2:** ~~Litho~~Stratigraphical column of the East Gobi Basin, including potential
1365 unconformities, depositional environments and tectonic episodes. Modified from
1366 Jerzykiewicz and Russell (1991); Prost (2004). 1= metamorphic rocks, 2= granitic
1367 rocks, 3= conglomerate, 4= coarse sandstone, 5= medium sandstone, 6= shale, 7=
1368 uncertain duration, 8= Zoovch Ovoo uranium deposit.

1369 **Figure 3:** Examples of studied samples distribution (green and blue dots for U-rich and
1370 carbonate cemented samples, respectively~~blue dots~~) along with two roll-front profiles.
1371 The background colours represent oxidized (yellow) versus reduced sand (white),
1372 clays (green) and uranium mineralization (red mesh texture). The vertical lines
1373 represent drilling-wells. The two profiles are not on the same vertical scale. The
1374 distance between wells is at the scale of tens of meters.

1375 **Figure 4:** Examples of typical core sequences in Zoovch Ovoo. **A)** Well, ZOOV_1142,
1376 depth 306.20 m. From left to right: reduced matrix-supported sandstone, oxidized
1377 matrix-supported sandstone, reduced matrix-supported sandstone with ~~O-~~Morganic
1378 matter, and reduced carbonate cemented sandstone. **B)** Well, ZOOV_1154, depth
1379 164.10 m. Reduced (left) and oxidized (right) consolidated facies ranging from silty
1380 claystone to very fine sand.

1381 **Figure 5:** Summary of the main siliciclastic and carbonate elements presented in the
1382 Zoovch Ovoo sands. (A, B) Monocrystalline and polycrystalline quartz. (C, D)
1383 Plagioclase and microcline with polysynthetic and cross-hatched twinning,
1384 respectively. The plagioclase with slight sericite alteration. (E, F) Detrital muscovite,
1385 chlorite, biotite. (G) Detrital dolomite grain, (H) Lithic element showing granophyric
1386 texture. All photographs under polarized/analyzed light; (G) under white light.

1387 **Figure 6:** Conceptual drawings of the ~~seven~~five FeS₂ generations identified in the
1388 Zoovch Ovoo sands. From left to right moving from the older to the younger generation:
1389 i) framboidal; ii) concentric (overgrowth); iii) euhedral pyrite 1 (pre-ore), iv) acicular
1390 FeS₂ (marcasite); ~~v) and~~ v) euhedral pyrite 2 (ore-stage); ~~vi) framboids in type IV~~
1391 ~~anhedral dolomite and vii) euhedral pyrite in type IV anhedral dolomite are~~
1392 ~~discriminated.~~

1393 **Figure 7:** Examples of the uranium ore replacing the euhedral pyrite 1 (pre-ore)
1394 generation while crystallized contemporaneously with the euhedral pyrite 2 (ore-stage).
1395 All pictures are taken under SEM-EDS using back-scattered electron mode. The

Commented [R21]: I rotated the map in landscape orientation to maximize the size. I also used colours and a more efficient geographical map for Mongolia.

1396 uranium content is higher in the brighter zones. **(A)** A close view showing the corrosion
 1397 features of pyrite 1 as cement (pre-ore) systematically in contact with UO_2 . Quartz
 1398 cement post-dates UO_2 ; **(B)** In the lower half of the picture, detrital grains cemented by
 1399 pyrite and UO_2 . Note the corroded surface of pyrite, which is also the boundary to UO_2 .
 1400 In the upper half of the picture, matrix (clays) supported sandstone without UO_2 ; **(C)**
 1401 Framboidal pyrite with pyrite overgrowth followed by UO_2 rim and euhedral pyrite 2 (ore
 1402 stage). The whole cluster is encompassed by uranium-rich clay matrix; **(D)** Zoomed
 1403 image of (C), where the two pre-ore stage pyrite generations (framboidal pyrite and
 1404 overgrowth) can be discriminated by the ore-stage euhedral pyrite 2, separated by a
 1405 UO_2 coating; **(E)** An organic matter particle relic (encompassed by the yellow dotted
 1406 line) that was previously replaced by framboidal pyrite. The framboids are closely
 1407 packed to form pyrite cement. Eventually, pyrite cement is being replaced by uranium
 1408 (~~pitchblende~~uraninite). The contact between ~~pitchblende~~uraninite and remaining pyrite
 1409 shows a typical contorted feature suggesting replacement process; **(F)** Focus on the
 1410 contact between framboidal pyrite and UO_2 . Several rates of framboid replacement by
 1411 UO_2 are recognized from right to left: fully preserved framboids, framboid core
 1412 remnants within UO_2 , almost entirely replaced framboid and finally UO_2 cement without
 1413 any recognizable pyrite; **(G)** Telovitrinite particle with variable uranium content and no
 1414 observable U-mineral expression. The uranium content is higher in the brighter zones;
 1415 **(H)** Uranium as ~~pitchblende~~uraninite (UO_2) precipitating at the rims of a Collotelinite
 1416 particle. Uranium concentration is decreasing towards the inner part of the particle as
 1417 a function of increasing distance from the U-cement area;

1418 **Figure 8:** Co and Cd content of pyrite as measured by La-ICPMS. It is possible to
 1419 distinguish pyrite associated with uranium (in red circles) enriched in Co and Cd from
 1420 pyrite not linked to uranium (in grey squares), which is depleted. Euhedral pyrite
 1421 associated with marcasite (blue triangles) is enriched in Co, while the euhedral pyrite
 1422 associated with sphalerite (green rhombs) enriched in Cd.

1423 **Figure 9:** Frequency histogram presenting the distribution of $\delta^{34}\text{S}$ for the different iron
 1424 disulfide occurrences: framboidal pyrite (in blue), euhedral/cubic pyrite (in red),
 1425 framboidal pyrite replacing organic matter (in green), euhedral/cubic to anhedral FeS_2
 1426 cement replacing organic matter (in purple) and marcasite.

1427 **Figure 10:** The Rayleigh fractionation model of framboidal pyrite at Lost Creek (LC)
 1428 from Hough et al., 2019 (blue dots), cross-plotted with the results of this study (red

dots) and pyrite data from Bonnetti et al., 2020 (green dots). The dashed line models $\delta^{34}\text{S}$ value of sulfate in solution with progressive sulfur depletion. The solid black line is the $\delta^{34}\text{S}$ value of pyrite produced at a specific level of depletion. According to the authors, the data corresponds to 88.5% depletion of sulfate in solution. The fractionation from Lost Creek is higher by about 100‰ than Zoovch Ovoo.

Figure 11: Summary of the macerals identified in the Zoovch Ovoo sands. Polished block photomicrographs under oil-immersion (x50) and reflected light. A) Fusinite with framboidal pyrite; B) Telovitrinite associated with euhedral pyrite and semifusinite; C) Very oxidized particle of telovitrinite (collotelinite); D) Fusinite containing uranium minerals, also euhedral pyrite, showing significantly higher reflectance.

Figure 12: The different forms of uranium petrographic types. (A) Uranium crystals as small spheres (U-balls) on organic matter (O.M). The maceral gelovitrinite (completely filled cells) appears to be more resilient to its replacement by U. (B) Elongated U-crystals termed U-flakes and U-aggregates. (C) U-balls of 1 μm size inside sphalerite cement. (D) U-flakes are growing at the rim of a quartz grain.

Figure 13: Ternary plot of $\text{P}_2\text{O}_5\text{-UO}_2\text{-SiO}_2$ (in wt% oxide) indicating the stoichiometric U-mineral compositions (striped squares) PitchblendeUraninite, Phosphorus enriched PitchblendeUraninite, Coffinite and Phospho-coffinite.

Figure 14: SEM-EDS analysis of a telovitrinite particle from sample 9704-8 (clay and organic matter intraclast in very coarse-grained mineralized sand). Three macerals can be discriminated, telinite, collotelinite and gelovitrinite. (A) Point measurements across the particle focusing on the areas of different brightness. The uranium content is uniformly fluctuating between 7.9-13.1 wt%. (B, C) High magnification of the bright regions of the telohuminite particle. Uranium distribution is not uniform at this scale.

Figure 15: The complete paragenesis of the diagenetic phases encountered in the Zoovch Ovoo sands.

Figure 16: Abiogenic redox model for pyrite dissolution and uranium reduction. (a) Pyrite is first partially dissolved; (b) Uranium is reduced from reduced sulfur and (c) by reduced iron.

Figure 17: The proposed metallogenic model for uranium formation and associated diagenetic phases in Zoovch Ovoo. The overall thickness of the reservoir has a maximum of 100 m. The oxidization part of the roll front provides sulfates (inspired by

1461 Rackley, 1972) and micro-organisms. In the sub-oxic part of the roll-front, three major
1462 intricate processes are involved in the mineralization formation: 1. Sulfate
1463 (bio)reduction leading to pyrite formation, 2. Pyrite epigenesis by pitchblendeuraninite
1464 3. Organic matter reactivity through complexation and sustainment of biological
1465 activity, responsible for uranium precipitation. Titanium oxide epigenesis by
1466 pitchblendeuraninite is also a common feature at Zoovch Ovoo. Organic matter
1467 sustains biological activity, which controls uranium precipitation either directly or
1468 through pyrite formation. It plays, therefore, a significant role in the biogeochemical
1469 process of uranium ore formation of Zoovch Ovoo.

1470

1471 TABLES

1472 **Table 1:** Rock-Eval data for different samples lithologies, namely: sand with organic
1473 matter (OM), black claystone and carbonate-cemented sandstone with organic matter.
1474 Radioactivity measurement in CPS (counts of radioactivity per second) using a
1475 Radiagem SPP2 detector. Background radioactivity 70 cps. Rock-Eval indices: S1
1476 amount of free hydrocarbons (mg of hydrocarbons per gram of sample); S2 oil potential
1477 (mg hydrocarbon per gram of sample); TOC Total organic Content (in weight %); Tmax:
1478 thermal maturity index in degree Celcius; HI: Hydrogen Index (mg of hydrocarbons per
1479 gram of organic carbon); OI: Oxygen index (mg of CO₂ per gram of organic carbon).

1480 **Table 2:** Sulfate and iron-reducing bacteria, as well as the methanogens, can
1481 enzymatically reduce uranium to form uranium oxides such as pitchblendeuraninite.

1482

1483

1484

1485 ANNEX (SUPPLEMENTARY MATERIAL)

1486 **Figure A1:** Clustered bar chart indicating the lithofacies distribution in Zoovch Ovoo,
1487 expressed in percent, as identified by point-counting method on the basis of 97
1488 samples.

1489 **Figure A1A2:** The log(Fe₂O₃/K₂O) versus log(SiO₂/Al₂O₃) after Herron, 1988. Data
1490 from bulk rock analysis (ICP-MS).

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Figure A3: A Diffractogram of oriented section under air-dried (AD) conditions and after ethylene-glycol (EG) treatment, for the sample 9704-45 (black silty-clay from the mineralized zone).

Figure A2A4: Cross-plot between Hydrogen Index and Oxygen index. Symbols coloured according to radioactivity (cps- counts per second) content of the whole rock. Data indicate that kerogen is of Type III (higher plants derived), consistent with organic petrography observations. The zoomed part of the diagram on the right suggests no relationship between kerogen's oxygen content and alteration by radioactivity.

Figure A3A5: Chondrite-normalized rare earth element patterns for UO_2 in three different petrographic situations: A) UO_2 replacing organic matter; B) associated with pyrite and C) within the clay matrix). In D, a comparison between the average REE concentrations of uranium oxides compared to the bulk rock.

Figure A4A6: SEM-BSE (A, D, G) and their respective cathodoluminescence images under black-white (B, E, H) and coloured mode (C, F, I). In A, B, C, quartz grains, and other silicate detrital minerals, the absence of pleochroic halos indicates the lack of radiolytic alteration. In D, E, F, uranium cement in part around a quartz grain, which shows radiolytic alteration features, i.e. zonations of specific distance from the grain edge towards the inner part. When radiation damage rims are observed in the absence of uranium minerals, they indicate former long-term contact. Uranium minerals were precipitated and then dissolved, a process typical of uranium displacement and re-concentration linked to roll-front movement. G, H, I: quartz cement crystals have grown inside a vug of pyrite that was partially replaced by uranium cement. The zonations and the jagged and ingrown shape of the crystal point out its authigenic character.

Figure A5A7: Cross-plot between total organic carbon (TOC) and total sulfur content (bulk rock analysis). The diagram shows a significant relationship suggesting that organic matter is a prerequisite for pyrite growth.

Figure A6A8: Examples of framboids being embedded by euhedral pyrite. **A, B:** Typical example of a pyrite cluster with framboids within euhedral crystals, located in the intergranular porosity of a matrix-supported sandstone. The framboids (20 μm) are densely packed and highly amalgamated with the euhedral grains, but they can be still discriminated against since they are composed of submicron pyrite crystals. The individual cubic crystals that form the aggregate are at the size of 10 μm (BSE). **C:** Again, framboids encompassed by euhedral pyrite, this time growing on organic

1524 matter, particularly fusinite. Euhedral crystals not associated with framboids are also
1525 recognized (BSE). **D:** A cluster of framboidal pyrite encompassed by a generation of
1526 euhedral pyrite that contains uranium. The cluster is cemented by type III subhedral
1527 dolomite. **E:** Well-developed pyritospheres (15 μm) surrounded by
1528 pitchblendeuraninite, followed by euhedral pyrite (10-15 μm) with pitchblendeuraninite
1529 inclusions. The whole assemblage is within the clay matrix, where pitchblendeuraninite
1530 is also contained. There appears to be one euhedral pyrite generation (BSE). **F:** Group
1531 of well-developed framboids (up to 10 μm) encompassed first by concentric
1532 overgrowth, then by euhedral pyrite at the size range of 5-10 μm , followed by
1533 pitchblendeuraninite precipitation and another a few μm thick euhedral pyrite
1534 generation (BSE).

Conditions for uranium biomineralization during the formation of the Zoovch Ovoo roll-front-type uranium deposit in East Gobi Basin, Mongolia

Dimitrios Rallakis¹, Raymond Michels¹, Michel Cathelineau¹, Olivier Parize² and Marc Brouand²

¹Université de Lorraine, CNRS, CREGU, GeoRessources, 54504, Vandoeuvre-lès-Nancy, France

²ORANO Mining, Le Prisme, 125 Avenue de Paris, 92320, Chatillon, France

Abstract

The Zoovch Ovoo uranium rollfront-type deposit is hosted in the Sainshand Formation, a Late Cretaceous siliciclastic reservoir, which constitutes the upper part of the post-rift infilling of the Mesozoic East Gobi Basin in SE Mongolia. The Sainshand Formation consists of unconsolidated medium-grained sand, silt and clay intervals deposited in fluvial-lacustrine settings. The uranium deposit is confined within a 60-80 m thick siliciclastic sequence inside aquifer-driven systems. The overall system experienced shallow burial and was never subjected to temperatures higher than 40°C. This study proposes a comprehensive metallogenic model for this uranium deposit. Sedimentological and mineralogical observations from drill core samples to the microscopic scale (optical and Scanning Electron Microscopy) together with in situ geochemistry of late-formed phases (Laser Ablation–Inductively Coupled Plasma Mass Spectrometry, Electron Probe Microanalysis, Fourier Transform–Infrared Spectroscopy) were considered for the reconstruction of the main stages of U trapping.

In the mineralized zone, the uranium ore is expressed as Ca–enriched uraninite (UO₂) and less commonly as Ca–enriched phospho-coffinite (U, P)SiO₄. Trapping mechanisms include i) complexation (i.e. uranyl-carboxyl complexes), ii) adsorption on organic or clay particles) and

iii) reduction by pyrite and by bacterial activity to amorphous uraninite. In all cases, the organic matter plays either the role of trap for uranium or nutrient for bacteria that can trap uranium through their metabolism. The shallow burial diagenesis conditions do not allow direct reduction of U(VI) by organic carbon. The $\delta^{34}\text{S}$ values of the iron disulfide are very diverse, fluctuating in extreme cases between -50 to +50‰, with an average $\delta^{34}\text{S}$ value for framboidal pyrite at 2‰, and -20‰ for euhedral pyrite. The positive and negative values reflect close versus open fractionation systems, while bacterial sulphate reduction (BSR) is active during the whole diagenetic history of the deposit as an essential source of reduced sulfur. Therefore, using detrital organic matter as a carbon source, microorganisms play a significant role in uranium trapping, either as a direct reducing agent for uranium or pyrite formation, which will trap uranium redox driven epigenetic processes.

Keywords: roll-front, uranium, bioreduction, organic matter, sulfur isotopes, East Gobi Basin, Mongolia

1 Introduction

The Central Asia Uraniferous Province, one of the most strategic areas in the world for uranium reserves, extends from Kazakhstan to the West towards the Transbaikial region to the East (Dahlkamp, 2009; Le Goux et al., 2015; IAEA 2018). Significant roll-front deposits exist all over this region, examples include the Chu-sarysu and Syrdarya basins in Kazakhstan (Aubakirov, 1998; Petrov 1998; Jaireth et al., 2008; Munara, 2012; Lach et al., 2015), the Songliao, Ordos and Erlian basins in China (Huang Xian-Fang et al., 2005; Min et al., 2005; Cai et al., 2007; Bonnetti et al., 2015a,b; Cao et al., 2016; Akhtar et al., 2017; Bonnetti et al., 2017; Jiao et al., 2018; Zhang et al., 2018; Yue et al., 2019) and the Unegt and Zuunbayan basins in Mongolia (Le Goux et al., 2015; Grizard et al., 2018; Boissezon et al., 2020; Rallakis et al., 2019; 2020).

Although these roll-front type uranium deposits might appear similar in terms of geochemical signatures and deposit geometry, there are significant differences in their paragenesis. The pre-ore uranium concentration in the sediments, the amount of detrital organic matter, the nature of uranium reducing agents, microorganisms' role, and uranium-hydrocarbon phase interactions may vary from one deposit to the other.

For instance, mineralization in the Chu-Sarysu basin in Kazakhstan occurs in Paleocene continental arkosic sands deposited in fluvial settings, sourced from volcanic rocks (Aubakirov, 1998; Petrov, 1998; Munara, 2012). Uranium mineralization is associated with hydrothermal and biogenic pyrite (Lach et al., 2015). Although the proportion of organic matter in the mineralized grey sandstones is low (generally 0.03-0.05% C), Petrov (1998) suggests that this proportion is enough with a minor contribution of iron sulfides to produce large U-deposits in sandstone. Later studies (Jaireth et al., 2008) indicate that the redox conditions were favoured by the upward migration of gases from the oil field (including H₂S) located below the Cretaceous sediments. U-deposits in sandstones located close to hydrocarbon reservoirs were also identified in the Ordos and Songliao basins in China (Huang Xian-Fang et al., 2005). The formation of uranium deposits in organic poor lithologies has been attributed to the input of H₂S, along faults from deep hydrocarbon reservoirs (Reynolds and Goldhaber, 1978). Yet, the role of hydrothermal fluid in the systems is ambiguous and rarely proven, with the rare exception of deposits where fluid inclusions attest to the circulation of hot brines, sometimes with hydrocarbons or gases (Zhu et al., 2012).

Some of these deposits were intensively studied in the last decade, and several results point out the contribution of biological activity within the sedimentary reservoirs to explain the U reduction. For example, in the Nuheting deposit in the Erlian basin, hydrocarbons and associated gases were invoked as potential reductants (Niu et al., 1995; Zhang and Ding, 1996 cited in Bonnetti, 2013 and Bonnetti et al., 2015a). The data, however, do not support the hypothesis of hydrocarbons migrations as reducing agents for uranium mineralization. Thus, Bonnetti et al. (2015) indicated that the Nuheting deposit underwent three main stages of

mineralization: (i) a synsedimentary/early diagenetic uranium concentration and mineralization, (ii) a late diagenetic *in situ* uranium remobilization and deposition on pyrite and (iii) epigenetic cementation. Another example is the Baxingtuo uranium deposit in the Songliao Basin. It is hosted in the Late Cretaceous Yaojia Formation in medium to fine-grained channel sandstone with abundant type III and IV kerogen detrital organic matter. In rare cases, uranium mineralization was attributed mostly to bacterial processes responsible for uranium reduction (Bonnetti et al., 2017).

The present paper aims to fully characterize the U-minerals and their relationships with organic matter and sulfides. Specifically, the petrography of the detrital and diagenetic phases as well as the crystal chemistry of the latter help to build the paragenesis and identify the uranium mineralization episodes. The crystal chemistry of uranium phases reveals the presence of U-minerals, while the trace element content of pyrite seems to be a very effective index to distinguish between pre-ore and syn-ore pyrite generations. The stable isotopes, in particular the *in situ* $\delta^{34}\text{S}$ isotopic analysis of pyrite provide information on the origin of reduced sulfur, while its fractionation signifies the availability of reduced sulfur in the system during the evolution of the deposit. Organic petrography and Rock-Eval pyrolysis are used for the qualitative assessment of kerogen and its thermal maturity. By combining the above, it is possible to understand the mechanisms responsible for the formation of uranium mineralization, while their interplay yields a geochemical model for the Zuoovch Ovoo deposit.

2 Geological setting

2.1 The East Gobi Basin

Mongolia is separated into four metallogenic provinces that host U mineralization, the Gobi-Tamtsag where the study area is located, the Khentei-Daur, the North Mongolian and the Mongol-Priargun. These provinces host over forty U mineralization areas that differ in terms of geological setting, mineralization type and age and associated minerals (Figure 1A, B; Dahlkamp, 2009).

The East Gobi Basin is located in southeastern Mongolia (Figure 1). It includes four morpho-tectonic elements: the Unegt and Zuunbayan sub-basins as shown on the map and the Sainshand and Khovsgol sub-basins located SW and NE of the map, respectively (Prost, 2004). The 700 km-wide by 300 km-long northeast-southwest trending East Gobi Basin was formed during Mesozoic extension (Meyerhoff and Meyer, 1987; Prost, 2004; Johnson and Ritts, 2012). The Zuunbayan sub-basin hosts the Zoovch Ovoo uranium deposit (Figure 1C). The Mesozoic-Cenozoic sedimentary sequence is estimated to approach about 4000 m in thickness. The granitic outcrops in the NE and S parts of the basin are probably the quartz arenite sandstone sources (Prost, 2004). In the Gobi-Tamtsag province, U deposits are found within the Upper Cretaceous (Cenomanian) Sainshand Formation from the Zuunbayaan sub-basin. This post-rift sedimentary infill of the East Gobi Basin is composed of medium to coarse-grained sand, deposited in fluvial to flood-dominated delta and lacustrine systems (Cardon et al., 2015; Le Goux et al., 2015).

2.2 Tectonic history

The East Gobi Basin is a multiphase deformation area (plate interior poly-phase basin) that, according to recent studies and petroleum-exploration seismic profiles, was subjected to four cycles of deformation and subsidence (Prost, 2004; Johnson and Ritts, 2012; Heumann et al., 2014), lasting from Late Paleozoic to Cenozoic:

- Due to the Paleo-Asian Ocean's closure, the Late Permian post-collisional basin produced highly deformed and metamorphosed turbiditic sequences that are unconformably overlain by undeformed non-marine Permo-Triassic fluvial and alluvial sediments (Phase 1).
- A Late Triassic major sinistral shear zone (East Gobi fault zone), southern Mongolia that formed major foreland and intramontane basins along with thrust sheets that carried Precambrian and early Paleozoic carbonate klippe over Permian and Triassic units. (Phase 2).

- The Late Mesozoic rift basin, lasting from the Late Jurassic to Late Cretaceous, is marked by the development of high angle normal faults (Phase 3).
- The Late Cretaceous post-rift succession and the development of a strike-slip basin marked by the regional unconformity and basin inversion. Although the sediments overlying the Late Cretaceous are characterized as a post-rift thermal sag phase, there were probably left-lateral strike-slip faults developing during the Early Cenozoic (Phase 4).

Finally, the Mesozoic sequence is covered by Tertiary-Quaternary fine to coarse-grained alluvial sediments, which form deposits of up to 5 km long and 1-2 km wide. Uplift episodes during the Early Cenozoic are also likely as older units outcrop locally among the Tertiary-Quaternary deposits (Prost, 2004) and are probably linked to the initiation of the Altyn Tagh fault in China during Oligocene-Miocene (Johnson and Ritts, 2012).

2.3 Stratigraphy of the East Gobi Basin

The lithostratigraphy of the East Gobi basin is presented in Figure 2. The Paleozoic basement stratigraphy (Devonian-Permian) consists of metamorphosed Paleozoic arc-related volcanics and marine siliciclastics forming the Tavan Tolgoi Unit (Traynor and Sladen, 1995; Lamb and Badarch, 1997; Graham et al., 2001). It is overlain unconformably by a 1000-4000 m thick continental sequence from Jurassic to Tertiary (Meyerhoff and Meyer, 1987; Prost, 2004). A hiatus of variable thickness exists between Permian and Middle Jurassic due to repeated episodes of block faulting and multiphase deformation (Johnson, 2004; Itterbeeck et al., 2005). The Khamar Khovoor Formation was deposited during the Middle and Upper Jurassic and is 750 m thick. The depositional setting at that time was paralic to marginal marine, with a combination of fluvial, lacustrine, deltaic and swamp-organic sedimentation. The fluvial character is expressed by braided rivers depositing sand and the paralic by dominant shale deposits. The Khamar Khovoor Formation forms a hiatus with the overlying Upper Jurassic (Tithonian-Kimmeridgian) Sharlyn Formation that consists of 200 m of well-defined braided

157 fluvial sandstones, conglomerates and to a lesser extent finer sediments, as lacustrine shales
158 (Graham et al., 2001; Prost, 2004).

159 This was followed by a 300-700 m thick sequence consisting mainly of shales interbedded with
160 coarser fractions (dark-coloured sandstones, conglomerates, siltstones) and volcanics (red-
161 coloured tuffs, basalts) forming the Tsagaan Tsav Formation of Early Cretaceous (Valanginian)
162 age. The Tsagaan Tsav Formation is composed of a fining upwards sequence of alluvial fan
163 and braided stream deposits, which is topped by fine material deposited during flooding events
164 (overbank deposits) and lacustrine facies (Graham et al., 2001; Johnson, 2004). The coarser
165 sandstone part of the Tsagaan Tsav Formation is the reservoir unit for the Tsagaan Els and
166 the Zuunbayan oil fields. The Zuunbayan Formation is Hauterivian to Albian and comprises
167 970 m of non-marine poorly compacted sandstones, interbedded with shales and volcanic tuff.
168 The Zuunbayan Formation is divided into three different units. i) the organic-rich basal unit,
169 which contains bituminous shales considered as potential source rock, ii) the central and upper
170 units, which include coals and sandstones with channel geometry along with basaltic flows
171 (Prost, 2004).

172 Within the Zuunbayan sub-basin, the Sainshand Formation hosts the Zoovch Ovoo uranium
173 deposit (Parize, 2013; Le Goux et al., 2015). The Sainshand Formation is of Cenomanian age,
174 and its thickness varies between 100-350 m. The sub-units reflect different lacustrine and
175 alluvial sedimentation cycles, setting up a combination of conglomerate, sand, silt, and clay
176 sediments (Dahlkamp, 2009). The Sainshand Formation is overlain by the Late Cretaceous
177 (Santonian-Turonian) Bayanshiree Formation, consisting mainly of reddish to greyish shales
178 with minor sandstones with channel-shaped geometry (Graham et al., 2001; Johnson, 2004).
179 The thickness of the next two Late Cretaceous lacustrine coarse clastic units, namely the
180 Santonian-Campanian Baruungoyot Formation and the Campanian-Maastrichtian Nemegt
181 Formation, is variable. The Upper Cretaceous post-rift sequence was deposited in a sag basin
182 period (sediment starvation) and was affected by strike-slip tectonics later in Cenozoic. The
183 series dip significantly along the faulted boundaries, whereas they are sub-horizontal in the

core of the syncline. Locally, Tertiary and Quaternary strata are present due to vertical movements of the East Gobi Fault Zone (Johnson and Ritts, 2012; Heumann et al., 2014). They are generally undifferentiated with very fine to coarse sediments that unconformably overlie the Late Cretaceous strata (Prost, 2004).

In this tectonic framework, the burial history of the regional area of Zoovch Ovoo as well as the geothermal gradient (4.5°C/100m) were based on Graham et al. (2001), Prost (2004), Rallakis et al. (2019; 2020).

3 Materials and methods

3.1 Uranium in the Sainshand Formation – Sampling

As the uranium distribution varies with the development of redox fronts in roll-front systems, samples were recovered from drill-cores along profiles crossing oxidized, active roll-front as well as reduced zones (Figure 3). The locations of Profile 1 and 2 in the roll-front are indicated in Figure 1. The Zoovch Ovoo depocenter is mostly composed of unconsolidated sediments, such as silts and sands. Few consolidated facies are clay matrix-supported, and less commonly dolomite-cemented sandstones (Figure 4). The Sainshand Formation features record depositional conditions ranging from fluvial to flood-dominated delta and lacustrine systems (Dahlkamp, 2009; Parize, 2015; Le Goux et al., 2015).

3.2 Petrography and chemistry

The petrographic characteristics of the different types of minerals were studied in detail on polished thin sections (~30 µm thick), using optical microscopy in transmitted and reflected light modes. The two methodologies used for their classification were based on Dott (1964) for petrography and Wentworth (1922) for granulometry.

A PHILIPS XL30 Scanning Electron Microscope (SEM), equipped with an energy dispersive spectrometer using a Si-(Li) semiconductor detector, coupled with a HITACHI S-4800 scanning electron microscope (SEM), to better observe the mineral paragenesis.

Electron probe microanalyses were carried out using a CAMECA SX100. The calibration was made using natural and synthetic oxides or alloys (orthoclase, albite, MnTiO₃, wollastonite, hematite and olivine). The analytical conditions were: 10 nA current, accelerating voltage of 15 kV, 10 s counting time for K, Na, Ca, 20 s for Al, Fe, Mn and 40 s for Mg and U.

The mineralogical analyses (XRD) were performed on bulk rock powder of carbonate cemented sandstones and on oriented clay extracts using a Bruker D2 Phaser equipped with a LynxEye XE-T detector. The interpretation software package used for the evaluation of the diffractograms was Diffrac.Suite along with EVA.

For the bulk rock geochemistry, the samples were initially dissolved in a microwave oven Milestone MLS 1200 Mega, using a solution of HF-HClO₄-HNO₃-H₂O₂ (Cheburkin and Shotyk, 1996). The concentrations of the major elements (Ca, Fe, K, Mg and Na) were determined by Atomic Absorption Spectroscopy (AAS); trace elements (As, B, Ba, Co, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Rb, Sr, U, V and Zn) were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

3.3 *Stable isotopes analysis*

In situ $\delta^{34}\text{S}$ isotopic analysis was performed on samples containing different pyrite habits. The analytical instrument used was a CAMECA IMS 1270 ion probe at the Jean Lamour Institute of the School of Mines (Nancy). The results were normalized using an in-house pyrite standard (Spain) and then treated using the formula described in Kitayama et al. (2012). The thin sections were gold coated before mounting. During the analysis, the pyrite crystals were sputtered with a Cs⁺ beam source of 2-3 nA intensity inside a vacuum chamber, with 10 kV acceleration voltage. Each spot analysis was performed under 40 cycles of 5 seconds each.

3.4 *Rare earth elements (REE) in uranium minerals and trace elements in pyrite*

Rare Earth Elements (REEs) of uranium minerals were analyzed by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at GeoRessources (Nancy).

Laser ablation was performed with a 193 nm GeoLas Pro ArF Excimer laser (Microlas®, Göttingen, Germany) equipped with beam homogenization optics by focusing the beam at the sample surface with a constant fluency of 10 J/cm² and constant repetition rate of 5 Hz. Helium was used as a carrier gas to transport the laser-generated aerosols from the ablation cell to the ICP-MS. Ablated material was analyzed by an Agilent 7500c Quadrupole ICP-MS (Agilent®, Santa Clara, California) equipped with an Octopole Reaction System with enhanced sensitivity optional lenses (Cs type, Agilent). The certified glass standards NIST610, NIST612 and NIST614 SRM, were used as reference materials (concentrations from Pearce et al., 1997) for the calibration of the LA-ICP-MS. The protocol for routine analysis of REE in uranium minerals was checked using an in-house reference uraninite standard. Absolute concentrations and detection limits were obtained from the equations developed by Longerich et al. (1996).

The suite of elements analyzed by LA-ICP-MS was La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Detection limits range from a few ppm for Ce to down to 0.5 ppm for heavy rare earth elements. The REE spectra were normalized to the chondrite standard (Masuda et al., 1973; Anders and Grevesse, 1989).

The elements analyzed by LA-ICP-MS were V, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Pb) in pyrite and Na, Mg, Si, P, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Ba and Pb in U-bearing minerals.

3.5 Organic matter

The macerals were identified using oil immersion microscopy (nomenclature after ICCP, 1963, 1971, 1975, 1998, 2001; Sýkorová et al., 2005; Suárez-Ruiz et al., 2012; Pickel et al., 2017). In core intervals enriched in organic carbon, coal is present as thin laminae within clays or is dispersed inside carbonate-cemented or un-cemented sands. Mechanical concentrates representing organic matter (40-70 mg), crushed down to 45 µm, of 14 samples namely, 9 sands with coal fragments, 3 organic matter-rich clays and 2 carbonate-cemented sandstones with organic matter were selected for Rock-Eval pyrolysis to determine their main geochemical

parameters (Espitalie et al., 1985). The analyses were carried out in the Institute of Earth Sciences in Orléans (ISTO), France,

4 Results

4.1 Nature of the sediments of the Sainshand Formation at the Zuunbayan sub-basin

The upper part of the Cenomanian Sainshand Formation was sampled for this study. The lithologies encountered in the Zoovch Ovoo depocenter have a vast granulometric range from silty clays to gravels for the unconsolidated facies and from silty claystones to micro-conglomerates for the cemented facies. Based on 93 samples analyzed by point-counting, the lithologies encountered in Zoovch Ovoo were by order of abundance: a) 47% sands to sandstones with matrix content between 15-75%, b) 32%, sands with less than 15% matrix, c) 10% pyrite-cemented sandstones, d) 5% sandstones cemented by iron oxides, e) 3% silty clays and f) 3% carbonate-cemented sandstones (Figure A1). Based on the ICP-MS bulk rock data and the equations from Herron (1988), the lithologies are classified as sub-arkoses, arenites and silty claystones (Figure A2 in the annex).

Two distinct units are identified in the sedimentological study (Parize et al., 2013). The first lithological unit consists of finely laminated to stratified monomict to polymict silty to sandy clay, corresponding to varves. The second unit is coarse-grained, sandy to (micro)-conglomeratic, monomict, with granules of intraclasts originating from the first unit. The coarse sediments indicate sudden episodes of sedimentation (floods). Sand dunes are intercalated between the two units that serve as uranium reservoirs, and uranium mineralization is confined in between the coarse (sand, conglomerate) and fine (silt, clay) units.

Detrital quartz, feldspars, biotite, muscovite and commonly lithic elements are the main detrital grains or clasts. Feldspar grains are often chemically altered by sericitization. Their shapes range from angular to sub-rounded with a maximum grain size of about 1mm (Figure 5). Clay intraclasts up to pebble size are often present in sand layers and detrital rounded

289 dolomite grains. Dolomite is microcrystalline and often associated with siderite (Rallakis et al.,
290 2020).

291 The sandstones are, for the most part, composed of quartz (40 to 80%), feldspars as K-
292 feldspars (microcline, orthoclase, some % to 25%) and plagioclases (5 to 20%), minor phases
293 (apatite, ilmenite) and a few accessories of magmatic origin (monazite, zircon, xenotime, rutile,
294 and anatase). The clay/phylosilicate fraction (biotite, chlorite, muscovite in the coarse-grained
295 fraction) is not abundant and not systematically present. Some tests on the clay mineralogy
296 were conducted by means of X-Ray Diffraction. The analysis was repeated twice, one before
297 (air-dried) and one after ethylene-glycol treatment, since swelling clays were identified (Figure
298 A3 in the annex). It was concluded that the predominant clay fraction is smectite (recognized
299 by the typical swelling at 14-17 Å followed by kaolinite. In total 6 clay samples were analyzed,
300 revealing the same pattern.

301 The consolidated lithologies are only a few dm thick and correspond to dolomite and pyrite
302 cemented sandstones, the cement accounting for 30% of sandstone volume on average. Four
303 successive generations of dolomite are distinguished (Rallakis et al., 2020): type I
304 (microcrystalline, pre-roll-front), type II (euhedral, pre-roll-front), type III (active roll-front) and
305 type IV (post-roll-front).

306 Organic matter as detrital coal particles is widespread in all lithologies. The organic matter
307 can be found as dispersed particles in sand, silt, and clay or concentrated within sandy laminae
308 (Rallakis et al., 2019). Coal layers are absent in the reservoir zone, and the organic matter
309 contained in the sediments occurs as detrital particles deposited along the sedimentary
310 bedding. The coarse, angular and poorly sorted organic particles are linked to medium-sized
311 lithologies (coarse to fine-grained sands). Organic matter particles encountered in fine clay
312 (organic-rich) layers are better preserved and linked to calm depositional conditions under less
313 oxygenated conditions. Well preserved phytoclasts, such as root remains, are often associated
314 with fine-grained organic-rich lithofacies, which could indicate higher plants that grew within
315 the depositional setting (no significant transport). Roll front mineralogy and zonation

Uranium mineralization is confined to sand dunes between the coarse (sand, conglomerate) and fine (silt, clay) units. In the oxidized part of the roll-front, Fe-hydroxides and oxides, namely limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$), goethite ($\text{FeO}(\text{OH})$), and hematite (Fe_2O_3), are present. Entire layers of originally reduced grey claystone can become partially to totally red due to the introduction of iron oxides with the oxidizing roll-front waters (Figure 4).

In the reduced part, euhedral pyrite is the most common authigenic mineral and was recognized in three forms, as framboids, as concentric overgrowth formed around framboids and as euhedral crystals (cubic). In a few cases, the polymorph of FeS_2 , marcasite can be identified, developing locally around euhedral pyrite.

Sphalerite is the second most common sulfide after pyrite and was encountered in many mineralized samples. Other sulfides include galena (PbS), greenockite (CdS) and acanthite (Ag_2S). These associated minerals are found rarely, and mainly contained in uranium-rich samples. Furthermore, barite (BaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and the selenides, namely, clausthalite (PbSe) and stilleite (ZnSe), were recognized in minute quantities. Native selenium is often found associated with organic matter, mainly contained inside cell-walls.

4.2 FeS_2 petrography

A detailed study of the petrographic relationships between FeS_2 , detrital elements and other diagenetic mineral phases allowed us to identify several habits of pyrite: i) isolated framboids within the mineral network, ii) framboids within organic matter particles, iii) concentric overgrowth of framboids, iv) framboids embedded within cubic (euhedral) pyrite, v) series of cubic (euhedral) pyrite, vi) isolated euhedral pyrite, vii) marcasite on isolated euhedral pyrite and viii) framboidal and euhedral pyrite inside post-uranium dolomite.

The pyrite habits allowed us to identify a pyrite paragenetic succession (Figure 6). Five different FeS_2 (mainly pyrite) were recognized in the following chronological order: i) framboidal pyrite, ii) concentric overgrowth, iii) euhedral pyrite 1 (pre-ore), iv) marcasite and v) euhedral pyrite 2 (ore-stage) often containing uraninite (UO_2) micro-inclusions.

342 The first euhedral pyrite generation, which is formed during a pre-ore stage, shows corrosion
343 features, hence suffered destabilization by circulating fluids (Figure 7A, B). The corrosion is
344 lacking from the second euhedral pyrite generation, ore-stage pyrite, which, on the contrary,
345 presents well-developed cubic crystals and may contain uraninite micro-size inclusions (Figure
346 7C, D). Marcasite was identified as pre-ore, precipitating directly after euhedral pyrite
347 generation 1 (pre-ore). Sphalerite can contain pitchblende as fracture-filling cement or as
348 spherical micro-inclusions. It definitely postdates the euhedral pyrite that does not contain
349 uranium inclusions but is probably also post-diagenetic with regards to the pyrite that contains
350 uranium inclusions, according to petrographic observations. Sphalerite is also separated in two
351 categories, the Cadmium rich and the Cadmium poor with the Cd concentration in the first
352 being up to 14 wt% and down to 3 wt% in the latter. Both sphalerite types may contain
353 pitchblende inclusions.

354 Framboidal pyrite is commonly found inside or at the rim of organic particles, isolated or in
355 groups (polyframoids). Typically, the cell lumens are used as nucleation sites controlling the
356 morphology of the growing crystal. The degree of epigenetic replacement of organic matter by
357 framoids and their overgrowths (concentric and euhedral pyrite generation 1) vary from a few
358 dispersed framoids to full replacement. Pyrite has a higher affinity with the maceral collotelline
359 (fused homogenous cell walls without defined cell structure) compared to the maceral telinite
360 (fully or partially fused cell walls) or corpogelinite (discrete homogenous vitrinitic bodies
361 representing the infilling of cell lumens). Even when the internal part of the cell-walls is empty,
362 i.e. fusinite, the framoids use it as a nucleation site and grow until they reach the borders of
363 the cell-walls that act as barriers to further crystal growth. Eventually, when uranium enters the
364 system, the framoids and their overgrowths that have previously replaced organic matter will
365 be gradually replaced by uranium. This epigenetic process is well demonstrated in Figure 7E,
366 F.

4.3 Trace elements in FeS₂

Examples of different forms of pyrite, pyrite associated with U cement, and sphalerite were analyzed for trace elements by LA-ICPMS. The concentric pyrite overgrowth could not be analysed as a separate phase from the framboids due to analytical limitations of the laser beam.

Vanadium and Zn concentrations in all pyrites are usually below 50 ppm and sometimes reach 200 and 100 ppm, respectively. Mo concentrations are more variable, from below detection limit (1 ppm) to up to 3300 ppm.

Copper contents of framboidal pyrite range from 20 ppm up to 1000-3000 ppm. Copper is below 100 ppm for the other pyrite types but can occasionally reach up to 500 ppm. Selenium is usually below the detection limit, but in some instances, both in framboidal pyrite and the other types, it can reach 2000 ppm. Cadmium and Sb are most of the times below 100 ppm. Lead was detected in many different concentrations up to 6600 ppm and may correspond partially to radiogenic Pb. The geochemical plot of Co and Cd plot (Figure 8) distinguishes the different sulfide groups. Pyrite not associated with uranium is depleted in both Co and Cd, irrespective of their morphology. On the contrary, pyrite associated with uranium show an enrichment trend in Cd (from a few ppm to 90 ppm) and Co (from a few ppm to 5500 ppm). The euhedral pyrite associated with marcasite contains around 1000-3000 ppm Co and high Cd contents in between 100-190 ppm, while marcasite itself has low contents in Cd and Co. Finally, the euhedral pyrite associated with sphalerite has a low Cd concentration but up to 10 000 ppm of Co, as sphalerite.

4.4 Isotopic chemistry - $\delta^{34}\text{S}$ of pyrite

The *in-situ* micrometer scale $\delta^{34}\text{S}$ analyses were performed on the various pyrite habits described above (Figure 9). The distribution of all the framboidal pyrite occurrences for $\delta^{34}\text{S}$ (n=22) ranges between -40 and +52‰. The absolute distribution of $\delta^{34}\text{S}$ of all the euhedral/cement pyrite (n=34) ranges from -50 to +34‰. More specifically, uranium-

associated pyrite (ore-stage pyrite) $\delta^{34}\text{S}$ ranges between -42 and -22‰. Data for framboidal and euhedral pyrites are overlapped over a vast range of values. The distinction between framboidal and euhedral pyrite is more pronounced for the extreme values, as the highest (positive) values were obtained in framboids and the lowest (negative) values in euhedral pyrite (Figure 9). In general, the framboids tend to be slighter heavier in $\delta^{34}\text{S}$ than euhedral or cement pyrite. This feature is even more apparent for framboids associated with organic matter ($\delta^{34}\text{S}$ ranges between +5 to +55‰).

4.5 Organic matter

The macerals identified in the Zoovch Ovoo sands using oil immersion microscopy are presented in Figure 11. Most of the organic matter is, in general, highly altered due to oxidation and weathering, inherited by sedimentation or introduced by roll-front waters. The kerogen is mainly of type III (vitrinite) and type IV (inertinite). Few occurrences of type II (liptinite) and cutinite could be recognized (Rallakis et al., 2019).

In terms of Rock-Eval analysis (Table 1 and Figure A5), all kerogen samples studied present a very low Hydrogen Index and a linear trend for the Oxygen Index, indicating type III (vitrinite) and IV (inertinite) kerogens. At whole-rock scale, since uranium is very often associated with organic matter particles, an attempt was made to correlate the geochemical composition of kerogen with uranium content expressed by radioactivity (counts per second using a Radiagem SPP2 detector). Indeed, uranium can significantly modify kerogen's geochemical composition (Rouzaud, 1980; Jaraula et al., 2015; Schulz et al., 2018; Zhang et al., 2019). Alteration processes that affect the organic matter associated to uranium deposits include weathering (surface), meteoric water influx (leaching by oxygenated waters), bacterial alteration and radiolysis (Landais et al., 1987; Forbes et al., 1988; Landais, 1996). As a result, the organic matter in U-deposits shows abnormal values which do not reflect their origin or thermal maturity. In other words, it displays very low HI and progressively higher OI due to radiolysis and probably due to alteration/oxidation processes; i.e. Tmax 420-450°C. In Zoovch Ovoo uranium content does not seem to be directly related to the Oxygen Index (Figure A4).

However, as the radioactivity measurements were performed at core scale, they may not represent the uranium concentration in the specific organic particles analyzed by Rock-Eval.

4.6 Petrography of uranium minerals

Uranium crystals were recognized in three forms: i) As independent spheres at the size range of 1 μm , ii) as elongated flakes iii) as large aggregates that resemble epigenetic replacement features of former organic matter particles, pyrite crystals or Fe-Ti oxides (Figure 12). Uranium can be contained in organic matter (OM) from very low (0.5 wt%) to very high concentration grades (about 80 wt%). In the last case, uranium replaces OM while preserving primary maceral textures. Isolated inclusions of uranium oxides are also found inside sphalerite and in one of the euhedral pyrite generations. U-oxides were also seen as dispersed inclusions within the clay matrix, deposited in the intergranular pores of dolomite-cemented sandstones, within the fractures of feldspar grains and as epigenetic replacement of pyrite. U-oxides can also totally replace Fe-Ti oxides while preserving the former mineral texture.

Based on these observations, it was possible to identify eight different types of uranium occurrences from the studied dataset.

4.7 Geochemistry of uranium

a. The (U+Ca)-Si-P ternary diagram

Analyses of representative of U-phases are plotted in the ternary diagram of P_2O_5 - UO_2 - SiO_2 (Figure 13) as a function of their host phase: U-rich organic matter; U-replaced organic matter; U-replaced Fe-Ti oxides; U associated to subhedral dolomite cement; U associated with pyrite cement; U associated with anhedral dolomite; U in euhedral (cubic) pyrite; U associated to corroded pyrite cement; U in sphalerite and finally U in a clay matrix.

Most of the data are distributed close to the uraninite endmember, with some P enrichment which causes a slight deviation from the stoichiometric formula UO_2 . Other analyses plot close to the phospho-coffinite stoichiometry, yet with slight P deficiency, and are interpreted as Phospho-coffinite. Pure coffinite is absent, and there is no continuous set of data from uraninite

to phospho-coffinite, suggesting the absence of an overall uraninite to coffinite transformation. U in clay matrix shows anomalous enrichment in SiO₂ due to analytical interference with phyllosilicates. P₂O₅ content tends to indicate that the composition is similar to the samples plotting below phospho-coffinite composition (non-stoichiometric phospho-coffinite described above).

b. The relationships between U and organic matter

The organic matter at Zoovch Ovoo is derived from land plants and occurs as detrital particles concentrated into clay layers, clay intraclasts or sandy laminae. Biological features of the particles are preserved depending on their transportation (proximal or distal origin). The thermal maturity of the organic matter is very low (peat to lignite stage). In the studied samples, U is intimately associated with organic matter. Very high concentration (up to 20 wt%) with no expression of uranium minerals was found in macerals (Rallakis et al., 2019) (Figure 14). Organic particles conserving their textural features are in some cases entirely replaced by U-oxides.

Also, UO₂ can entirely replace organic matter particles with partial preservation of organic structure (suggesting epigenesis). As burial diagenesis is too low to envisage the reduction of U(VI) by carbonaceous moieties (maximum temperature in the reservoir < 40°C), the role of micro-organisms for the reduction of U(VI), either directly through their physiological activity or by providing, reduced sulfur could be inferred. Finally, Fe(II) carboxylates were also considered as possible reducing agents (Boyanov et al., 2007).

b. Geochemistry of uranium – REE patterns

The REE pattern of the uranium minerals hosted in particular type of deposits i.e. roll-front, volcanic related, vein type and others may provide information linked to their genetic mechanism, thus permitting classifications in salinity, temperature and source. This approach became possible by studying and comparing the REE patterns of major uranium deposits worldwide for which the genetic mechanism is already known i.e. roll-front, volcanic-related, unconformity-related, intrusive etc. (Mercadier et al., 2011). The REE content of uraninite (UO₂)

in Zoovch Ovoo was studied relative to different occurrences, i.e. (A) UO_2 replacing organic matter, (B) UO_2 associated with pyrite and (C) UO_2 in a clay matrix. The REE content was measured using LA-ICP/MS (Figure A5), and the data were normalized relative to chondrite (Anders and Grevesse, 1989). In all cases, the REE concentrations range between 10^3 - 10^4 that of chondrite. Overall, two REE profiles were distinguished: one LREE enriched for the UO_2 -organic matter and UO_2 -pyrite and another HREE enriched for the UO_2 -organic matter and UO_2 -clay matrix. Both types of REE profile show a significant negative anomaly for Eu.

Comparing the average REE concentrations on UO_2 crystals and the bulk rock REE concentration (Figure A5), it appears that the average spectrum acquired on UO_2 is approximately 100 times richer in REE than the bulk rock. Furthermore, the average spectrum of UO_2 shows enrichment in HREE, while bulk rock data show the opposite trend. Both cases show a significant negative Eu anomaly. By comparing our data with Mercadier et al. (2011) it could be concluded that there is a good fit between the REE spectra of Zoovch Ovoo and the roll-fronts of Kazakhstan. The water source in the latter is meteoric, the U-source is monazite and the temperature of formation does not exceed 50°C .

5 Discussion

5.1 Mineral paragenesis in Zoovch Ovoo

The complete sequence of paragenesis from sedimentation through early diagenesis, roll-front formation, to late diagenesis processes at Zoovch Ovoo is summarized in Figure 15.

Early diagenetic stage

The organic matter observed in Zoovch Ovoo sediments is detrital and comes from two sources, one distal and one proximal, as suggested by the organic particles' preservation status. The low burial temperature conditions lead to the organic matter's low thermal maturity, which reached the lignite stage ($\%R_r \approx 0.4$; Rallakis et al., 2019).

Detrital sediments are neither affected by diagenesis nor by cementation. The dolomite cemented sandstone layers are an exception and their formation is linked to proto-dolomite deposition (Rallakis et al., 2020).

Dolomite types I (microcrystalline) and II (euhedral) were formed during early diagenesis and are associated with siderite. Siderite is the earliest expression of reduced iron implicated in diagenesis, indicating reducing conditions in the absence of a reduced sulfur source. The appearance of the first framboidal pyrite generation is diagnostic of the triggering of bacterial sulfate reduction. The overgrowth of pyrite and dolomite and the formation of the first euhedral pyrite generation and marcasite also belong to the pre-ore stage. Sphalerite 1 occurs after marcasite and marks the input of Zn enriched waters.

Effect of roll-front waters

The partial dissolution of ~~the~~ dolomite I and II due to the reactivity with the roll-front waters is responsible for forming secondary porosity and is followed by the formation of subhedral (type III) dolomite (Rallakis et al., 2020). The roll-front also affects the first euhedral pyrite and sphalerite generations, causing their epigenetic replacement by UO_2 . Furthermore, both the second euhedral pyrite and sphalerite generations are co-genetic to the first uranium precipitation episode since they contain uraninite inclusions (uraninite 1). The first uranium episode refers to the incipient stages of U precipitation, followed by the second uranium episode, which refers to the massive introduction of U in the system (uraninite 2). During the second U episode, uraninite tends to be accumulated as follows:

- i. as uranium oxides at the rims of the organic particles (UO_2): decreasing concentration gradients towards the inner part of the particles are observed, but the full replacement of the organic particle is possible.
- ii. as uniform cement inside the clay matrix, preferentially on parts that were previously pyrite-cemented.
- iii. in the intergranular porosity between the detrital grains or in the secondary porosity caused by dolomite dissolution.

iv. and finally, by epigenesis of the first pyrite and sphalerite generations and the pyrite associated with organic matter.

Late diagenetic stage

The late diagenetic stage is characterized by the formation of anhedral (type IV) dolomite, precipitated from formation fluids very lean in REE. The strong negative Eu anomaly of this anhedral dolomite (Fowler and Doig, 1983; Rallakis et al., 2020) and the newly formed framboidal and euhedral pyrite found inside its lattice indicate post-roll-front reducing conditions, most likely during the uplift stage (Rallakis et al., 2019). Furthermore, type IV dolomite cement was confirmed in samples collected from the area outside the roll-front. Anhedral dolomite is therefore disconnected from the roll-front influence. It is also found in coarse to micro-conglomeratic lithologies suggesting a link with high permeability layers, in contrast with dolomite type I and II present in fine-grained sediments.

During late diagenesis, phospho-coffinite and quartz cement (authigenic quartz) formed locally, indicating mobility of Si and P from unknown sources (Figure 13). Mobilization of phosphorus may be linked to bacterial activity. Indeed, previous studies (Gächter and Meyer, 1993; Hutchens et al., 2006; Bonnetti et al., 2015b) have shown that microorganisms are responsible for the release of P from organic compounds as well as from the dissolution of apatite during BSR, where bacteria use P for their metabolism. Apatite is an accessory mineral that is very often encountered in Zoovch Ovoo.

The direct long-term contact of detrital grains, i.e. quartz, feldspars and micas with uraninite cement, induced radiation damage that formed pleochroic halos around these minerals, visible under cathodoluminescence (Figure A6). In particular, radiation halos were identified in quartz grains, not in contact with phospho-coffinite cement. Keeping in mind that direct contact is needed between uranium minerals and quartz for alpha particles to penetrate the mineral lattice, this feature is evidence for uraninite cement deposition around detrital grains followed by dissolution and redistribution. Such processes were already described by Meunier et al. (1990a) and are characteristic of roll-front systems.

5.2 Significance of the sulfide mineral habits and mineral chemistry

Although euhedral pyrite is interpreted as abiotic in origin, framboidal pyrite may be related either to abiotic or biotic processes. Experiments on abiotic pyrite formation showed that framboids obtained in the laboratory are unstable and easily converted to euhedral pyrite (Sawlowicz, 2000). On the contrary, biologically derived framboids are stable in the presence of organic matter (MacLean et al., 2008). Therefore, pyrite occurring as stable framboids observed in sedimentary rocks is most often interpreted as derived from bacterial activity (Álvarez-Iglesias and Rubio, 2012; Cavalazzi et al., 2014; Bonnetti et al., 2017; Hough et al., 2019). Also, low crystallinity iron sulfide (as mackinawite and greigite) has been detected in association with organic matter particles in our samples (Rallakis et al., 2019), a feature consistent with the activity of microbial sulfate reducers (Watson et al., 2000; Wolthers et al., 2000; Veeramani, 2013). Finally, at Zoovch Ovoo, pyrite is exclusively concentrated in laminae enriched in organic matter (Figure A7), while it is not present in surrounding facies. Hough et al. (2019) suggest that in roll-front systems, such a situation is a sign of pyrite formation in the presence of microorganisms. For all these reasons, we consider pyrite framboids in our samples as derived from sulfate-reducing bacteria (SRB) feeding on the detrital organic matter.

The first euhedral generation (pre-ore) pyrite seems to have formed as continuous overgrowths on framboids (framboidal pyrite 1) and their concentric overgrowths if present (Figure A8). This transformation is caused by minimizing the crystal surface energy during growth to become more stable (Sawlowicz, 1993; 2000). The genetic relationship is known because pyrite clusters of embedded framboids were found in the central part of euhedral crystals (Figure 8C-F).

Marcasite can sometimes be observed at a paragenetic position between the first (pre-ore) and second (ore stage) euhedral pyrite generations. Therefore, it is the last pre-roll-front iron disulfide. As marcasite forms under a pH of 5 in the roll-front waters (Murowchick and Barnes, 1986; Anthony et al., 2003), it frequently has a specific position within the geometry of roll-fronts (Hough et al., 2019), which may explain its occasional observation in our samples.

All four pre-roll-front iron disulfides are characterized by a depletion in Cd, Co, Ni and to a lesser extent in V, Zn, Mo and Cu, relative to the second euhedral generation formed during the ore-stage (Figure 8). Marcasite is significantly enriched in As compared to all other iron disulfides. According to Savage et al. (2000), Lowers et al. (2007), and Ingham et al. (2014), reduced arsenic (As^{-1}) is incorporated in the iron disulfide lattice by substituting sulfur. Arsenic was probably scavenged due to low sulfur availability during the final iron disulfide formation before the roll-front waters recharge.

The petrographic analysis did not confirm any hydrothermal minerals or alterations. Hence, sphalerite must be attributed to the introduction of the roll-front waters that together with U carry metallic elements such as Ni, V, Co, Cd, Zn, As, Pb and others. Thus, this stage is marked by the ore-stage pyrite (euhedral generation 2) significantly richer in heavy metal elements, in contrast to pre-ore pyrite (framboids and euhedral generation 1) (Figure 8). Two reasons may explain the origin of the trace elements:

- 1) the roll-front waters are leaching these elements from host lithologies i.e. a combination of mafic rocks (Co, Ni; Goldschmidt, 1954; Clark et al., 2004), granitic rocks (Mo; Blevin et al., 1996) and organic-rich black shales (As, V; Brumsack, 2006) together with U. Indeed, meta-volcanic and intrusive rocks ~~are outcropping~~ in the vicinity of the Zoovch Ovoo depocenter, which could serve as potential sources (Graham, et al., 2001; Figure 1).
- 2) these trace elements are incorporated in ore stage sulfides after being leached from pyrite by oxidizing waters during the roll-front displacement. The trace metals would then concentrate in the roll-front waters and be available to crystallize ore stage pyrite in the more reduced part of the roll-front (Descostes et al., 2010; Ingham et al., 2014; Bonnetti et al., 2020).

Concerning native Se found with organic matter, Ingham et al. (2014) proposed that in roll-front systems, Se is being scavenged from the dissolution of pre-ore pyrite or ideally from other

Se-bearing minerals. Indeed, there are selenides in the Zoovch Ovoo reservoir, such as clausthalite (PbSe) and stilleite (ZnSe), potentially a source for Se.

5.3 Interpretation of sulfur isotopes

In the Sainshand Formation, detrital sediments (Figure 5) are dominated by quartz, feldspar and micas. Apart from the mineralized laminae enriched in organic matter, no pyrite is detected in the rocks. Therefore, the source and transport of sulfur available for mineralization must be related to the circulation of roll-front waters. Two possible sources may be considered:

1) Sulfates dissolved from evaporite deposits leached by the circulating waters. Considering that the Sainshand Formation temperature at Zoovch Ovoo never exceeded 40°C (Graham et al., 2001; Prost, 2004, Rallakis et al., 2019; 2020), reduced sulfur species could be obtained through bacterial activity. Such activity would lead to the formation of framboidal pyrite.

2) Sulfur species derived from the oxidative alteration of pyrite by roll-front waters. Indeed, (bio)-oxidation of pyrite in roll-front systems liberates intermediate valence sulfur species, which will contribute in the formation of pyrite in the roll-front (Granger and Warren, 1969; Rackley, 1972; Hough et al., 2019). In Zoovch Ovoo, the pre-ore pyrite present in the organic-rich laminae (framboidal pyrite 1, euhedral overgrowth and euhedral pyrite 1) would then become a possible initial pool of sulfur.

The $\delta^{34}\text{S}$ ranges from +52‰ to -52‰, which is very large but not unusual in roll fronts worldwide. There are examples of other roll-front deposits (Ingham et al., 2014; Bonnetti et al., 2015b; Lach et al., 2015; Hough et al., 2019; Bonnetti et al., 2020) that demonstrate similar values for the $\delta^{34}\text{S}$ of pyrite as those observed at Zoovch Ovoo (Figure 9). For instance, the deposit from Pepegona and Pannikan (Lake Eyre Basin-South Australia) has pyrite with a range of $\delta^{34}\text{S}$ from -43.9 to +32.4‰ (Ingham et al., 2014). Another example is Lost Creek and Willow Creek Mine Unit 10 (Wyoming-USA) deposits that have $\delta^{34}\text{S}$ from -68.1 to +142.8‰

and from -48.1 to +68.2‰, respectively (Hough et al., 2019). Bonnetti et al. (2020), in their study of the roll-front systems of the Mesozoic, found values between -30.5‰ to +18.8‰.

At first glance, very negative $\delta^{34}\text{S}$ values in pyrite from roll-front deposits are attributed to bacterial activity and more positive to abiotic pyrite precipitation mechanisms (Bonnetti et al., 2020). However, sulfur isotope values in roll-fronts also depend on redistribution mechanisms. Therefore, we plotted our data within the diagram proposed by Hough et al. (2019) in Figure 10 for comparison.

In our study, pyrite shows heavy $\delta^{34}\text{S}$ values (+10 to +52‰). According to literature, evaporites have a $\delta^{34}\text{S}$ range from +20 to +35‰ (Makhnach et al., 2000) and can be considered a potential S source. Yet, pyrite $\delta^{34}\text{S}$ values higher than the mean evaporites composition imply an additional condition to fractionation. Alternately, according to the diagram of Hough et al. (2019), the highly positive $\delta^{34}\text{S}$ pyrite may also derive from a Rayleigh fractionation in closed isotopic systems. It is therefore suggested that pyrite (Figure 9) showing heavy $\delta^{34}\text{S}$ values (framboidal pyrite 1) may have been fractionated from evaporites-derived sulfate in a semi-closed isotopic system. Pyrite isotopic compositions also show $\delta^{34}\text{S}$ values expanding to lighter isotopic values (+10 to -52‰). According to Hough et al. (2019), this might be linked to more open-system conditions.

These authors also suggest that strong fractionation to negative values may suggest the effects of precipitation under neutral pH conditions and inheritance of light sulfur isotopes linked to multiple stages of pyrite dissolution/precipitation. Indeed, oxidation of pyrite deposited during previously occurring roll-fronts activity and subsequent sulfur disproportionation reactions may provide reduced sulfur species of light isotopic composition, even though dissolution and transport can both influence the isotopic distribution of sulfur (Seibert, 2017).

Pyrite habitus (euhedral vs framboids) are well separated spatially and isotopically in other study cases (Hough et al., 2019). In the Erlian basin, pre-ore vs ore pyrite is well divided into pre-ore (framboids) vs ore (colomorph + subidiomorphic) pyrite generations with distinct isotopic signatures (Bonnetti et al., 2017). In our case, euhedral and framboids are spatially

associated and (present multiple overgrowths) in the same mineralized laminae and have the same large span of isotopic compositions.

The large span of $\delta^{34}\text{S}$ values observed for all pyrite ~~habitus~~ in our samples may be tentatively linked to fluctuating sulfate-containing water recharge periods alternating between open (high sulfate availability, recycling of isotopically light sulfur derived from altered pyrite) and a closed system (low sulfate availability, heavy isotopic enrichment). Both bacterial (framboids) or abiotic (euhedral) pyrite precipitation processes would have been submitted to this hydrological regime to lead to the very intricate pyrite petrography, and isotope geochemistry observed.

Framboidal pyrite 1 is the earliest pyrite generation observed and is followed by euhedral pyrite 1 (pre-ore) and euhedral pyrite 2 (contemporaneous to U ore). Framboidal pyrite 1 would then be the primary episode of reduced sulfur occurrence (hence controlled by bacterial sulfate reduction - BSR). Euhedral pyrite 1 and 2 (both of abiotic origin) would then derive from the recycling of framboidal pyrite 1 by the roll-front (since no other sulfur source is observed). However, pyrite is always located in the close vicinity of organic matter rich laminae, which suggests that whatever the pyrite generation, microbial activity controls the overall fate of reduced sulfur in the system (Figure A7).

The fate of sphalerite is very similar to euhedral pyrite (sphalerite 1 is pre-ore, sphalerite 2 contains micro-inclusions of uraninite). Yet, the origin of Zn is unknown.

5.4 Uranium trapping processes involving pyrite

The petrographic study of sulfides in the Zoovch Ovoo samples revealed widespread U-pyrite association. In many cases, epigenetic replacement of pyrite by uranium oxides is observed (Figure 7). Also, pyrite dissolution features exist (Figure 16). ~~In both instances, they concern pre-ore pyrite (framboidal pyrite 1 and euhedral pyrite 2; Figure 7), suggesting sulfide instability in roll-front waters during uranium precipitation.~~

Dissolution of pyrite by roll-front waters would lead to Fe(II) liberation and reduced sulfur species (S_0 , HS^- , polysulfides). Fe(II) in solution may be considered as an efficient reducer for uranium (Boyanov, 2007; Du et al., 2011) as reduced sulfur species might be (Hua et al., 2006; Boonchayaanant et al., 2010). However, if dissolution occurs before uranium precipitation, the solute dispersion in the aqueous solution may prevent uraninite growth at the expense of pyrite.

It is more likely that the uranium reduction process may have happened at the contact with solid FeS_2 as explained by Wersin et al. (1994) or Eglizaud et al. (2006). According to these authors, the interaction between pyrite and U(VI) is a two-step process. First, U(VI) is adsorbed on the pyrite surface, and then the redox reaction is initiated. Reduced uranium can be found either sorbed or precipitated as UO_2 (Eglizaud et al., 2006; Bruggeman et al., 2010). Progressive oxidation of Fe(II) and S_2^{2-} by U(VI) at the surface of the pyrite crystals lead from partial to complete replacement of FeS_2 by UO_2 (Figure 7E-F). This microsite redox chemistry would not preclude syn-ore euhedral pyrite to precipitate with UO_2 (Figure 7C, D) since overall pyrite precipitation is driven by the presence of reduced sulfur provided by thiosulfate disproportionation (Hough et al., 2019) and by BSR, as explained earlier.

Similar observations concern sphalerite: Sphalerite 1 generation occurs before U precipitation in the diagenetic sequence and may show epigenetic replacement by uraninite. The second ZnS generation is co-genetic with U deposition and contains uraninite microsize inclusions (Figure 12C).

The biogenic iron sulfides, mackinawite and greigite, detected in association with organic matter particles (Rallakis et al., 2019), are also able to act as reducers of U(VI) to UO_2 (Hua and Deng, 2008; Veeramani et al., 2013). It is also known that sulfate-reducing bacteria can generate reduced sulfur species such as H_2S and native sulfur (Gruner et al., 1953; Kochenov et al., 1977; Picard et al., 2017). These compounds can induce a reduction of dissolved uranium (Spirakis, 1996).

The sulfur isotopes data obtained on the Zoovch Ovoo pyrites give evidence of the availability of reduced sulfur produced through bacterial sulfate reduction. Indeed, pyrite,

sphalerite mackinawite, and greigite are strongly associated with organic matter. Petrographic study of the uranium-sulfides relationships evidenced epigenesis and hence reduction of U(VI) by sulfides. Thus, even though sulfides are responsible for U precipitation, the sulfate-reducing bacterial community is the primary control of the precipitated uranium ore pool.

5.5 Uranium trapping processes involving organic matter

Uranium occurs at Zoovch Ovoo very intimately associated with organic matter particles at high concentration without expression of a mineral phase or as UO_2 replacing partially macerals with partial preservation of the original biological woody texture (Figure 14). Such U concentrations in wood material are the highest reported in literature (Rallakis et al., 2019). Simple adsorption/complexation cannot be ruled out but may not explain such concentrations.

U(VI) trapping mechanism in interstitial waters by organic matter was for many decades not very clearly understood when dealing with low-temperature abiotic systems. Nakashima et al. (1984) and Nakashima (1992) and Cumberland et al. (2018) suggested that organic matter can trap uranium by complexation, forming uranyl-carboxyl functional groups. Such a process is possible for immature organic matter, such as peat, which may scavenge uranium by a factor of 10^4 from groundwater containing uranium at ppb levels (Idiz et al., 1986; Owen and Otton, 1995). However, this process is not reduction [as U remains under the oxidized state as U(VI)] but adsorption/complexation by carboxylic acids and phenolic groups of the immature organic matter (Warwick et al., 2005; Bryan et al., 2012).

Also, Nakashima et al. (1984) and Nakashima (1992) proved that direct reduction of U(VI) by organic matter (in particular by hydrocarbonaceous moieties) is only possible at $T > 120^\circ\text{C}$. Such a process is unlikely to have occurred within the Sainshand formation since the temperature never exceeded 40°C (Graham et al., 2001; Prost, 2004; Rallakis et al., 2019; 2020).

5.6 Organic matter and bacteria as redox trap for uranium

The high concentration of U in the organic matter without expression of uranium minerals can be achieved via direct reduction of U(VI) by bacteria, leading to the formation of amorphous U(IV) (Bhattacharyya et al., 2017). The mechanism of U reduction through biomineralization by bacteria and fungi was also studied by Lovley et al. (1991) and by Min et al. (2005) in laboratory experiments and the case of Chinese roll-front systems, respectively. Micro-organisms consortia can play a significant role in the control of the redox conditions for uranium precipitation as shown by these studies.

Biomineralization of uranium occurs then in two steps. First, the complexation of uranium, attributed to the bacterial excreted ligands around their cells as non-crystalline U(IV) (Bhattacharyya et al., 2017), whereas the precipitation that follows is accredited to the redox change, driven by enzymatic reactions (Gadd, 1996; Suzuki and Banfield, 1999; Wilkins et al., 2006). Such a process would lead to organic matter rich in U, presenting no expression of UO₂ minerals as observed in our samples (Figure 14). Yet, Meunier et al. (1990b) considered that U was dispersed in the organic matter in similar cases, occurring under its reduced state U(IV), forming very probably tiny-sized U oxide crystals. Such micro-minerals could not be observed at the highest SEM magnification yet cannot be excluded (Figure 14). Bhattacharyya et al. (2017) located U trapped in non-crystalline form, using synchrotron, in similar cases.

Uranium can be reduced by sulfate-reducing bacteria (Lovley et al., 1993; Wilkins et al., 2006; Cardenas et al., 2010) and to some extent by the methanogenic strains (Holmes et al., 2018). The chemical reactions and the bacteria species that could occur in such a process are presented in Table 2. In Zoovch Ovoo, bacteria could thrive in the low-temperature environment (T<80°C), using the abundant coal fragments concentrated in laminae (Rallakis et al., 2019) as nutrients.

We might propose that organic matter is essential in trapping uranium through its role as a nutrient for micro-organism communities that control the trapping of uranium either by complexation-adsorption of U(IV) or direct reduction of U(VI). The continuous bacterial activity

would progressively lead uranium to concentrate in the organic matter up to 20 weight%, eventually under amorphous U(VI) form. U(VI) may also be reduced by microorganisms into UO₂, as uraninite intimately associated with the fine organic structures (i.e. cellular walls geometry). With further organic carbon consumption by bacteria, UO₂ may entirely replace the organic particles (Figure 7; Figure 14).

Pyrite is an efficient uranium reducing agent in Zoovch Ovoo (Rallakis et al., 2019), and is intimately associated with organic matter. Petrography and sulfur isotopes suggest that reduced sulfur present is derived from bacterial sulfate-reducing communities. Yet, such communities also need organic carbon as a nutrient. Therefore, the presence of organic matter is essential: 1) to BSR, which induces the formation of pyrite, a redox trap for U; 2) to microbial communities, which act as a trap for U. In other words, organic matter plays a primary role in the formation of the ore deposit of Zoovch Ovoo since it sustains microbial activity and provides an efficient biogeochemical trap for uranium (Lovley et al., 1991; Detmers et al., 2001; Min et al., 2005; Menor-Salván et al., 2010).

5.7 The model: biogeochemical roll-front trap of the Zoovch Ovoo uranium deposit

The combination of the various biogeochemical processes described in this paper is summarized within a conceptual roll-front system in Figure 17.

Bio-reduction of sulfur, S-recycling in the roll-front and reduced iron availability

Meteoric waters bearing sulfate and uranium percolate downdip through the permeable sandy horizons of the reservoir. In Zoovch Ovoo's case, sulfate could derive from the dissolution of sulfates (gypsum or celestite formed at the surface during evaporation), as was suggested by the strong positive $\delta^{34}\text{S}$ isotopic values of framboids (Figure 9). Sulfates might also derive from the oxidation of pyrite by dissolved oxygen (Stumm and Lee, 1961) and the activity of micro-organisms like *Thiobacillus ferrooxidans* present in the percolating surface waters (Rackley, 1972). Consequently, Fe(III) precipitates as hydroxides (goethite/limonite) and oxides (hematite) (Schwertmann, 1991).

In the suboxic part of the roll-front, dissolution of phyllosilicates (e.g. biotite) and ilmenite, abundant in the Sainshand formation (Figure 5), may release Fe(II). Updip pyrite dissolution may also provide Fe(II) and reduced sulfur species available for the precipitation of euhedral pyrite (Granger and Warren, 1969; Boulegue, 1981; Brunner and Bernasconi, 2005; Hough, 2019). The subsequent pH drop would explain the dolomite dissolution features observed in dolomite types that were formed prior to the introduction of roll-front waters i.e. microcrystalline (type I) and euhedral (type II) dolomite.

In the reduced part of the roll-front, bacteria like the genus *Desulfovibrio* would be present and reduce sulfate (the dominant sulfur source) into sulfides (Rackley, 1972), producing intermediate valence species of sulfur (such as S_2^- , HS^- , H_2S , S_0) (Figure 17, sulfate reduction). Reduced iron would then react with the reduced sulfur leading to the formation of framboidal pyrite. The resulting pH increase would allow subhedral (type III) dolomite, indicative of roll-front activity, to precipitate if the Mg concentration and carbonate activity in the waters is sufficiently high (Rallakis et al., 2020).

U reduction process and deposit formation

Bio-reduction of U is an essential process for reducing uranium at near-surface temperatures (Rackley, 1972; Huang, 1978; Lovley et al., 1991). Bacteria would then reduce U(VI) to form non-crystalline U(IV) (Bhattacharyya et al., 2017) and uraninite/coffinite. Thus, organic matter plays a central role in the metallogenic system. It concentrates uranium by adsorption or complexation and is also a source of nutrients to sustain bacterial activity responsible for metal reduction.

Importance of uplift

The relatively shallow aquifers probably underwent a nearly continuous bacterial activity responsible for many chemical features and processes controlling the U and sulfide precipitation. However, the main uranium deposition events occur since the beginning of uplift when enhanced fluid movement sustained roll-front activity.

The rifting phase in East Gobi Basin ~~was~~ ceased at the end of Early Cretaceous. From Cenomanian and on, the sedimentary sequence in Zoovch Ovoo experienced uplift and erosion (estimated at 300 m at maximum), entering the thermal cooling phase (Prost, 2004; Graham et al., 2001). During Tertiary, the Zuunbayan fault system was reactivated with strike-slip movement (Johnson and Ritts, 2012; Heumann et al., 2014) moving the reservoir from 500 to 200 m – present day depth. These local tectonics could be responsible for opening the system, allowing meteoric waters to percolate through Sainshand Formation, carrying dissolved uranium in oxidized state as U(VI) as well as Fe(III), SO_4^{2-} and bacteria. This new water mass was certainly in disequilibrium with dolomite and had a higher oxidation state than the Sainshand aquifer. The disequilibrium is evidenced by the dissolution features of the pre-roll-front dolomite cements and the deposition of U minerals in the secondary porosity as well as by the appearance of the subhedral (type III) dolomite. With progressive uplift, parts of the roll-front were cut-off and reducing conditions were locally re-established. In sediments that are not leached by the roll-front waters, the type II dolomite does not show any dissolution features. Consequently, these parts were re-equilibrated with the aquifer waters which were saturated in respect to dolomite. Thus, the remaining uncemented sand layers, particularly the coarser units were percolated by the aquifer waters allowing the anhedral (type IV) dolomite cement to precipitate. In a previous study (Rallakis et al., 2020) the four dolomite petrographic types, as presented in the paragenesis table from type I to IV (Figure 15) and discussed chronologically in this chapter, were used to track the burial history of the reservoir.

To conclude the uplift episodes in Cenozoic displaced and combined the biochemical trap ingredients, allowing progressive enrichment in uranium through time.

Late processes

During the stages of the roll-front activity, uraninite often experienced coffinitization with phosphorus incorporation leading to phospho-coffinite (U, $\text{P}(\text{SiO}_4)$) (Figure 13). Previous studies (Gächter and Meyer, 1993; Hutchens et al., 2006; Bonnetti et al., 2015b) have shown that micro-organisms are responsible for releasing P from organic compounds as well as from

the dissolution of apatite during BSR. It remains, however, to determine whether P is coming from organic compounds or from the dissolution of apatite, which is a common accessory mineral in the Zoovch Ovoo sands.

6 Conclusion

The Zoovch Ovoo U-ore deposit was formed in uncemented sands deposited in fluvio-lacustrine settings, where relatively abundant coal particles were concentrated as laminae. This feature is a crucial parameter for the precipitation of sulfides and uranium ores.

The mineral sequence proposed in this study highlights multiple episodes of sulfides (essentially pyrite, sphalerite) and uranium deposition (non-crystalline, uraninite, phosphocoffinite). Sulfides precipitated during pre-, syn- and post-ore stages as reflected by specific contents in trace metals. The δS^{34} compositions changes are, however, not consistent with pyrite morphology or generation. The heavy $\delta^{34}S$ values of pyrite between +10‰ to +52‰ are controlled by sulfate inputs, sulfur recycling from sulfides, and bacterial sulfate reduction under conditions of open and closed systems.

Regarding the very close association of sulfides with organic matter particles, bacterial activity is suspected as a significant provider of reduced sulfur. Since the burial temperature of Sainshand formation never exceeded 40°C, direct reduction of uranium by organic matter could be excluded, considering that temperatures over 120°C are required for direct reduction. Unusually high concentrations of up to 20 wt% of uranium within organic matter without crystalline expression (amorphous) suggests that bacteria play an essential direct role in the trapping process. The continuous bacterial activity would increase the uranium concentration until the uraninite mineral is expressed, accompanied by the destruction of organic carbon, leading to total replacement features resembling epigenesis.

Pyrite epigenesis by uranium is also the central trapping mechanism, implying the reduction of U(IV) by solid reduced sulfur (and Fe(II) to some extent). It appears that the significant

reducing agents for uranium in the Zoovch Ovoo are micro-organisms and sulfides. Also, bacteria have a major influence on the sulfur cycle, controlling a part at least. Their intimate association to organic matter-rich laminae is explained ~~in consideration of micro-organisms using coal particles as a carbon source.~~ Therefore, the Zoovch Ovoo uranium ore deposit may be considered as a (bio)-geochemical trap. It appears that the relatively shallow aquifers probably underwent a nearly continuous bacterial activity which is responsible for many chemical features and processes controlling U and sulfide precipitation. However, major uranium deposition events occurring since the beginning of uplift (Oligocene-Miocene) triggered enhanced fluid movements, sustaining roll-front activity. The latter displace and combine the bio-(geo)chemical trap ingredients, allowing progressive enrichment in uranium through time.

The exact uranium source is not easy to identify; however, the following formations outcrop in the region and have strong potential to act as such: 1) the granitic, 2) metamorphic and 3) volcanic basement rocks and 4) the volcanic ash/glass that covers Sainshand Formation.

The enrichment of ore-stage sulfides in certain trace elements is a probably a gradual process (Ni, V, Co, Cd, Zn, As, Pb and others). It is linked to the continuous dissolution of pre-ore sulfides in the oxidized zone of the roll-front and the formation (re-precipitation) of ore-stage sulfides at the roll-front interface, in the same sense that the concentration gradient of uranium ore increases as the roll-front evolves.

Deposition of the ore is therefore dependent on circulating fluids carrying U reaching the organic-rich laminae. This hydrologic factor is controlled by the permeability network inherited from sedimentation allowing the input of S, U and micro-organisms by percolating waters. Knowledge of the spatial sedimentary organization of the most transmissive layers and distribution of organic matter are, therefore, two crucial parameters for further prospection.

7 Acknowledgements

This work was performed and funded in the research framework between ORANO Mining and CREGU (*Centre de Recherches sur la Géologie des Matières Premières Minérales et Énergétiques*), in the Laboratory of GeoRessources in Nancy, France (contract number 40077759 of 15/03/2016). We are grateful to COGEOBI's geological team for the hospitality and the equipment provided during the field work as well as for taking care of the shipping of the samples from Mongolia to France. People from the laboratory of GeoRessources, in particular Marie Christine Boiron and Chantal Peiffert, are acknowledged for their contribution to the REE *in situ* analysis. Andreï Lecomte and Olivier Rouer are acknowledged for the crystal chemistry analyses and the manipulation of the analytical means. A special thanks to Denis Mangin from the Institute of Jean Lamour of the School of Mines in Nancy (France) for the *in situ* analysis of the S isotopes and to Mohammed Boussafir from the Institute of Earth Sciences in Orleans (France) for the Rock-Eval analyses. Finally, the authors would like to acknowledge the two anonymous reviewers that played a catalytic role in polishing the present manuscript.

8 References

- AKHTAR, S., YANG, X., PIRAJNO, F. (2017). Sandstone type uranium deposits in the Ordos Basin, Northwest China: A case study and an overview. *Journal of Asian Earth Sciences* 146, 367-382.
- ÁLVAREZ-IGLESIAS, P., & RUBIO, B. (2012). Early diagenesis of organic-matter-rich sediments in a ría environment: organic matter sources, pyrites morphology and limitation of pyritization at depth. *Estuarine, Coastal and Shelf Science*, 100, 113-123.
- ANDERS, E., GREVESSE, N. (1989). Abundances of the elements – Meteoritic and solar. *Geochimica et Cosmochimica Acta*, vol. 53, pp. 197-214.
- ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W. NICHOLS, M.C. (2003). Eds., *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, VA 20151-1110, USA. <http://www.handbookofmineralogy.org/>.
- AUBAKIROV, KH.B. (1998). On the deep origin of ore-forming solutions in the uranium deposits in platform sequence of depressions (with Chu-Sarysu Province as an example). *Geology of Kazakhstan* 2(354), pp. 40-47.

919 BLEVIN P.L., CHAPPELL B.W. AND ALLEN C.M. (1996). Intrusive metallogenic provinces in eastern
 920 Australia based on granite source and composition. *Trans. R. Soc. Edinb. Earth Sci.* 87, 281-290.

921 BHATTACHARYYA, A., CAMPBELL, K.M., KELLY, S.D., ROEBBERT, Y., WEYER, S., BERNIER-LATMANI, R.,
 922 BORCH, T. (2017). Biogenic non-crystalline U(IV) revealed as major component in uranium ore
 923 deposits. *Nature communications*, 8, doi.10.1038/ncomms15538

924 BOISSEZON, H.DE., LEVY, L., JAKYMIW, C., DISTINGUIN, M., GUERIN, F., DESCOSTES, M. (2020).
 925 Modeling uranium and ²²⁶Ra mobility during and after an acidic in situ recovery test (Dulaan
 926 Uul, Mongolia). *Journal of Contaminant Hydrology*, 103711, ISSN 0169-7722,
 927 <https://doi.org/10.1016/j.jconhyd.2020.103711>.

928 BONNETTI, C., CUNEY, M., MALARTRE, F., MICHELS, R., LIU, X., PENG, Y. (2015a). The Nuheting Deposit,
 929 Erlian Basin, China: Synsedimentary vs Diagenetic Uranium Mineralization. *Ore Geology*
 930 *Reviews*, 69, pp. 118–139. doi.org/10.1016/j.oregeorev.2015.02.010

931 BONNETTI, C., CUNEY, M., MICHELS, R., TRUCHE, L., MALARTRE, F., LIU, X., YANG, J. (2015b). The
 932 Multiple Roles of Sulfate-Reducing Bacteria and Fe-Ti Oxides in the Genesis of the Bayinwula Roll
 933 Front-Type Uranium Deposit, Erlian Basin, NE China. *Economic Geology*, V. 110, pp. 1059-1081.

934 BONNETTI, C., LIU, X., ZHAOBIN, Y., CUNEY, M., MICHELS, R., MALARTRE, F., MERCADIER, J., CAI, J.
 935 (2017). Coupled uranium mineralization and bacterial sulphate reduction for the genesis of the
 936 Baxingtuo sandstone-hosted U deposit, SW Songliao Basin, NE China. *Ore Geology Reviews*, 82,
 937 pp. 108-129.

938 BONNETTI, C., LINGLI, Z., RIEGLER, T., BRUGGER, J., FAIRCLOUGH, M. (2020). Large S isotope and trace
 939 element fractionations in pyrite of uranium roll from systems result from internally-driven
 940 biogeochemical cycle. *Geochimica et Cosmochimica Acta*, vol. 282, pp. 113-132.
 941 doi.org/10.1016/j.gca.2020.05.019

942 BOONCHAYAANANT, B., GU, B., ORTIZ, M.E., CRIDDLE, C.S. (2010). Can microbially-generated hydrogen
 943 sulfide account for the rates of U(VI) reduction by a sulfate-reducing bacterium?.
 944 *Biodegradation*, 21, pp.81-95.

945 BOULÈGUE, J. (1981). Simultaneous Determination of Sulfide, Polysulfides and Thiosulfate as an Aid to
 946 Ore Exploration. *Developments in Economic Geology*, 15, pp. 21-36. doi.org/10.1016/0375-
 947 6742(81)90053-4

948 BOYANOV, M., O'LOUGHLIN, E.J., RODEN E.E., FEIN, J.B., KEMMETH, K.M. (2007). Adsorption of Fe(II)
 949 and U(VI) to carboxyl-functionalized microspheres: The influence of speciation on uranyl
 950 reduction studied by titration and XAFS. *Geochimica et Cosmochimica Acta*, vol. 71, pp. 1898-
 951 1912. DOI : [10.1016/j.gca.2007.01.025](https://doi.org/10.1016/j.gca.2007.01.025)

952 BRYAN, N.D., ABRAHAMSEN, L., EVANS, N., WARWICK, P., BUCKAU, G., WENG, L., VAN RIEMSDIJK W.H.
 953 (2012). The effects of humic substances on the transport of radionuclides: recent improvements

in the prediction of behaviour and the understanding of mechanisms, *Applied Geochemistry*, 27 (2), pp. 378-389.

BRUGGEMAN, C., MAES, N. (2010). Uptake of Uranium(VI) by Pyrite under Boom Clay Conditions: Influence of Dissolved Organic Carbon. *Environ. Sci. Technol.* 2010, 44, 11, 4210–4216

BRUMSACK H.J. (2006). The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232, 344-361.

BRUNNER B., BERNASCONI S. (2005) A revised isotope fractionation model for dissimilatory sulphate reduction in sulphate reducing bacteria. *Geochim. Cosmochim. Acta* 69, 4759–4771.

CAI, C.F., LI, H.T., QIN M.K., LUO, X.R., WANG, F.Y., OU, G.X. (2007). Biogenic and petroleum-related ore-forming processes in Dongsheng uranium deposit, NW China. *Ore Geology Reviews* 32, 262-274.

CAO, B.F., BAI, G.P., ZHANG, K.X., HE, B. (2016). A comprehensive review of hydrocarbons and genetic model of sandstone-hosted Dongsheng uranium deposit, Ordos Basin, China. *Geofluids*, 16, pp. 624-650.

CARDENAS, E., WU, W.M., BETH LEIGH, M., CARLEY, J., CARROLL, S., GENTRY, T., LUO, J., WATSON, D., GU, B., GIN DER-VOGEL, M., KITANIDIS, K.P., JARDINE, P.M., ZHOU, J., CRIDDLE, C.S., MARSH, T.L., TIEDJE, J.M. (2010). Significant Association between Sulfate-Reducing Bacteria and Uranium-Reducing Microbial Communities as Revealed by a Combined Massively Parallel Sequencing-Indicator Species Approach. *Applied and Environmental Microbiology*, 20, pp. 6778-6786; DOI: 10.1128/AEM.01097-10

CARDON, O., LE GOUX, F., SALABERT, J. (2015). Prospection d'uranium en Mongolie: découverte majeure dans le désert de Gobi [Uranium exploration in Mongolia: important discovery in the Gobi Desert]. *Revue Générale Nucléaire*, vol. 47, pp. 12-19.

CAVALAZZI, B., AGANGI, A., BARBIERI, R., FRANCHI, F., & GASPAROTTO, G. (2014). The formation of low-temperature sedimentary pyrite and its relationship with biologically-induced processes. *Geology of Ore Deposits*, 56(5), 395-408.

CHEBURKIN, A. and SHOTYK, W. (1996). An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius Journal of Analytical Chemistry*, vol. 354, pp. 688-91.

CLARK, C., GRGURIC B., SCHMIDT, M.A. (2004). Genetic implications of pyrite chemistry from the Palaeoproterozoic Olary Domain and overlying Neoproterozoic Adelaidean sequences, northeastern South Australia. *Ore Geology Reviews*, 25, pp. 237-257.

CUMBERLAND, S.A., ETSCHMANN, B., BRUGGER, J., DOUGLAS, G., EVANS, K., FISCHER, L., KAPPEN, P., MOREAU, J.W. (2018). Characterization of uranium redox state in organic-rich Eocene sediments. *Chemosphere*, 194, pp. 602-613.

989 DAHLKAMP, F.J. (2009). Uranium Deposits of the World: Asia, Berlin Heidelberg: Springer-Verlag, 493
990 pp.

991 DESCOSTES, M., SCHLEGEL, M.L., EGLIZAUD, N., DESCAMPS, F., MISERQUE, F., SIMONI, E. (2010).
992 Uptake of uranium and trace elements in pyrite (FeS₂) suspensions. *Geochimica et*
993 *Cosmochimica Acta*, 74, pp. 1551-1562.

994 DETMERS J., BRÜCHERT V., HABICHT K. S., KUEVER J. (2001). Diversity of sulfur isotope fractionations
995 by sulfate-reducing prokaryotes. *Applied Environmental Microbiology*, 67, pp. 888-894.

996 DOTT, R. H. JR. (1964). Wacke, greywacke and matrix-What approach to immature sandstone
997 classification?. *Journal of Sedimentary Petrology*, vol. 34, No. 3. pp. 625-632.

998 DU, X., BOONCHAYANANT, B., WEI-MIN, W., FENDORF, S., BARGAR, J., CRIDDLE, C.S. (2011).
999 Reduction of Uranium(VI) by Soluble Iron(II) Conforms with Thermodynamic Predictions.
1000 *Environmental Science & Technology*, American Chemical Society, 45, pp. 4718-4725.

1001 EGLIZAUD, N., MISERQUE, F., SIMONI, E., SCHLEGEL, M.L., DESCOSTES, M. (2006). Uranium (VI)
1002 interaction with pyrite (FeS₂): chemical and spectroscopic studies. *Migration 2005*, Avignon,
1003 France, pp. 651-656. DOI : [10.1524/ract.2006.94.9-11.651](https://doi.org/10.1524/ract.2006.94.9-11.651)

1004 ESPITALIE, J., DEROO, G., MARQUIS, F. (1985). Rock-eval pyrolysis and its applications. *Oil Gas Sci.*
1005 *Technol. -Rev IFP* 40–6, 755–784.

1006 FORBES, P., LANDAIS, P., BERTRAND, P., BROSE, E., ESPITALIÉ, J., YAHAYA, M. (1988). Chemical
1007 transformations of type-III organic matter associated with the Akouta uranium deposit (Niger):
1008 Geological implications. *Chemical Geology*, 71, pp. 267-282.

1009 FOWLER, A.D., DOIG, R. (1983). The significance of europium anomalies in the REE spectra of granites
1010 and pegmatites, Mont Laurier, Quebec. *Geochimica et Cosmochimica Acta*, 47, pp. 1131-1137.

1011 GÄCHTER, R., MEYER, J.S. (1993). The role of microorganisms in mobilization and fixation of
1012 phosphorus in sediments. *Hydrobiologia*, 253, pp. 103-121.

1013 GADD, G.M. (1996). Influence of microorganisms on the environmental fate of radionuclides.
1014 *Endeavour*, 20, pp. 150-156.

1015 GOLDSCHMIDT V. M. (1954). *Geochemistry*. The Clarendon Press, Oxford, p. 730.

1016 GRAHAM, S.A., HENDRIX, M.S. JOHNSON, C.L., BADAMGARAV, D., BADARCH G., AMORY, J., PORTER,
1017 M., BARSBOLD, R., WEBB, L.E., and HACKER B.R. (2001). Sedimentary record and tectonic
1018 implications of Mesozoic rifting in southeast Mongolia. *Geological Society of America Bulletin*,
1019 vol. 113, pp. 1560–1579.

1020 GRANGER, H.C.; WARREN, C.G. (1969). Unstable sulfur compounds and the origin of roll-front type
1021 uranium deposits. *Economic Geology*, 64 (2), pp. 160-171.

GRIZARD, P., SCHMITT, J.M., GOBLET, P. (2018). Hydrogeology of an arid endorheic basin (Tsagaan Els, Dornogobi, Mongolia): field data and conceptualization, three-dimensional groundwater modeling, and water budget. *Hydrogeology Journal*, doi.org/10.1007/s10040-018-1868-1

GRUNER, J.W., GARDINER, L., SMITH, D.K (1953). Studies relating to the origin and distribution of uranium deposits on the Colorado Plateau. Annual Report for July 1, 1952 to March 31. Division of Raw Materials, Washington 25, D.C., 58 p.

HERRON, M.M. (1988). Geochemical classification of terrigenous sands and shales from core or log data: *Journal of Sedimentary Petrology*, v. 58, no.5, pp. 820- 829.

HEUMANN, J.M., JOHNSON, L.C., WEBB, L.E., TAYLOR, P.J., JALBAA, U., MINJIN, C. (2014). Total and left–lateral displacement across the East Gobi Fault Zone, southern Mongolia: Implications for timing and modes of polyphase intracontinental deformation. *Earth and Planetary Science Letter* (392), pp. 1-15.

HOLMES, D.E., ORELANA, R., GILOTEUAX, L., WANG, L.Y., SHRESTHA, P., WILLIAMS, K., LOVLEY, D.R., ROTARU, A.E. (2018). Potential for *Methanosarcina* to Contribute to Uranium Reduction during Acetate-Promoted Groundwater Bioremediation. *Microbial Ecology*, 76, pp. 660-667.

HOUGH, G., SWAPP, S., FROST, C., FAYEK, M. (2019). Sulfur Isotopes in Biogenically and Abiogenically Derived Uranium Roll-Front Deposits. *Economic Geology*, v. 114, no. 2, pp. 353-373.

HUA, B, XU, H., TERRY, J., DENG, G. (2006). Kinetics of Uranium(VI) Reduction by Hydrogen Sulfide in Anoxic Aqueous Systems. *Environmental Science and Technology*, 40, 4666-4671.

HUA, B., DENG, B. (2008). Reductive immobilization of uranium (VI) by amorphous iron sulfide. *Environmental Science & Technology*, 42, pp. 8703-8708.

HUANG, W.H. (1978). Geochemical and Sedimentologic Problems of Uranium Deposits of Texas Gulf Coastal Plain. vol. 62, 6, pp. 1049-1062.

HUANG, XIAN-FANG., LIU, DE-CHANG., DU, LE-TIAN., ZHAO, YING-JUN. (2005). A new sandstone type uranium metallogenetic type—‘structure—oil, gas type’. In: JINGWEN, M., BIERLEIN, F.P. (eds), *Mineral Deposit Research: Meeting the Global Challenge. Proceedings of the Eighth Biennial SGA meeting, Beijing, China, August 2005*, 265–268.

HUTCHENS, E., VALSAMI-JONES, E., HAROUIYA, N., CHAÏRAT, C., OELKERS, E.H., McELDONEY, S. (2006). An Experimental Investigation of the Effect of *Bacillus megaterium* on Apatite Dissolution, *Geomicrobiology*, 23(3), pp. 177-182.

IDIZ, E.F., CARLISLE, D., KAPLAN, I.R. (1986). Interaction between organic matter and trace metals in a uranium rich bog, Kern County, California, U.S.A, *Applied Geochemistry*, 1, 573-590.

INGHAM, E.S., COOK, N.J., CLIFF, J., CIOBANU, C.L., HUDDLESTON, A. (2014). A combined chemical, isotopic and microstructural study of pyrite from roll-front uranium deposits, Lake Eyre Basin, South Australia. *Geochimica et Cosmochimica Acta*, 125, pp. 440-465.

1057 INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA) and NUCLEAR ENERGY AGENCY (NEA). (2018).
 1058 Uranium 2018: Resources, production and Demand, NEA No. 7413, © OECD 2018, pp. 462.

1059 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY (ICCP), 1963. International Handbook of Coal
 1060 Petrography, 2nd Edition. CNRS. Academy of Sciences of the USSR, Paris, Moscow.

1061 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY, (ICCP), 1971. International Handbook of Coal
 1062 Petrography, 1st Supplement to 2nd Edition. CNRS, Paris.

1063 INTERNATIONAL COMMITTEE FOR COAL PETROLOGY, (ICCP), 1975. International Handbook of Coal
 1064 Petrography, 2nd Supplement to 2nd Edition. CNRS, Paris.

1065 INTERNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY, (ICCP), 1998. The new vitrinite
 1066 classification (ICCP System 1994). Fuel 77, 349–358.

1067 INTERNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY, (ICCP), 2001. The new inertinite
 1068 classification (ICCP System 1994). Fuel 80, 459–471.

1069 ITTERBEECK, J.V., HORNE, D.J., BULTYNCK, P., VANDENBERGHE, N. (2005). Stratigraphy and
 1070 palaeoenvironment of the dinosaur-bearing Upper Cretaceous Iren Dabasu Formation, Inner
 1071 Mongolia, People's Republic of China, Cretaceous Research, Volume 26, Issue 4, August 2005,
 1072 pp. 699-725.

1073 JAIRETH, S., MCKAY, A., LAMBERT, I. (2008). Association of large sandstone uranium deposits with
 1074 hydrocarbons. Australian Government, Geoscience Australia, 89, 6 p.

1075 JARAULA, C.M.B., SCHWARK, L., MOREAU, X., PICKEL, W., BAGAS, L., GRICE, K. (2015). Radiolytic
 1076 alteration in the Mugla Rock (Australia) uranium deposit. Applied Geochemistry, vol. 52, pp. 97-
 1077 108.

1078 JERZYKIEWICZ, T., RUSSELL, D.A. (1991). Late Mesozoic stratigraphy and vertebrates of the Gobi Basin.
 1079 Cretaceous Research, 12, pp. 345-377.

1080 JIAO, Y.Q., WU, L.Q., RONG, H., ZHANG, F., YUE, L., TAO, Z.P., SUN, Y.H. (2018). Geological modeling of
 1081 uranium reservoir: The geological foundation of revealing the metallogenic mechanism and
 1082 solving “Remaining Uranium”. Earth Science 43, 3568-3583 (in Chinese with English abstract).

1083 JOHNSON, C.L. (2004). Polyphase evolution of the East Gobi basin: sedimentary and structural records
 1084 of Mesozoic-Cenozoic intraplate deformation in Mongolia. Basin Research (16), 79-99.

1085 JOHNSON, C.L. and RITTS, B.D. (2012). Plate interior poly-phase basins. In: BUSBY, C. and AZOR PEREZ,
 1086 A. (2012). Tectonics of Sedimentary Basins: Recent Advances. Wiley, Hoboken, ISBN:
 1087 9781444347135, pp. 567-582.

1088 KITAYAMA, Y., THOMASOT, E., O’NEIL, J., WING, B. (2012). Sulfur-and oxygen-isotopes, constraints on
 1089 the sedimentary history of apparent conglomerates from the Nuvvuagittuq Greenstone Belt
 1090 (Nuvanik, Quebec). Earth and Planetary Science Letters, 355, pp. 271-282.

1091 KOCHENOV, A.V., KOROLEV, K.G., DUBINCHUK, V.T., MEDVEDEV, Y.L. (1977). Experimental data on
 1092 precipitation of uranium aqueous solution. *Geochemistry International*, 14, pp. 82-87.

1093 LACH, P., CATHELINEAU, M., BROUAND, M., FIET, N. (2015). In-situ isotopic and chemical study of pyrite
 1094 from Chu-Sarysu (Kazakhstan) roll-front uranium deposit. *Procedia Earth and Planetary Science*,
 1095 13, pp. 207-210. doi.org/10.1016/j.proeps.2015.07.049

1096 LAMB, M.A. and BADARCH, G. (1997): Paleozoic sedimentary basins and volcanic-arc systems of
 1097 southern Mongolia: New stratigraphic and sedimentologic constraints: *International Geology*
 1098 *Review*, v. 39, p. 542-576.

1099 LANDAIS, P., CONNAN, J., DEREPEPE, J.M., GEORGE, E., MEUNIER, J.D., MONTHIOUX, M., PAGEL, M.,
 1100 PIRONON, J., POTY, B. (1987). Alterations of the organic matter, a clue for uranium ore genesis.
 1101 *Uranium*, 3, 307–342.

1102 LANDAIS, P. (1996). Organic geochemistry of sedimentary uranium ore deposits. *Ore Geol. Reviews*,
 1103 11, pp. 33-51.

1104 LE GOUX, F., BANZRAGCH, T.O., DELAUNAY A., NYAMDORJ, B.I., JAKUES, E., KORSHUNOV, A., PARIZE,
 1105 O. and BROUAND, M. (2015). The Major Gobi Uranium Deposits, Upper Cretaceous East Gobi
 1106 Basin, Mongolia: Geodynamical and Mineralogical Key Parameters of Uranium Ore Geology. In:
 1107 *Mineral Resources in a Sustainable World, 13th SGA Biennial Meeting 2015*, vol. 5, 1815-1818.

1108 LONGERICH H.P., JACKSON S.E. and GÜNTHER D. (1996). Laser Ablation Inductively Coupled Plasma,
 1109 Mass Spectrometric Transient Signal Data Acquisition and Analyte Concentration Calculation.
 1110 *Journal of Analytical Atomic Spectrometry*, vol. 11, p. 899-904.

1111 LOVLEY, D.R., PHILLIPS, E.J.P., GORBY, Y. A., LANDA, E.R. (1991). Microbial reduction of uranium.
 1112 *Nature*, 350, pp. 413-416. doi:10.1038/350413a0

1113 LOVLEY, D.R., RODEN, E.E., PHILLIPS, E.J.P., WOODWARD, J.C. (1993). Enzymatic iron and uranium
 1114 reduction by sulfate-reducing bacteria. *Marine and Petroleum Geology*, 113, pp. 41-53.

1115 LOWERS, H.A., BREIT, G.N., FOSTER, A.L., WHITNEY, J., YOUNT, J., UDDIN, M.N., MUNEEEM, A. (2007).
 1116 Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. *Geochimica et*
 1117 *Cosmochimica Acta*, 71, pp. 2699-2717.

1118 MACLEAN, L.C.W., [TYLISZCZAK](https://doi.org/10.1111/j.1472-4669.2008.00174.x), T., GILBERT, P.U.P.A., ZHOU, D., PRAY, T.J., ONSTOTT, T.C., SOUTHAM,
 1119 G. (2008). A high-resolution chemical and structural study of framboidal pyrite formed formed
 1120 within a low-temperature bacterial biofilm. *Geobiology*, 6(5), pp. 471-480.
 1121 <https://doi.org/10.1111/j.1472-4669.2008.00174.x>

1122 MAKHNACH, A., MIKHAJLOV, N., KOLOSOV, I., GULIS, L., SHIMANOVICH, V., DEMENEVA, O. (2000).
 1123 Comparative analysis of sulfur isotope behavior in the basins with evaporites of chloride and
 1124 sulfate types. *Sedimentary Geology*, 134, pp. 343-360.

1125 MASUDA A., NAKAMURA N., and TANAKA T. (1973). Fine structure of mutually normalized rare-earth
 1126 patterns of chondrites, *Geochimica et Cosmochimica Acta*, 37, pp. 239-248.
 1127 MENOR-SALVAN C., TORNOS, F., FERNANDEZ-REMOLAR, D., AMILS, R (2010). Association between
 1128 catastrophic paleovegetation changes during Devonian-Carboniferous boundary and the
 1129 formation of giant massive sulfide deposits. *Earth and Planetary Science Letters*,
 1130 doi:10.1016/j.epsl.2010.09.020.
 1131 MERCADIER, J., CUNEY, M., LACH, P., BOIRON, M.C., BONHOURE, J., RICHARD, A., LEISEN, M., KISTER,
 1132 P. (2011). Origin of uranium deposits revealed by their rare earth element signature. *Terra Nova*,
 1133 23, No.4, pp.264-268.
 1134 MEUNIER, J.D., SELLIER, E., PAGEL, M., (1990a). Radiation damage rims in quartz from uranium bearing
 1135 sandstones. *Journal of Sedimentary Petrology*, 60, pp. 53-58.
 1136 MEUNIER, J.D., LANDAIS, P., PAGEL, M. (1990b). Experimental evidence of uraninite formation from
 1137 diagenesis of uranium rich organic matter. *Geochimica et Cosmochimica Acta*, 54, pp. 809-817.
 1138 MEYERHOFF, A.A. and MEYER, R.F. (1987). Geology of heavy crude oil and natural bitumen in the USSR,
 1139 Mongolia, and China. In: MEYER, R. F, ed., *Exploration for heavy crude oil and natural bitumen:*
 1140 *AAPG Studies in Geology* 25, pp. 31-101.
 1141 MIN, M., XU, H., CHEN, J., FAYEK, M. (2005). Evidence of uranium biomineralization in sandstone-
 1142 hosted roll-front uranium deposits, northwestern China, *Ore Geology Reviews*, Volume 26,
 1143 Issues 3–4, July 2005, pp. 198-206.
 1144 MUNARA, A. (2012). Formation des gisements d'uranium de type roll : approche minéralogique et
 1145 géochimique du gisement uranifère de Muyunkum (Bassin de Chu-Sarysu, Kazakhstan). Thèse
 1146 soutenue le 9 Juillet 2012, PhD Univ. H. Poincaré Nancy. 327p.
 1147 MUROWCHICK, J. B., & BARNES, H. L. (1986). Marcasite precipitation from hydrothermal solutions.
 1148 *Geochimica et Cosmochimica Acta*, 50(12), 2615-2629.
 1149 NAKASHIMA, S., DISNAR, J.R., PERRUCHOT, A., TRICHET, J. (1984). Experimental study of mechanisms
 1150 of fixation and reduction of uranium by sedimentary organic matter under diagenetic or
 1151 hydrothermal conditions. *Geochimica et Cosmochimica Acta*, 48, pp. 2321-2329.
 1152 NAKASHIMA, S. (1992). Complexation and reduction of uranium by lignite. *Science of the Total*
 1153 *Environnement*, 117-118, pp. 425-437.
 1154 NIU, L., HUANG, S., YANG, G. (1995). The characteristics of uranium mineralization and genesis of
 1155 Nuheting uranium deposit in Erlian Basin, Inner Mongolia. *China Nucl. Sci. Technol. Rep.* 1995–
 1156 00 (in Chinese with English abstract).
 1157 OWEN D.E., OTTON J.K. (1995). Mountain wetlands: efficient uranium filters-potential impacts.
 1158 *Ecological Engineering*, 5, pp. 77-93.

1159 PARIZE, O. (2013). Le remplissage de la dépression de Tsagaan Els et les dépôts fluviaux associés
1160 (Crétacé moyen, Bassin de Zuunbayan). Implication stratigraphiques et sédimentologiques sur
1161 le gisement de Zoovch Ovoo – Synthèse des résultats 2012-2013. Octobre 2013, édition
1162 décembre 2014. Rapport technique AMS-DGS-TEC-SDYRT-0008, (Poster AMS-DGS-TEC-SDY-RT-
1163 0008_PosterZoovchA1_2013).

1164 PARIZE, O. (2015). Le remplissage de la dépression de Tsagaan Els et les dépôts fluviaux associés
1165 (Crétacé moyen, Bassin de Zuunbayan). Implication stratigraphiques et sédimentologiques sur
1166 le gisement de Zoovch Ovoo – Synthèse des résultats 2012-2013. Octobre 2013, édition
1167 décembre 2014. Rapport technique AMS-DGS-TEC-SDYRT-0008, (Poster AMS-DGS-TEC-SDY-RT-
1168 0008_PosterZoovchA1_2013).

1169 PEARCE N.J.G., PERKINS W.K., WESTGATE J.A., GORTON M.P., JACKSON S.E., NEAL C.R. AND CHENERY
1170 S.P. (1997). A compilation of new and published major and trace element data for NIST SRM 610
1171 and NIST SRM 612 glass reference materials. *Geostandards and Geoanalytical Research*, vol. 21,
1172 pp. 101-114.

1173 PETROV N.N. (1998). Les gisements épigénétiques du Kazakhstan. *Géologie du Kazakhstan*, 2(354): pp.
1174 22-39. (trans. from Russian).

1175 PICARD, A., GARTMAN, A., CLARKE, D.R., GIRGUIS, P.R. (2017). Sulfate-reducing bacteria influence the
1176 nucleation and growth of mackinawite and greigite. *Geochimica et Cosmochimica Acta*.
1177 doi.org/10.1016/j.gca.2017.10.006

1178 PICKEL, W., KUS, J., FLORES, D., KALAITZIDIS, S., CHRISTANIS, K., CARDOTT, B.J., MISZ-KENNAN, M.,
1179 RODRIGUES, S., HENTSCHEL, A., HAMOR-VIDO, M., CROSDALE, P., WAGNER, N. (2017).
1180 Classification of liptinite - ICCP System 1994. *International Journal of Coal Geology*, 169, pp. 40-
1181 61.

1182 PROST, G.L. (2004). Tectonics and hydrocarbon systems of the East Gobi basin, Mongolia, AAPG
1183 Bulletin, vol. 88, No. 4, pp. 483-513.

1184 RACKLEY, R.I. (1972). Environment of Wyoming Tertiary Uranium Deposits. *The American Association*
1185 *of Petroleum Geologists Bulletin*, v. 56. No. 4. Pp. 755-774.

1186 RALLAKIS, D., MICHELS, R., BROUAND, M., PARIZE, O., CATHELINEAU, M. (2019). The Role of Organic
1187 Matter on Uranium Precipitation in Zoovch Ovoo, Mongolia. *Minerals* 9(5), 310.
1188 [DOI: 10.3390/min9050310](https://doi.org/10.3390/min9050310)

1189 RALLAKIS, D., MICHELS, R., BROUAND, M., PARIZE, O., CATHELINEAU, M. (2020). Dolomite cements in
1190 Cenomanian continental sand deposits: time evolution and significance (Zoovch Ovoo U-deposit,
1191 East Gobi Basin, Mongolia). *Sedimentary Geology*, vol. 405(C), 105688.
1192 doi.org/10.1016/j.sedgeo.2020.105688

1193 REYNOLDS, R.L., GOLDBERGER, M.B. (1978). Origin of a South Texas roll-type uranium deposit; I,
 1194 Alteration of iron-titanium oxide minerals. *Economic Geology*, 73(8): 1677-1689.

1195 ROUZAUD, J.N., OBERLIN, A., TRICHET, J. (1980). Interaction of uranium and organic matter in
 1196 uriferous sediments. *Physics and Chemistry of the Earth*, vol. 12, pp. 505-516.

1197 SAVAGE, K.S., TINGLE, T.N., O'DAY, P.A., WAYCHUNAS, G.A., BIRD, D.K. (2000). Arsenic speciation in
 1198 pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County,
 1199 California. *Applied Geochemistry*, 15, pp. 1219-1244.

1200 SAWLOWICZ, Z. (1993). Pyrite framboids and their development: a new conceptual mechanism.
 1201 *Geologische Rundschau*, 82(1), pp. 148-156.

1202 SAWLOWICZ, Z. (2000). Framboids: from their origin to application. Polska Akademia Nauk – Oddział
 1203 w Krakowie, Prace Mineralogiczne, 88, 80 pp.

1204 SCHULZ, H.M., YANG, S., PANOVA, E., BECHTEL, A. (2018). The role of Pleistocene meltwater-controlled
 1205 uranium leaching in assessing irradiation-induced alteration of organic matter and petroleum
 1206 potential in the Tremadocian Koporie Formation (Western Russia), *Geochimica et Cosmochimica*
 1207 *Acta*, doi: <https://doi.org/10.1016/j.gca.2018.10.029>

1208 SCHWERTMANN, U. (1991). Solubility and dissolution of iron oxides. *Plant and soil*, 130, pp. 1-25.

1209 SEIBERT, S., DESOURVIERES, C., SKRZYPEK, G., DENG, H., PROMMER, H. (2017). Model-based analysis
 1210 of $\delta^{34}\text{S}$ signatures to trace sedimentary pyrite oxidation during managed aquifer recharge in a
 1211 heterogeneous aquifer. *Journal of Hydrology*, 548, pp. 368-381.
 1212 <https://doi.org/10.1016/j.jhydrol.2017.02.030>

1213 SPIRAKIS, C. (1996). The role of organic matter in the formation of uranium deposits in sedimentary
 1214 rocks. *Ore Geology Reviews*, 11, pp. 53-69.

1215 STUMM, W., LEE, G.F. (1960). The chemistry of aqueous iron. *Schweizerische Zeitschrift für Hydrologie*,
 1216 22(1), pp. 295-319.

1217 SUÁREZ-RUIZ, I., FLORES, D., MENDONÇA FILHO, J.G., HACKLEY, P.C. (2012). Review and update of the
 1218 applications of organic petrology: Part 1, geological applications. *International Journal of Coal*
 1219 *Geology*, 99, pp. 54-112.

1220 SUZUKI, Y., BANFIELD, J.F. (1999). Geomicrobiology of Uranium, chapter 8. In: Burns, P.C., Finch, R.
 1221 (1999). URANIUM: Mineralogy, Geochemistry and the Environment, *Reviews in Mineralogy*, 38,
 1222 673 p.

1223 SÝKOROVÁ, I., PICKEL, W., CHRISTIANIS, K., WOLF, M., TAYLOR, G.H., FLORES, D., 2005. Classification
 1224 of huminite—ICCP System 1994. *International Journal of Coal Geology* 62, 85–106.

1225 TRAYNOR, J.J. and SLADEN, C. (1995). Tectonic and stratigraphic evolution of the Mongolian People's
 1226 Republic and its influence on hydrocarbon geology and potential: Marine and Petroleum
 1227 Geology, v. 12, p. 35-52.

1228 VEERAMANI, H., SCHEINOST, A.C, MONSEGUE, N., OAFOKU, N.P., KUKKADAPU, R., NEWVILLE, M.,
 1229 LANZIROTTI, A., PRUDEN, A., MURAYAMA, M., HOCELLA, Jr. M.F. (2013). Abiotic Reductive
 1230 Immobilization of U(VI) by Biogenic Mackinawite. Environmental Science and Technology, 47, 5,
 1231 2361-2369.

1232 WARWICK, P., EVANS, N., HALL, A., WALKER, G., STEIGLEDER, E. (2005). Stability constants of U(VI) and
 1233 U(IV)-humic acid complexes. Journal of Radioanalytical and Nuclear Chemistry, 266(2), pp. 179-
 1234 190.

1235 WATSON, J., CRESSEY, B., ROBERTS, A., ELLWOOD, D., CHARNOCK, J., AND SOPER, A. (2000). Structural
 1236 and magnetic studies on heavy-metal-adsorbing iron sulphide nanoparticles produced by
 1237 sulphate-reducing bacteria. *J. Magn. Magn. Mater.* 214 (1-2), 13–30. doi:10.1016/s0304-
 1238 8853(00)00025-1

1239 WENTWORTH, C.K. 1922. A scale of grade and class terms for clastic sediments. Journal of Geology.
 1240 30:377-392. WORDEN, R.H. & BURLEY, S.D. (2003). Sandstone diagenesis: the evolution of sand
 1241 to stone, Sandstone Diagenesis: Recent and Ancient. International Association of
 1242 Sedimentologists, 44 pp. ISBN: 978-405-10897-3.

1243 WERSIN, P., HOCELLA, M.F., PERSSON, P., REDDEN, G., LECKIE, J.O., HARRIS, D.W. (1994). Interaction
 1244 between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence of sorption and
 1245 reduction. *Geochimica et Cosmochimica Acta*, 58(13), pp. 2829-2843.

1246 WILKINS, M.J., LIVENS, F.R., VAUGHAN, D.J., LLOYD, J.R. (2006). The impact of Fe(III)-reducing bacteria
 1247 on uranium mobility. *Biogeochemistry*, 78(2), pp. 125-150.

1248 WOLTERS, M., VAN DER GAAST, S. J., AND RICKARD, D. (2003). The structure of disordered
 1249 mackinawite. *Am. Mineral.* 88 (11-12), 2007–2015. doi:10.2138/am-2003-11-1245

1250 YUE, L., JIAO, Y., Wu, L., RONG, H., XIE, H., WANG, Q., YAN, Q. (2019). Selective crystallization and
 1251 precipitation of authigenic pyrite during diagenesis reservoir sandbodies in Ordos Basin. *Ore*
 1252 *Geology Reviews*, vol. 107, pp. 532-545.

1253 ZHANG, R., DING, W. (1996). Discussion on geological characteristics of Nuheting type uranium deposit
 1254 and the relation between oil and gas-bearing water and uranium metallogenesis. *Galaxy of*
 1255 *Research Achievements of Uranium Geology of China*. Bureau of Geology, CNNC, Beijing, pp.
 1256 205–214.

1257 ZHANG, F., JIAO, Y.Q., WU, L.Q., RONG, H., WANG, L.H. (2018). Relations of uranium enrichment and
 1258 carbonaceous debris within the Daying uranium deposit, northern Ordos Basin. *Journal of Earth*
 1259 *Science*, DOI: 10.1007/s12583-017-0952-0.

- ZHANG, F., JIAO, Y., WU, L., RONG, H., WANG, L., ZHANG, Z. (2019). In-situ analyses of organic matter maturation heterogeneity of uranium-bearing carbonaceous debris within sandstones: A case study from the Ordos Basin in China, *Ore Geology Reviews*, doi: <https://doi.org/10.1016/j.oregeorev.2019.03.021>
- ZHU, M., WU, R., LIU, X., NIE, F., YU, D. (2012). Geologic Setting of Interformational Braided Channel Type Sandstone Uranium Deposits in North China, East China Institute of Technology, 29/05/2012 IAEA Conference, PowerPoint Presentation. Available online from: <https://www.slideshare.net/monatom/05-xiaodong-liu-geologic-setting-of-interformationalbraidedchannel-type-sandstone-uranium-deposits-in-north-china>

FIGURES

Figure 1: Location map of Mongolia presenting A) the four metallogenic provinces hosting U, namely from North to South 1) North Mongolian, 2) Khentai-Daur, 3) Mongol-Priargun, 4) Gobi-Tamtsag (Dahlkamp, 2009); B) the study area and C) a simplified geological map of East Gobi Basin with the morpho-tectonic elements. The Zoovch Ovoo roll-front U deposit is located in the Zuunbayan sub-basin in East Hongor Tolgoy and Bayanshiree plateau (map modified from Graham et al., 2001).

Figure 2: Stratigraphical column of the East Gobi Basin, including potential unconformities, depositional environments and tectonic episodes. Modified from Jerzykiewicz and Russell (1991); Prost (2004). 1= metamorphic rocks, 2= granitic rocks, 3= conglomerate, 4= coarse sandstone, 5= medium sandstone, 6= shale, 7= uncertain duration, 8= Zoovch Ovoo uranium deposit.

Figure 3: Examples of studied samples distribution (green and blue dots for U-rich and carbonate cemented samples, respectively) along with two roll-front profiles. The background colours represent oxidized (yellow) versus reduced sand (white), clays (green) and uranium mineralization (red mesh texture). The vertical lines represent drilling-wells. The two profiles are not on the same vertical scale. The distance between wells is at the scale of tens of meters.

Figure 4: Examples of typical core sequences in Zoovch Ovoo. **A)** Well, ZOOV_1142, depth 306.20 m. From left to right: reduced matrix-supported sandstone, oxidized matrix-supported sandstone, reduced matrix-supported sandstone with organic matter,

and reduced carbonate cemented sandstone. **B)** Well, ZOOV_1154, depth 164.10 m. Reduced (left) and oxidized (right) consolidated facies ranging from silty claystone to very fine sand.

Figure 5: Summary of the main siliciclastic and carbonate elements presented in the Zoovch Ovoo sands. (A, B) Monocrystalline and polycrystalline quartz. (C, D) Plagioclase and microcline with polysynthetic and cross-hatched twinning, respectively. The plagioclase with slight sericite alteration. (E, F) Detrital muscovite, chlorite, biotite. (G) Detrital dolomite grain, (H) Lithic element showing granophyric texture. All photographs under polarized/analyzed light; (G) under white light.

Figure 6: Conceptual drawings of the five FeS₂ generations identified in the Zoovch Ovoo sands. From left to right moving from the older to the younger generation: i) framboidal; ii) concentric (overgrowth); iii) euhedral pyrite 1 (pre-ore), iv) acicular FeS₂ (marcasite) and v) euhedral pyrite 2 (ore-stage).

Figure 7: Examples of the uranium ore replacing the euhedral pyrite 1 (pre-ore) generation while crystallized contemporaneously with the euhedral pyrite 2 (ore-stage). All pictures are taken under SEM-EDS using back-scattered electron mode. The uranium content is higher in the brighter zones. **(A)** A close view showing the corrosion features of pyrite 1 as cement (pre-ore) systematically in contact with UO₂. Quartz cement post-dates UO₂; **(B)** In the lower half of the picture, detrital grains cemented by pyrite and UO₂. Note the corroded surface of pyrite, which is also the boundary to UO₂. In the upper half of the picture, matrix (clays) supported sandstone without UO₂; **(C)** Framboidal pyrite with pyrite overgrowth followed by UO₂ rim and euhedral pyrite 2 (ore stage). The whole cluster is encompassed by uranium-rich clay matrix; **(D)** Zoomed image of (C), where the two pre-ore stage pyrite generations (framboidal pyrite and overgrowth) can be discriminated by the ore-stage euhedral pyrite 2, separated by a UO₂ coating; **(E)** An organic matter particle relic (encompassed by the yellow dotted line) that was previously replaced by framboidal pyrite. The framboids are closely packed to form pyrite cement. Eventually, pyrite cement is being replaced by uranium (uraninite). The contact between uraninite and remaining pyrite shows a typical contorted feature suggesting replacement process; **(F)** Focus on the contact between framboidal pyrite and UO₂. Several rates of framboid replacement by UO₂ are recognized from right to left: fully preserved framboids, framboid core remnants within UO₂, almost entirely replaced framboid and finally UO₂ cement without any

recognizable pyrite; **(G)** Telovitrinite particle with variable uranium content and no observable U-mineral expression. The uranium content is higher in the brighter zones; **(H)** Uranium as uraninite (UO_2) precipitating at the rims of a Collotelinite particle. Uranium concentration is decreasing towards the inner part of the particle as a function of increasing distance from the U-cement area;

Figure 8: Co and Cd content of pyrite as measured by La-ICPMS. It is possible to distinguish pyrite associated with uranium (in red circles) enriched in Co and Cd from pyrite not linked to uranium (in grey squares), which is depleted. Euhedral pyrite associated with marcasite (blue triangles) is enriched in Co, while the euhedral pyrite associated with sphalerite (green rhombs) enriched in Cd.

Figure 9: Frequency histogram presenting the distribution of $\delta^{34}\text{S}$ for the different iron disulfide occurrences: framboidal pyrite (in blue), euhedral/cubic pyrite (in red), framboidal pyrite replacing organic matter (in green), euhedral/cubic to anhedral FeS_2 cement replacing organic matter (in purple) and marcasite.

Figure 10: The Rayleigh fractionation model of framboidal pyrite at Lost Creek (LC) from Hough et al., 2019 (blue dots), cross-plotted with the results of this study (red dots) and pyrite data from Bonnetti et al., 2020 (green dots). The dashed line models $\delta^{34}\text{S}$ value of sulfate in solution with progressive sulfur depletion. The solid black line is the $\delta^{34}\text{S}$ value of pyrite produced at a specific level of depletion. According to the authors, the data corresponds to 88.5% depletion of sulfate in solution. The fractionation from Lost Creek is higher by about 100‰ than Zoovch Ovoo.

Figure 11: Summary of the macerals identified in the Zoovch Ovoo sands. Polished block photomicrographs under oil-immersion (x50) and reflected light. A) Fusinite with framboidal pyrite; B) Telovitrinite associated with euhedral pyrite and semifusinite; C) Very oxidized particle of telovitrinite (collotelinite); D) Fusinite containing uranium minerals, also euhedral pyrite, showing significantly higher reflectance.

Figure 12: The different forms of uranium petrographic types. (A) Uranium crystals as small spheres (U-balls) on organic matter (O.M). The maceral gelovitrinite (completely filled cells) appears to be more resilient to its replacement by U. (B) Elongated U-crystals termed U-flakes and U-aggregates. (C) U-balls of 1 μm size inside sphalerite cement. (D) U-flakes are growing at the rim of a quartz grain.

Figure 13: Ternary plot of P_2O_5 - UO_2 - SiO_2 (in wt% oxide) indicating the stoichiometric U-mineral compositions (striped squares) Uraninite, Phosphorus enriched Uraninite, Coffinite and Phospho-coffinite.

Figure 14: SEM-EDS analysis of a telovitrinite particle from sample 9704-8 (clay and organic matter intraclast in very coarse-grained mineralized sand). Three macerals can be discriminated, telinite, collotelinite and gelovitrinite. (A) Point measurements across the particle focusing on the areas of different brightness. The uranium content is uniformly fluctuating between 7.9-13.1 wt%. (B, C) High magnification of the bright regions of the telohuminite particle. Uranium distribution is not uniform at this scale.

Figure 15: The complete paragenesis of the diagenetic phases encountered in the Zoovch Ovoo sands.

Figure 16: Abiogenic redox model for pyrite dissolution and uranium reduction. (a) Pyrite is first partially dissolved; (b) Uranium is reduced from reduced sulfur and (c) by reduced iron.

Figure 17: The proposed metallogenic model for uranium formation and associated diagenetic phases in Zoovch Ovoo. The overall thickness of the reservoir has a maximum of 100 m. The oxidization part of the roll front provides sulfates (inspired by Rackley, 1972) and micro-organisms. In the suboxic part of the roll-front, three major intricate processes are involved in the mineralization formation: 1. Sulfate (bio)reduction leading to pyrite formation, 2. Pyrite epigenesis by uraninite 3. Organic matter reactivity through complexation and sustainment of biological activity, responsible for uranium precipitation. Titanium oxide epigenesis by uraninite is also a common feature at Zoovch Ovoo. Organic matter sustains biological activity, which controls uranium precipitation either directly or through pyrite formation. It plays, therefore, a significant role in the biogeochemical process of uranium ore formation of Zoovch Ovoo.

TABLES

Table 1: Rock-Eval data for different lithologies, namely: sand with organic matter (OM), black claystone and carbonate-cemented sandstone with organic matter. Radioactivity measurement in CPS (counts of radioactivity per second) using a

Radiagem SPP2 detector. Background radioactivity 70 cps. Rock-Eval indices: S1 amount of free hydrocarbons (mg of hydrocarbons per gram of sample); S2 oil potential (mg hydrocarbon per gram of sample); TOC Total organic Content (in weight %); Tmax: thermal maturity index in degree Celcius; HI: Hydrogen Index (mg of hydrocarbons per gram of organic carbon); OI: Oxygen index (mg of CO₂ per gram of organic carbon).

Table 2: Sulfate and iron-reducing bacteria, as well as the methanogens, can enzymatically reduce uranium to form uranium oxides such as uraninite.

ANNEX (SUPPLEMENTARY MATERIAL)

Figure A1: Clustered bar chart indicating the lithofacies distribution in Zoovch Ovoo, expressed in percent, as identified by point-counting method on the basis of 97 samples.

Figure A2: The log(Fe₂O₃/K₂O) versus log(SiO₂/Al₂O₃) after Herron, 1988. Data from bulk rock analysis (ICP-MS).

Figure A3: A Diffractogram of oriented section under air-dried (AD) conditions and after ethylene-glycol (EG) treatment, for the sample 9704-45 (black silty-clay from the mineralized zone).

Figure A4: Cross-plot between Hydrogen Index and Oxygen index. Symbols coloured according to radioactivity (cps- counts per second) content of the whole rock. Data indicate that kerogen is of Type III (higher plants derived), consistent with organic petrography observations. The zoomed part of the diagram on the right suggests no relationship between kerogen's oxygen content and alteration by radioactivity.

Figure A5: Chondrite-normalized rare earth element patterns for UO₂ in three different petrographic situations: A) UO₂ replacing organic matter; B) associated with pyrite and C) within the clay matrix). In D, a comparison between the average REE concentrations of uranium oxides compared to the bulk rock.

Figure A6: SEM-BSE (A, D, G) and their respective cathodoluminescence images under black-white (B, E, H) and coloured mode (C, F, I). In A, B, C, quartz grains, and

other silicate detrital minerals, the absence of pleochroic halos indicates the lack of radiolytic alteration. In D, E, F, uranium cement in part around a quartz grain, which shows radiolytic alteration features, i.e. zonations of specific distance from the grain edge towards the inner part. When radiation damage rims are observed in the absence of uranium minerals, they indicate former long-term contact. Uranium minerals were precipitated and then dissolved, a process typical of uranium displacement and re-concentration linked to roll-front movement. G, H, I: quartz cement crystals have grown inside a vug of pyrite that was partially replaced by uranium cement. The zonations and the jagged and ingrown shape of the crystal point out its authigenic character.

Figure A7: Cross-plot between total organic carbon (TOC) and total sulfur content (bulk rock analysis). The diagram shows a significant relationship suggesting that organic matter is a prerequisite for pyrite growth.

Figure A8: Examples of framboids being embedded by euhedral pyrite. **A, B:** Typical example of a pyrite cluster with framboids within euhedral crystals, located in the intergranular porosity of a matrix-supported sandstone. The framboids (20 μm) are densely packed and highly amalgamated with the euhedral grains, but they can be still discriminated against since they are composed of submicron pyrite crystals. The individual cubic crystals that form the aggregate are at the size of 10 μm (BSE). **C:** Again, framboids encompassed by euhedral pyrite, this time growing on organic matter, particularly fusinite. Euhedral crystals not associated with framboids are also recognized (BSE). **D:** A cluster of framboidal pyrite encompassed by a generation of euhedral pyrite that contains uranium. The cluster is cemented by type III subhedral dolomite. **E:** Well-developed pyritospheres (15 μm) surrounded by uraninite, followed by euhedral pyrite (10-15 μm) with uraninite inclusions. The whole assemblage is within the clay matrix, where uraninite is also contained. There appears to be one euhedral pyrite generation (BSE). **F:** Group of well-developed framboids (up to 10 μm) encompassed first by concentric overgrowth, then by euhedral pyrite at the size range of 5-10 μm , followed by uraninite precipitation and another a few μm thick euhedral pyrite generation (BSE).

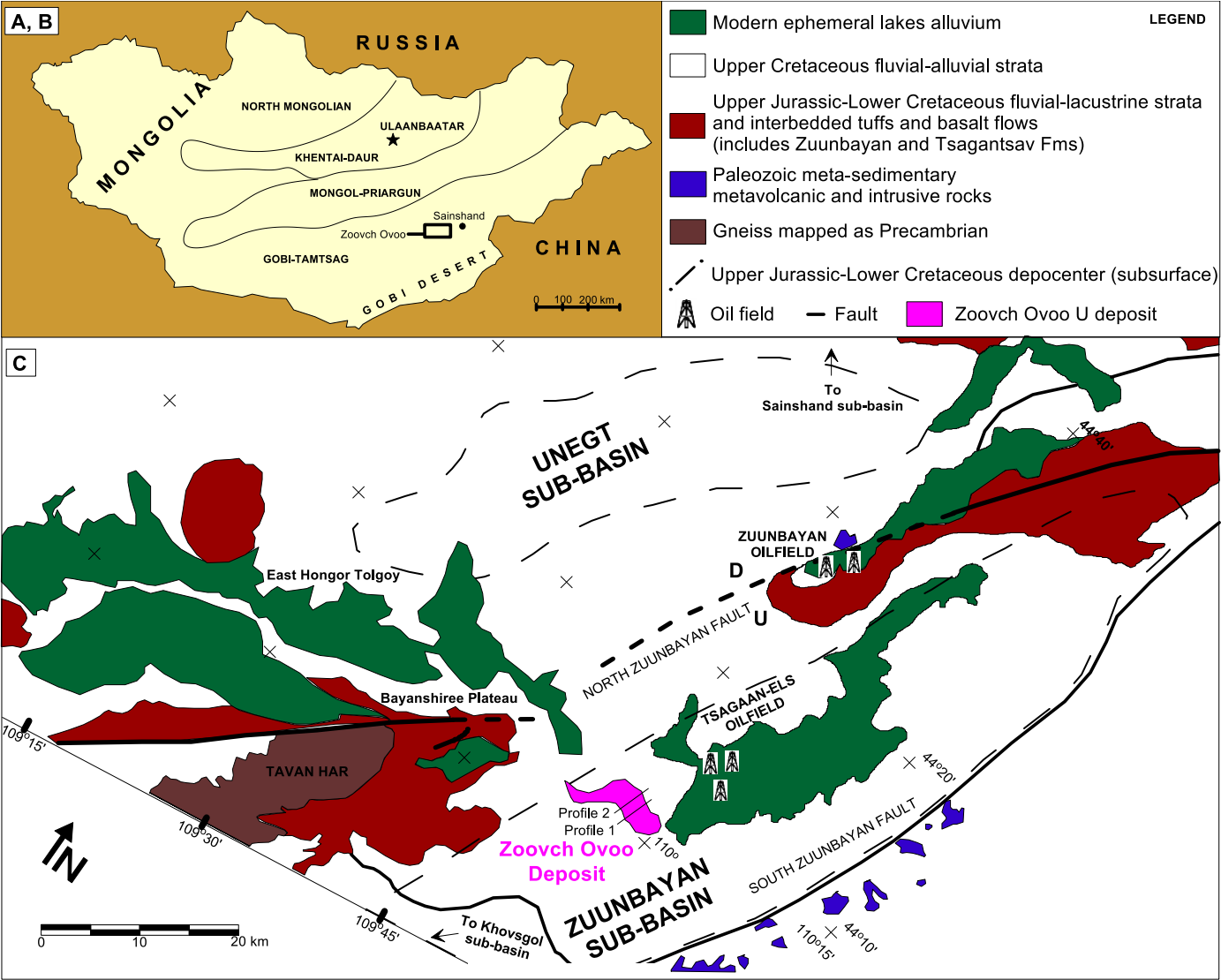


Figure 1

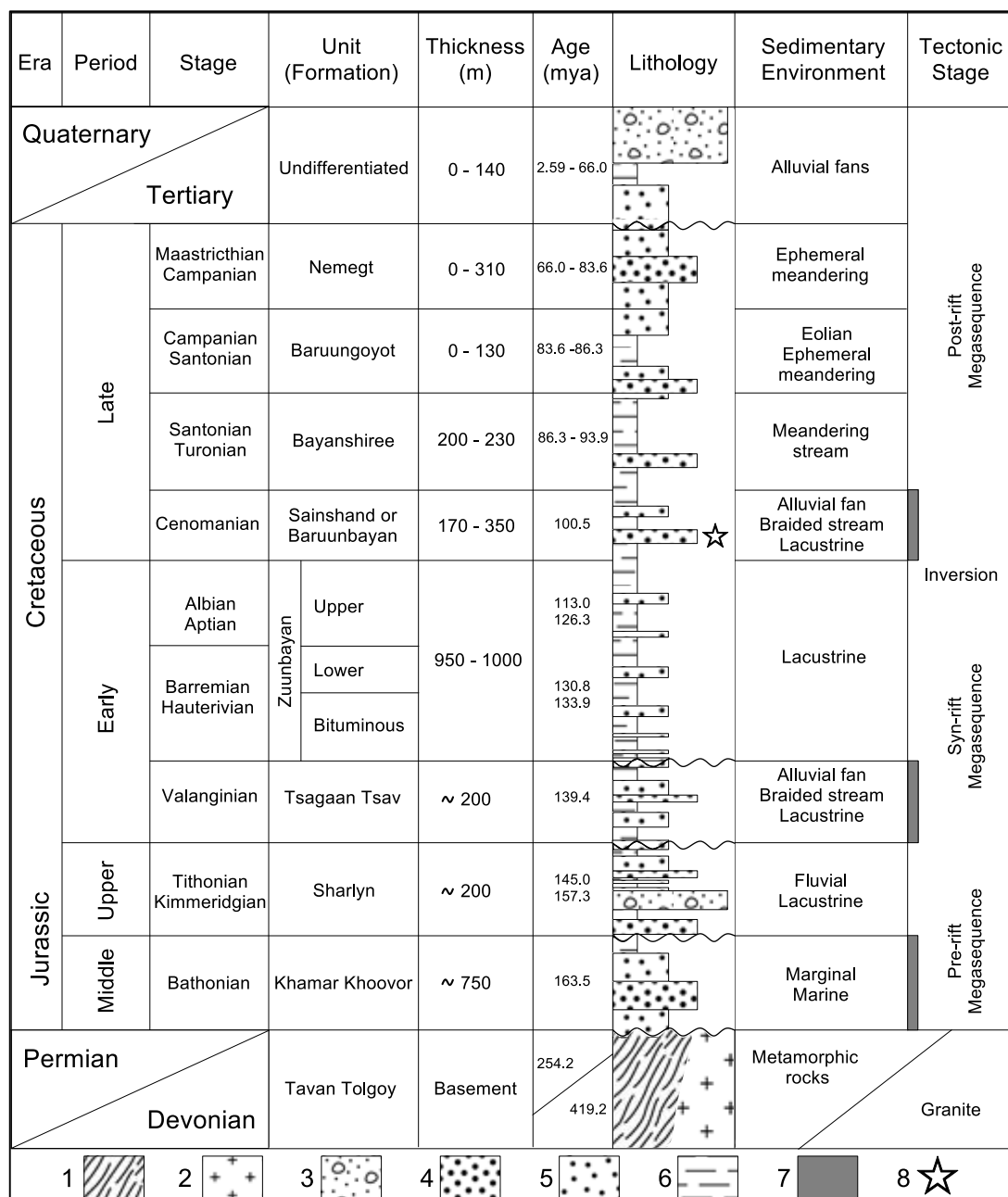


Figure 2

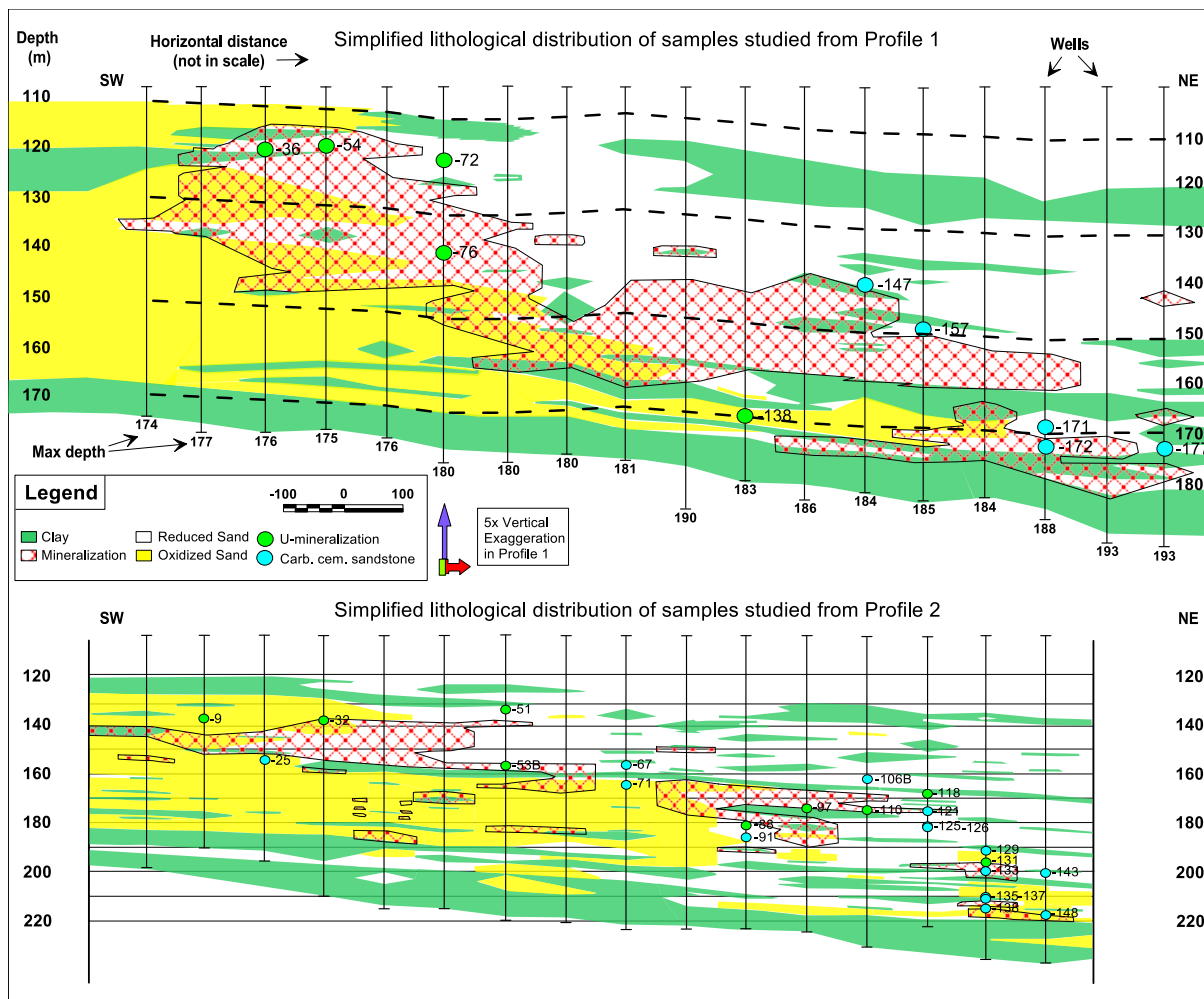


Figure 3

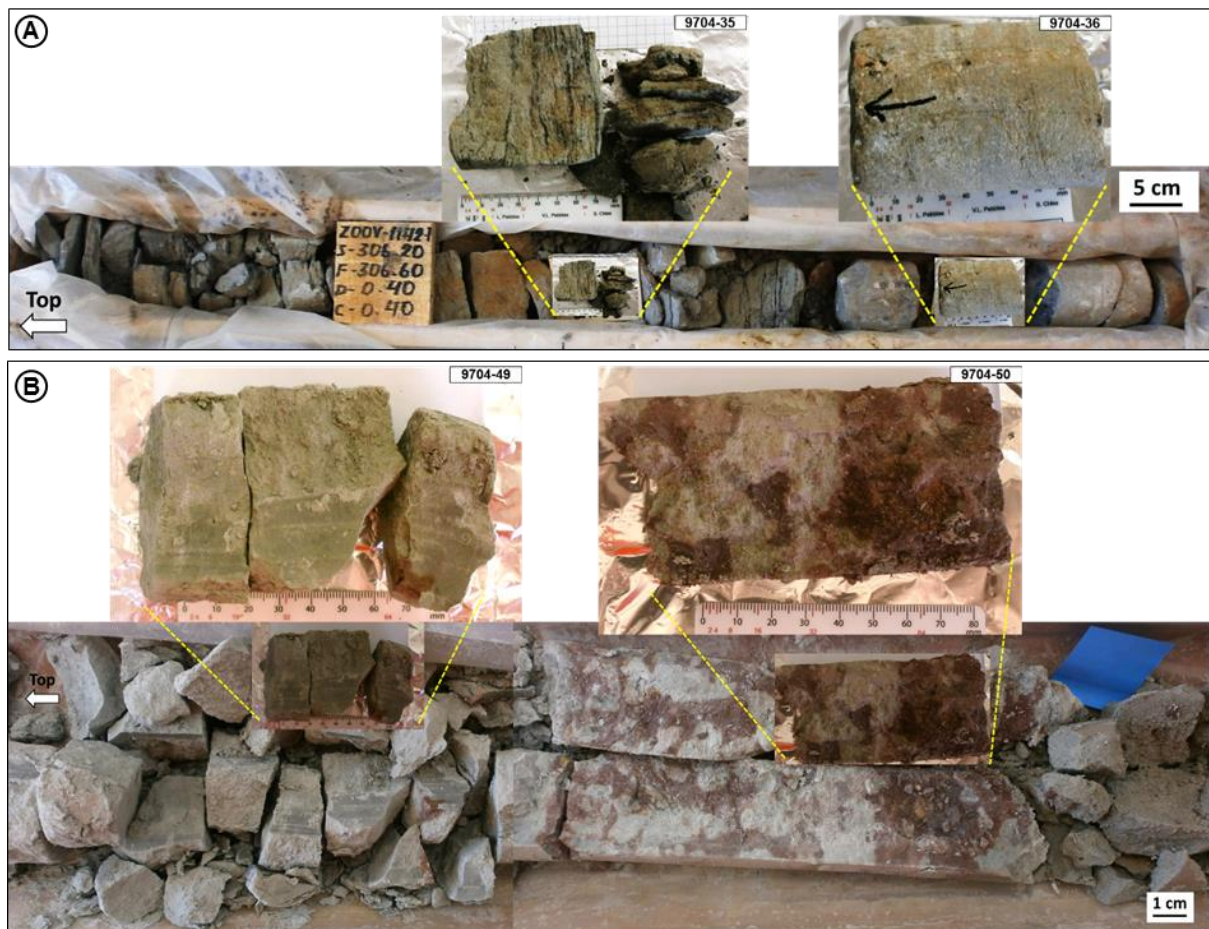


Figure 4

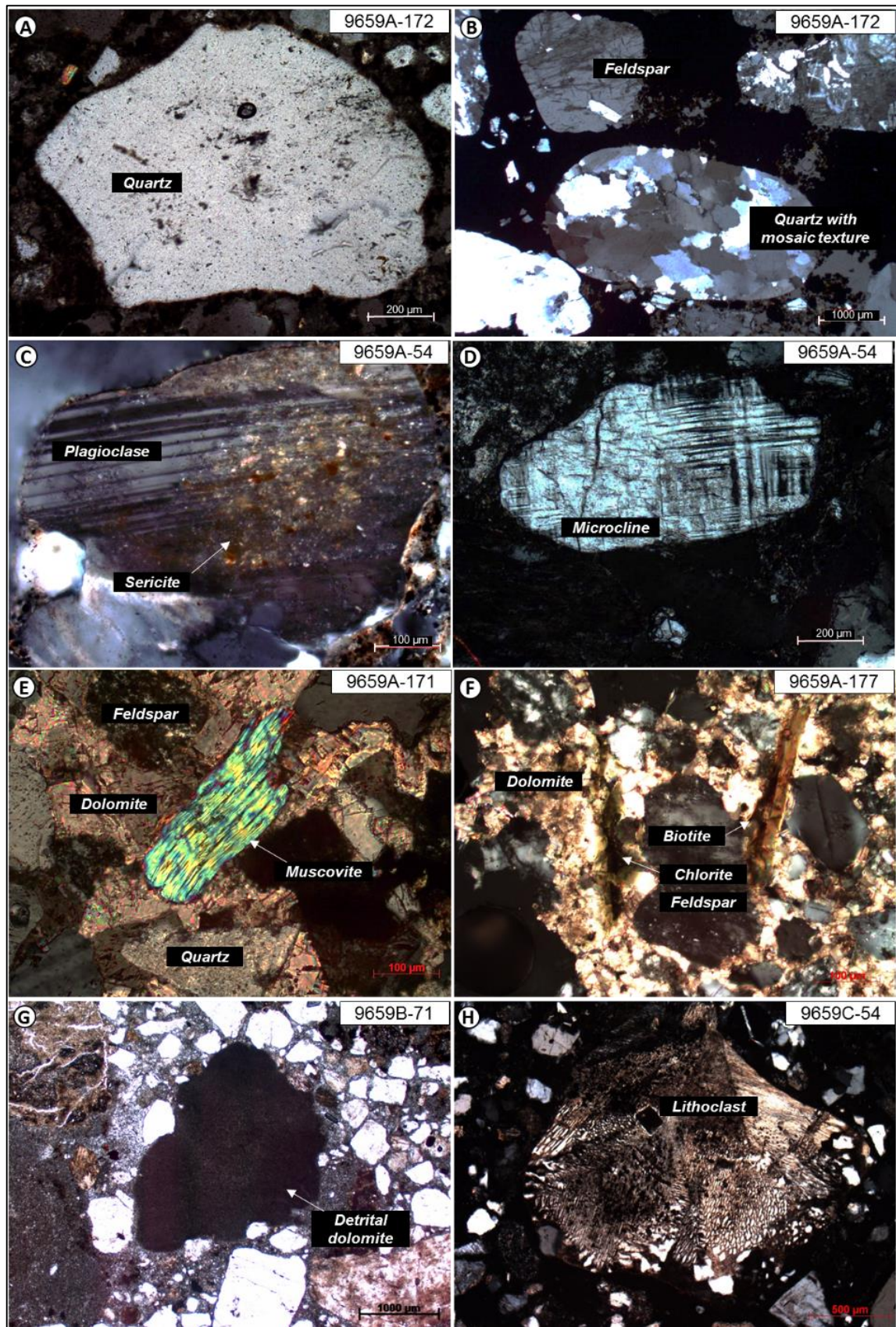


Figure 5

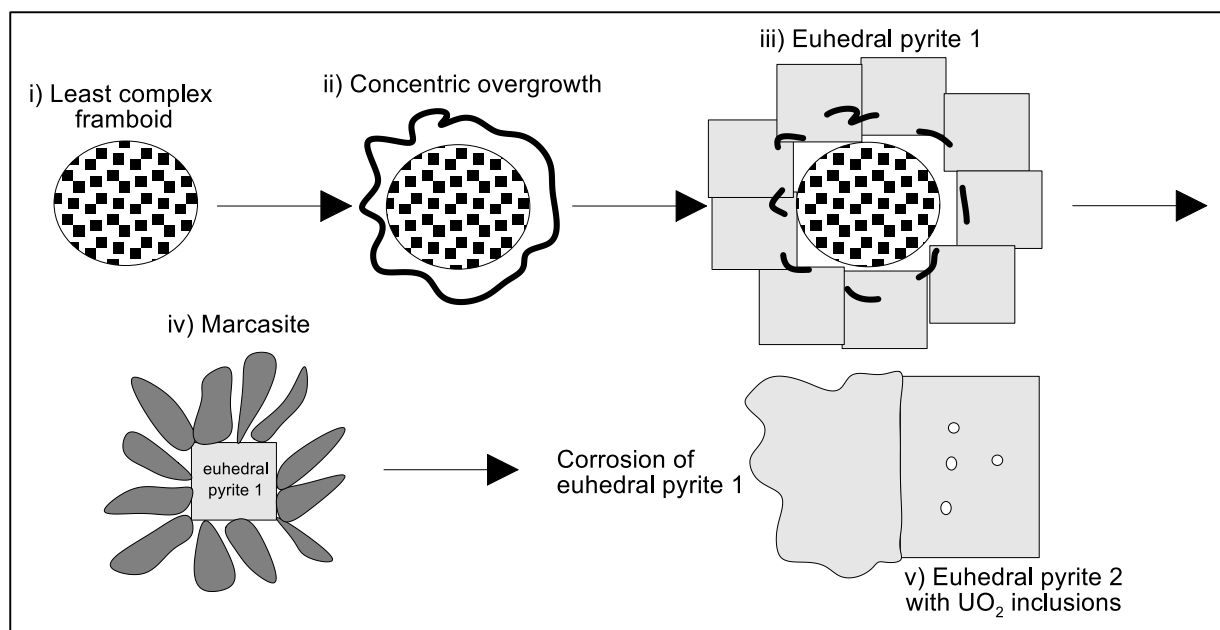


Figure 6

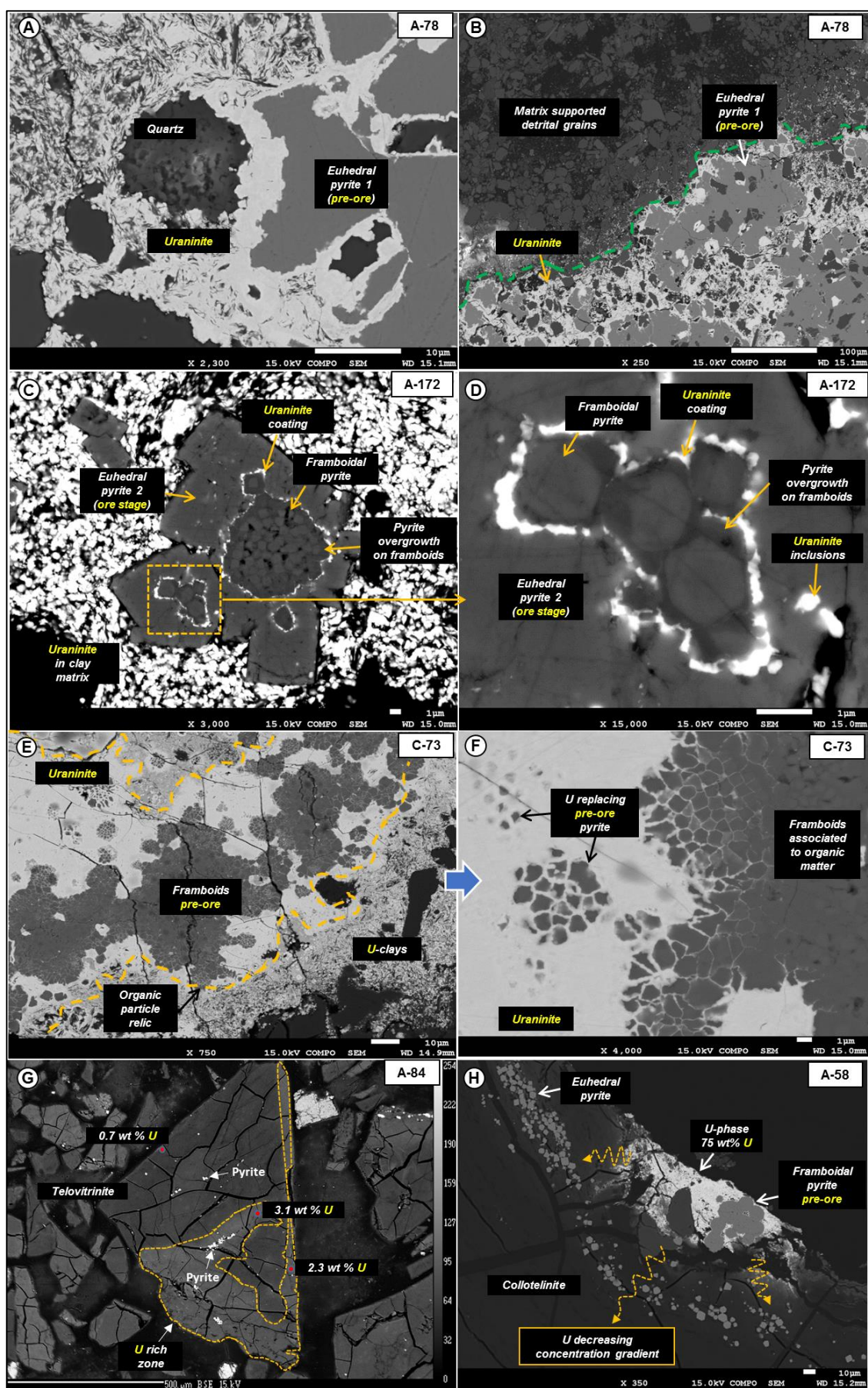


Figure 7

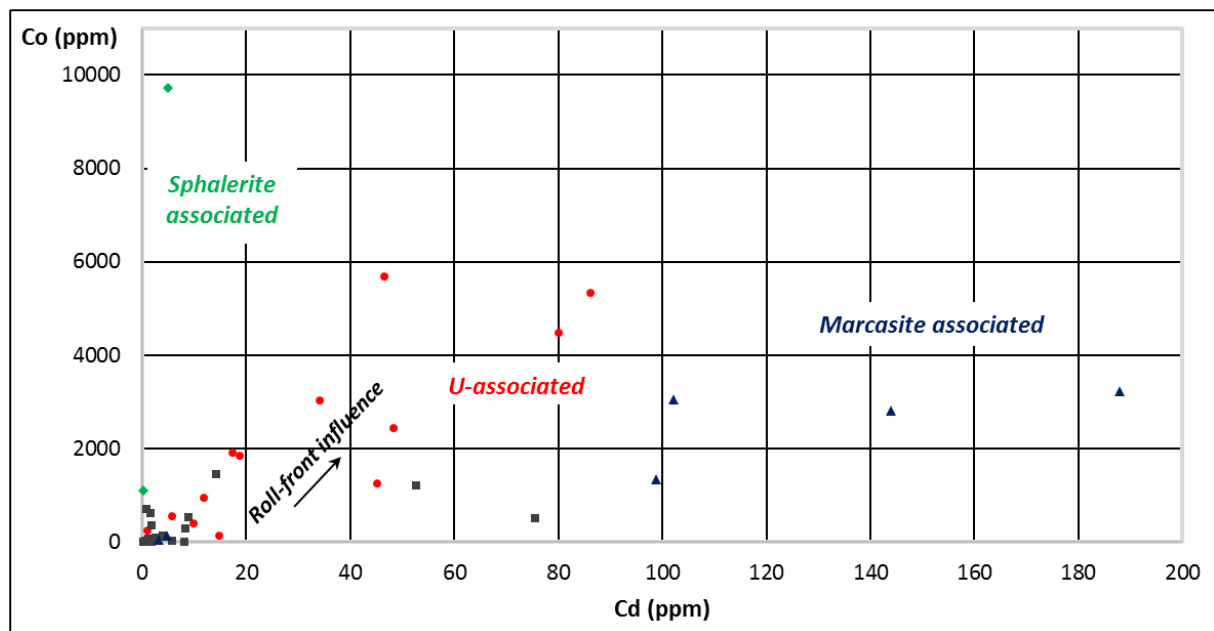


Figure 8

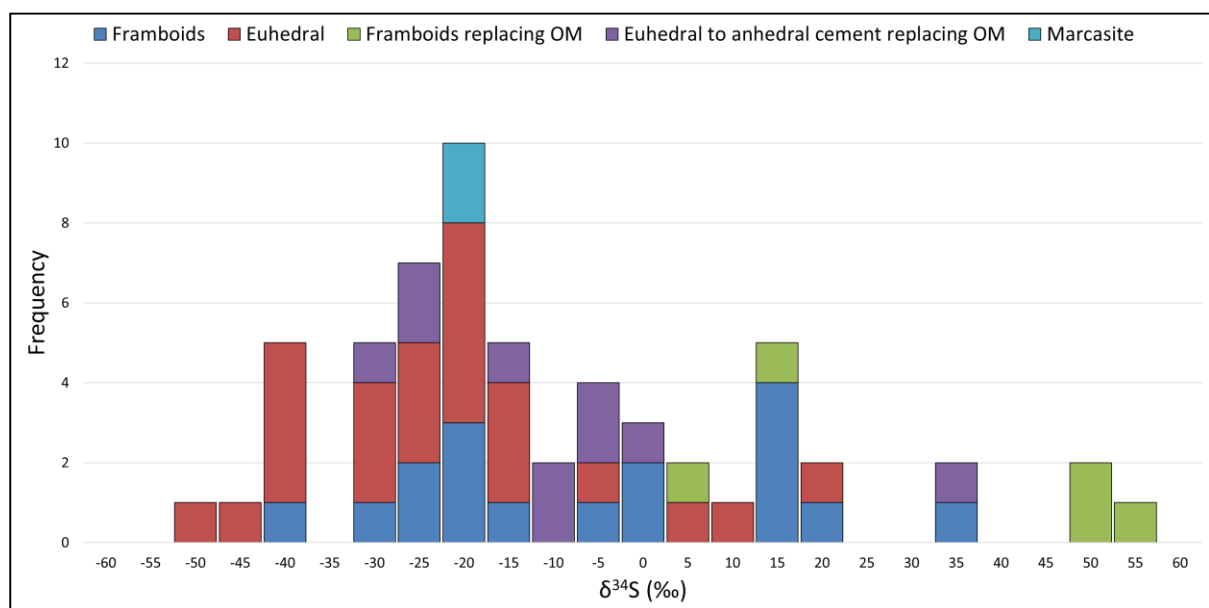


Figure 9

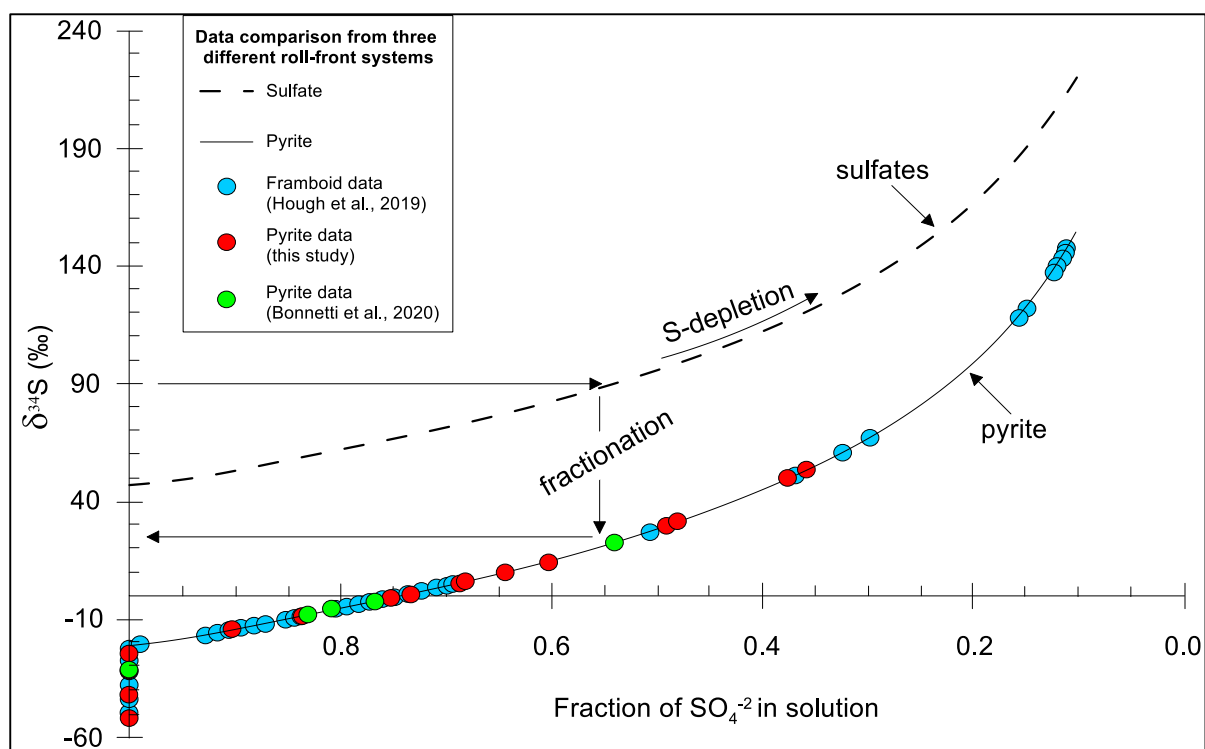


Figure 10

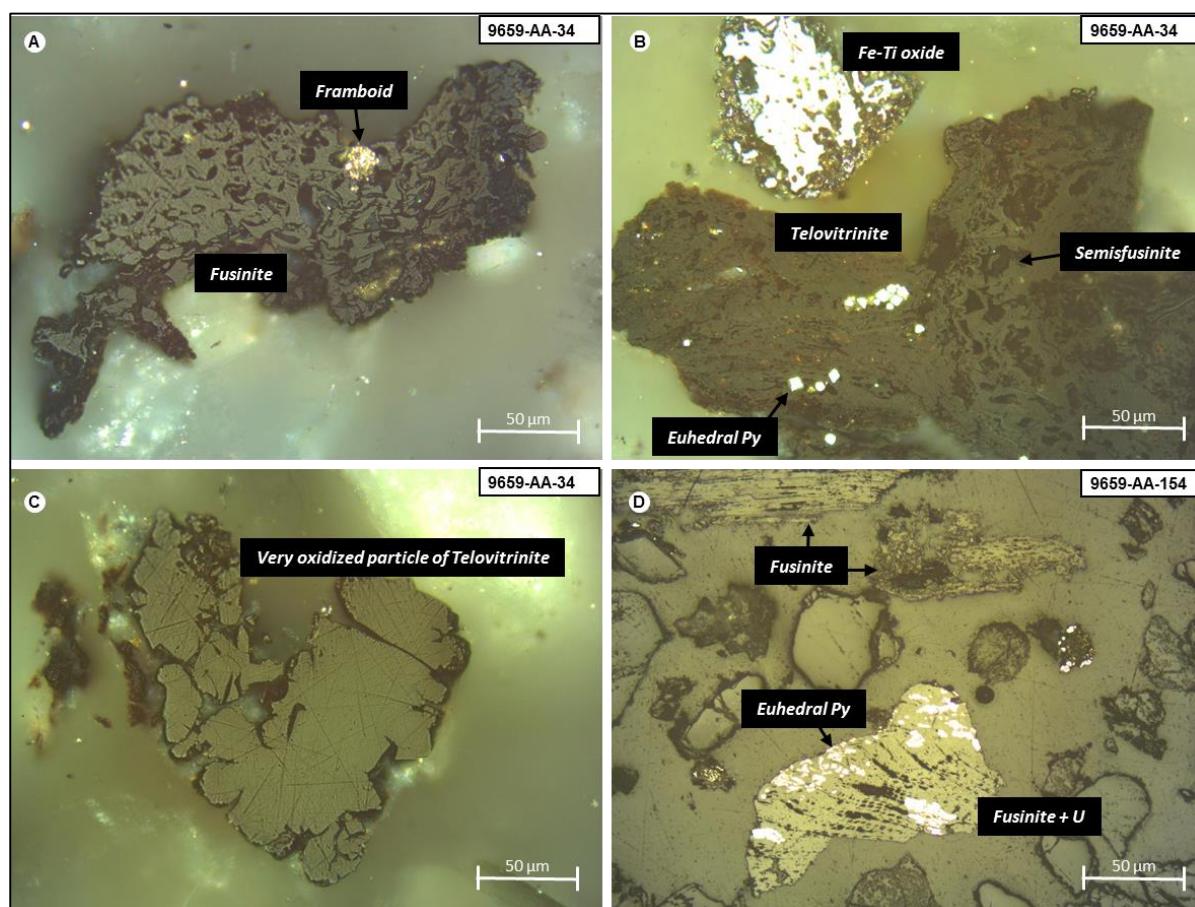


Figure 11

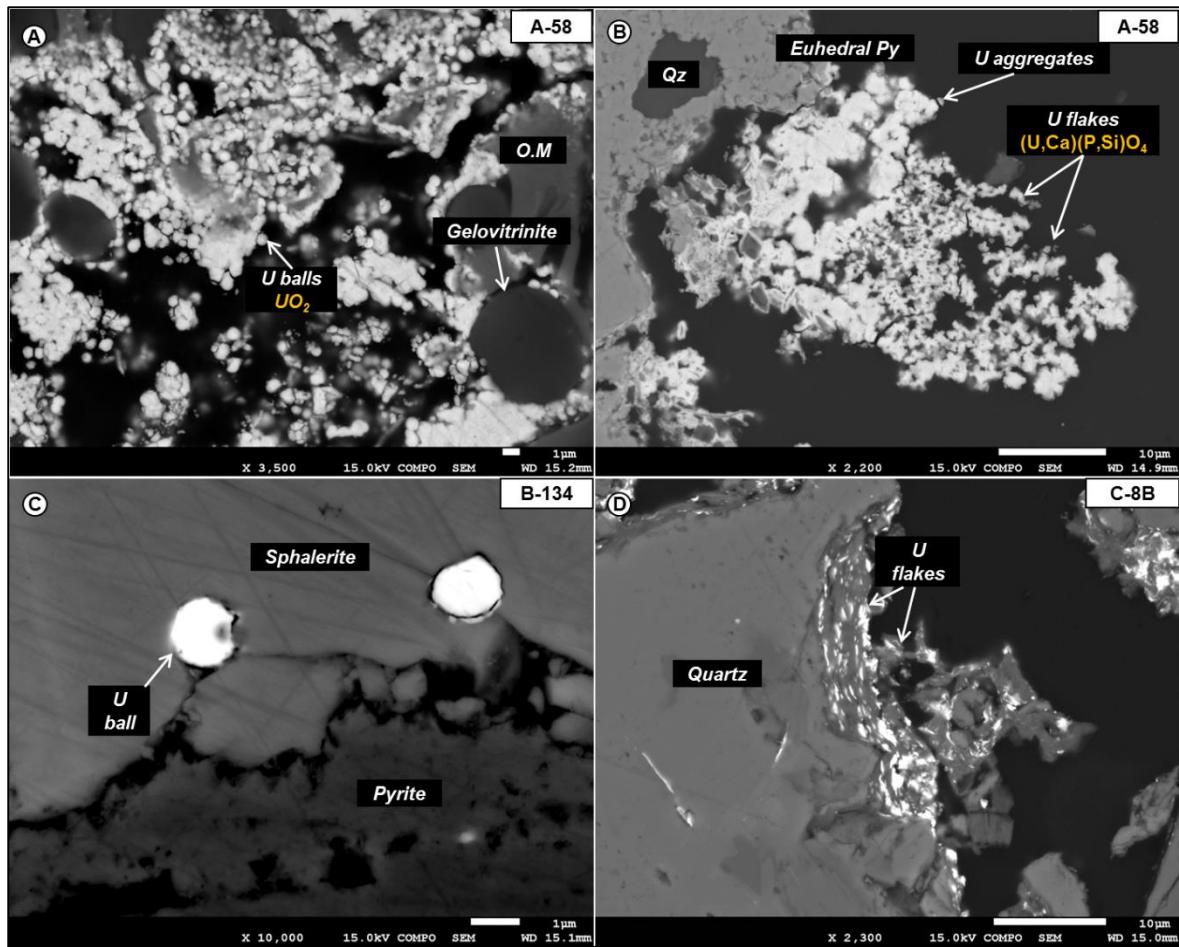


Figure 12

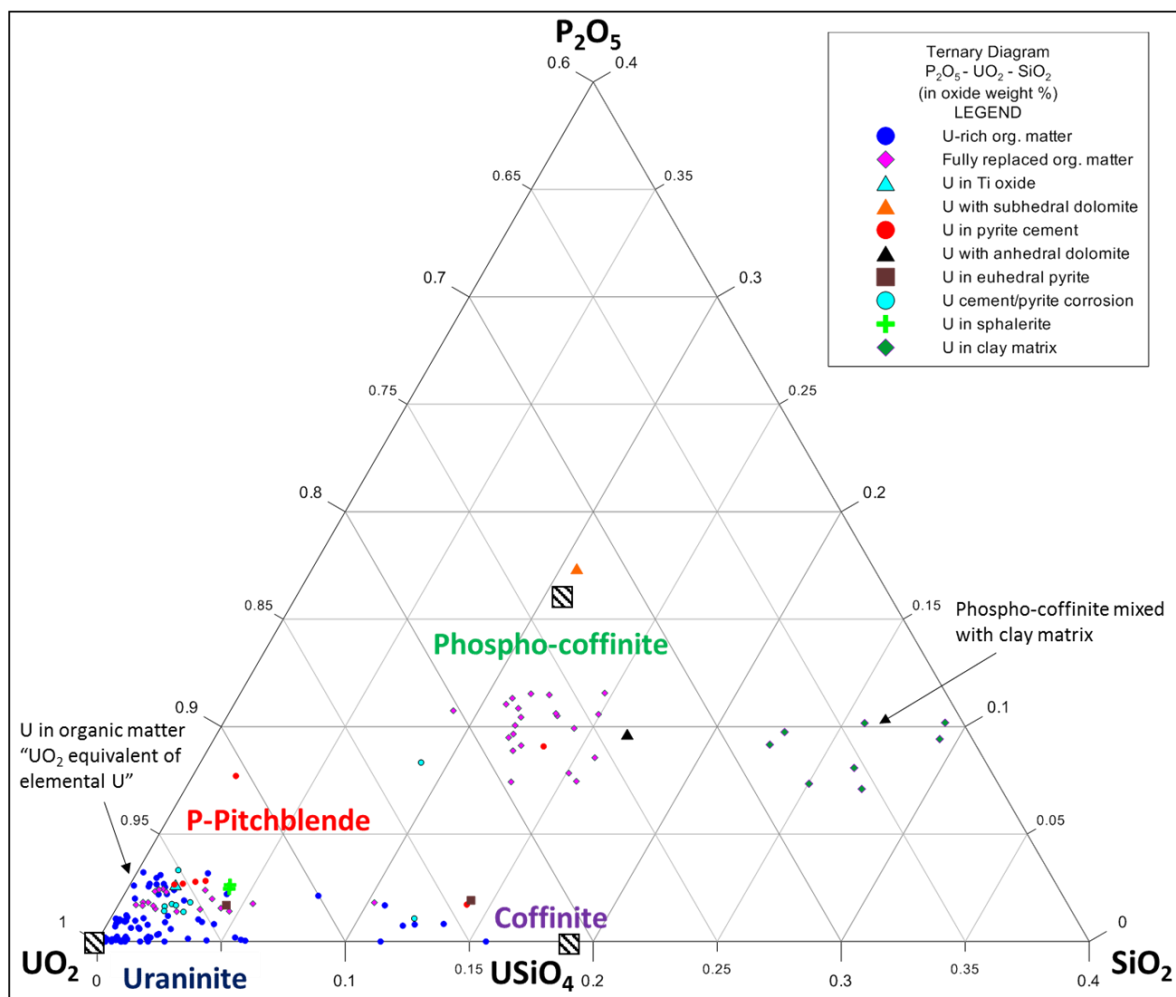


Figure 13

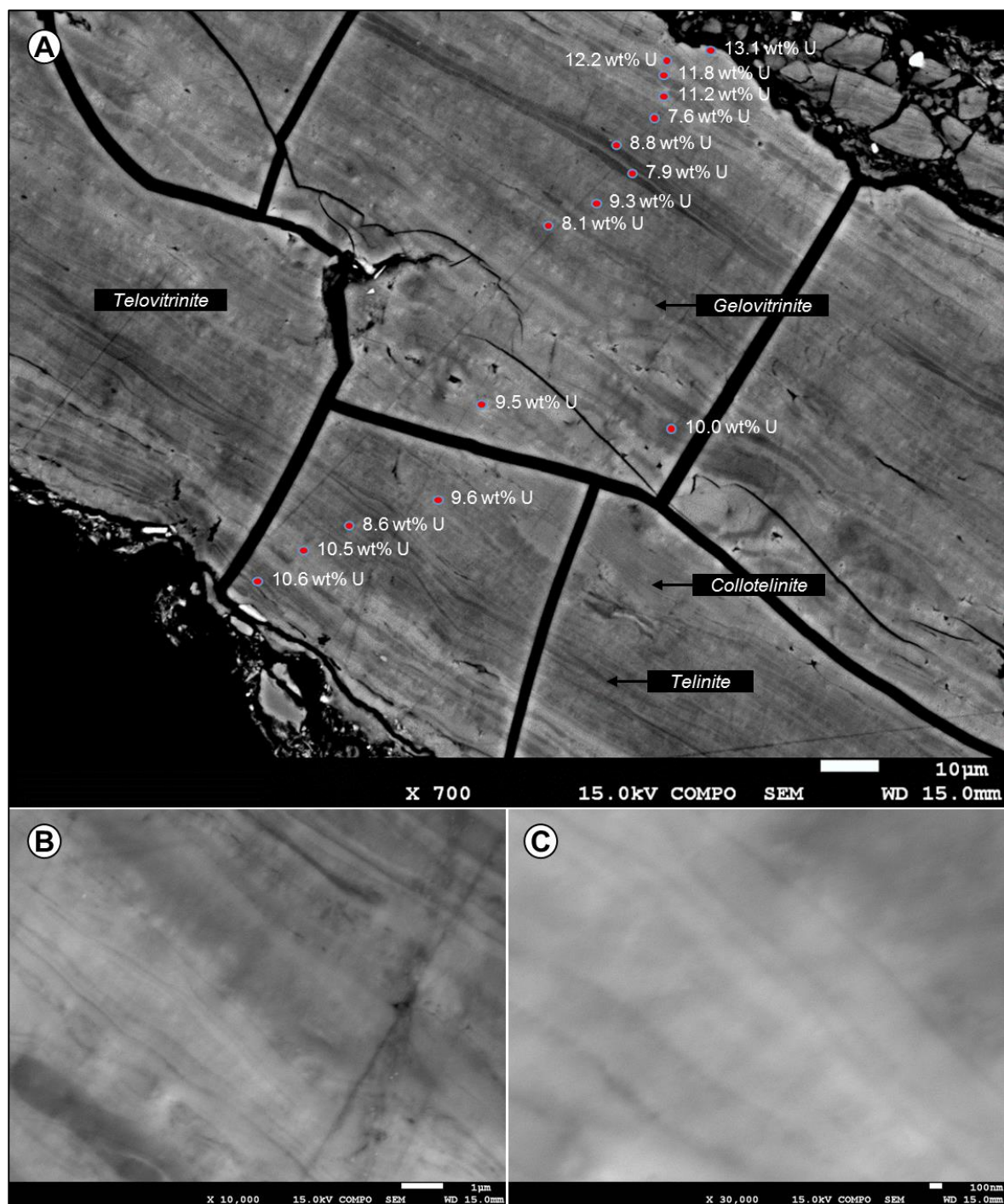


Figure 14

PARAGENETIC EVENT CHART				
Diagenetic events and minerals	Time →			
	Sedimentation / lowermost part of the basin	Early diagenesis	Roll-front	Late diagenesis
- Mg-rich calcite or dolomite precursor	—			
- I Microcrystalline dolomite + siderite	—			
- Framboidal pyrite 1	—			
- Siderite cores	—			
- II Euhedral dolomite + siderite zonations		—		
- Concentric overgrowth of pyrite		—	Partial dissolution of euhedral dolomite	
- II Poecilitic overgrowth of dolomite		—	↗	
- Euhedral pyrite 1		—		
- Marcasite		—		
- Sphalerite 1			—	
- III Subhedral dolomite			—	
- Euhedral pyrite 2			—	
- Sphalerite 2			—	
- Uraninite 1 (spherules)			—	
- Uraninite 2 (massive)		Org. mat. epigenization 1	Corrosion of Euhedral pyrite 1 & Sphalerite 1	—
- Phospho-coffinite		Org. mat. epigenization 2	Corrosion of Euhedral pyrite 1 & Sphalerite 1	—
- Quartz cement				—
- IV Anhydral dolomite				—
- Framboidal pyrite 2 (in Type IV dolomite)				—
- Euhedral pyrite 3 (in Type IV dolomite)				—

Figure 15

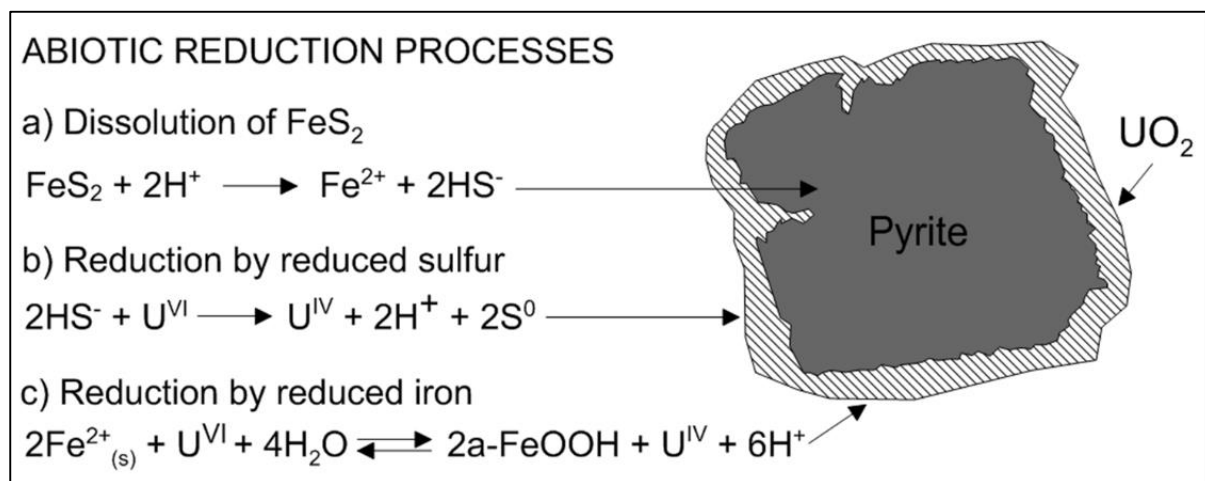


Figure 16

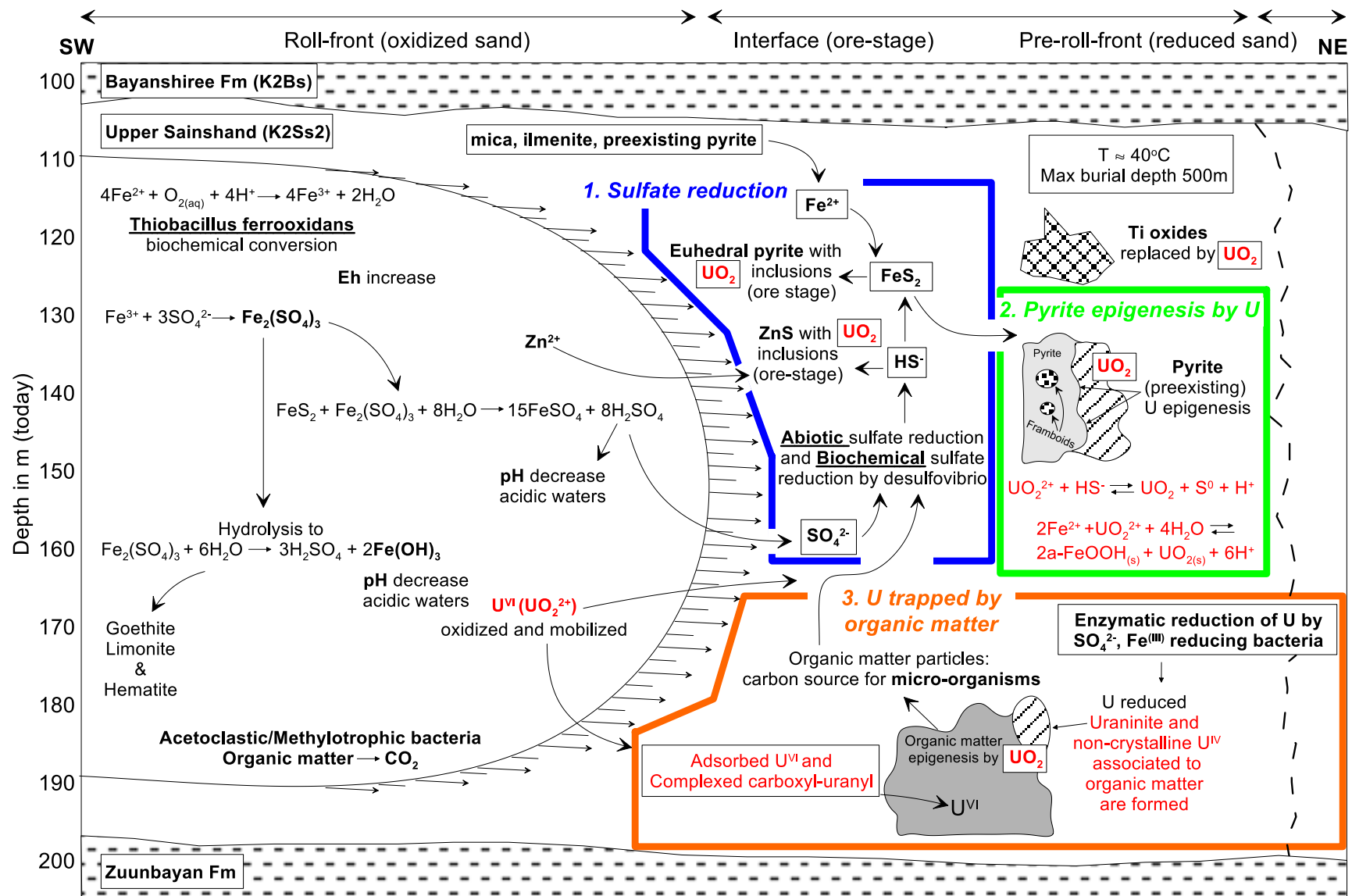


Figure 17

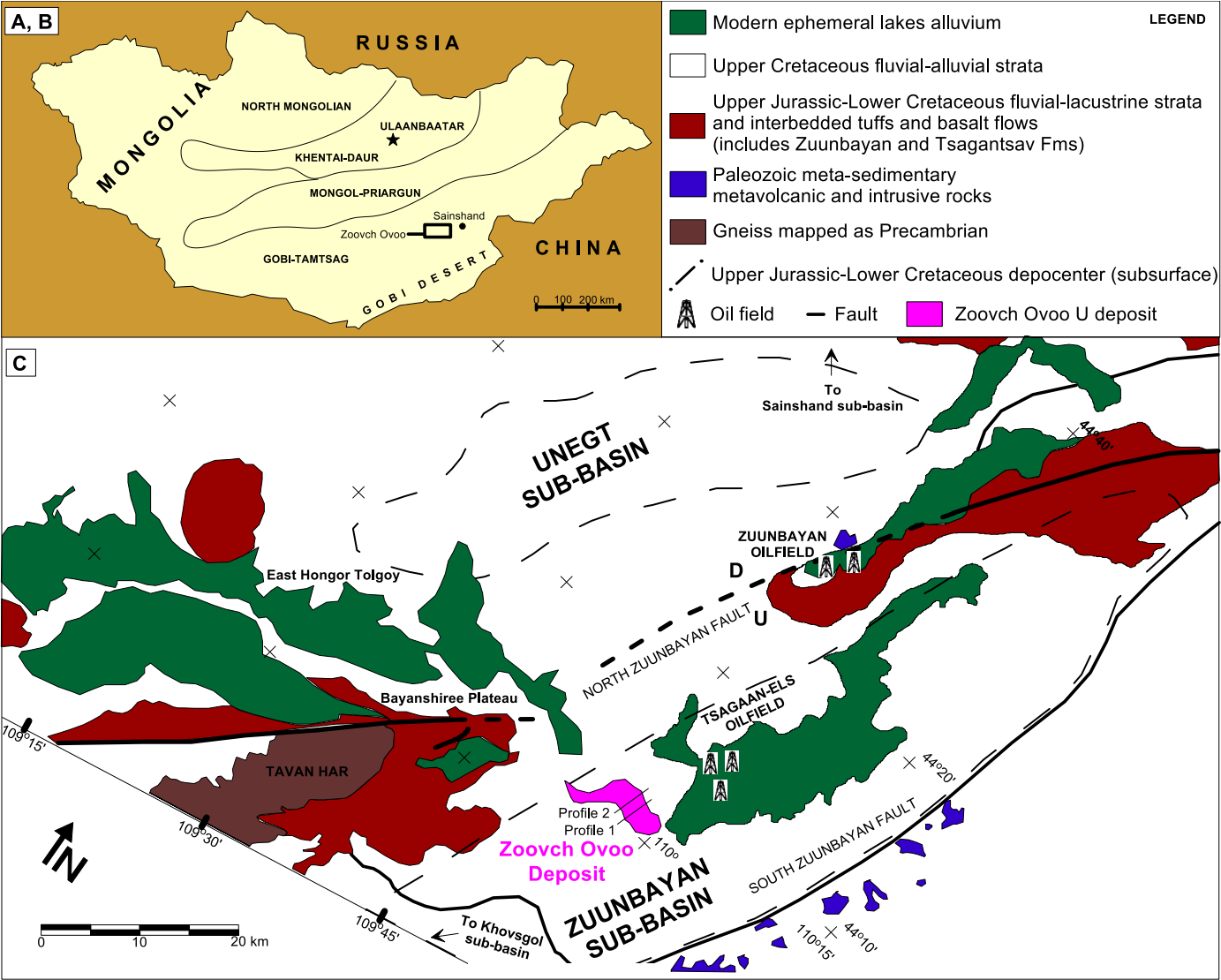


Figure 1

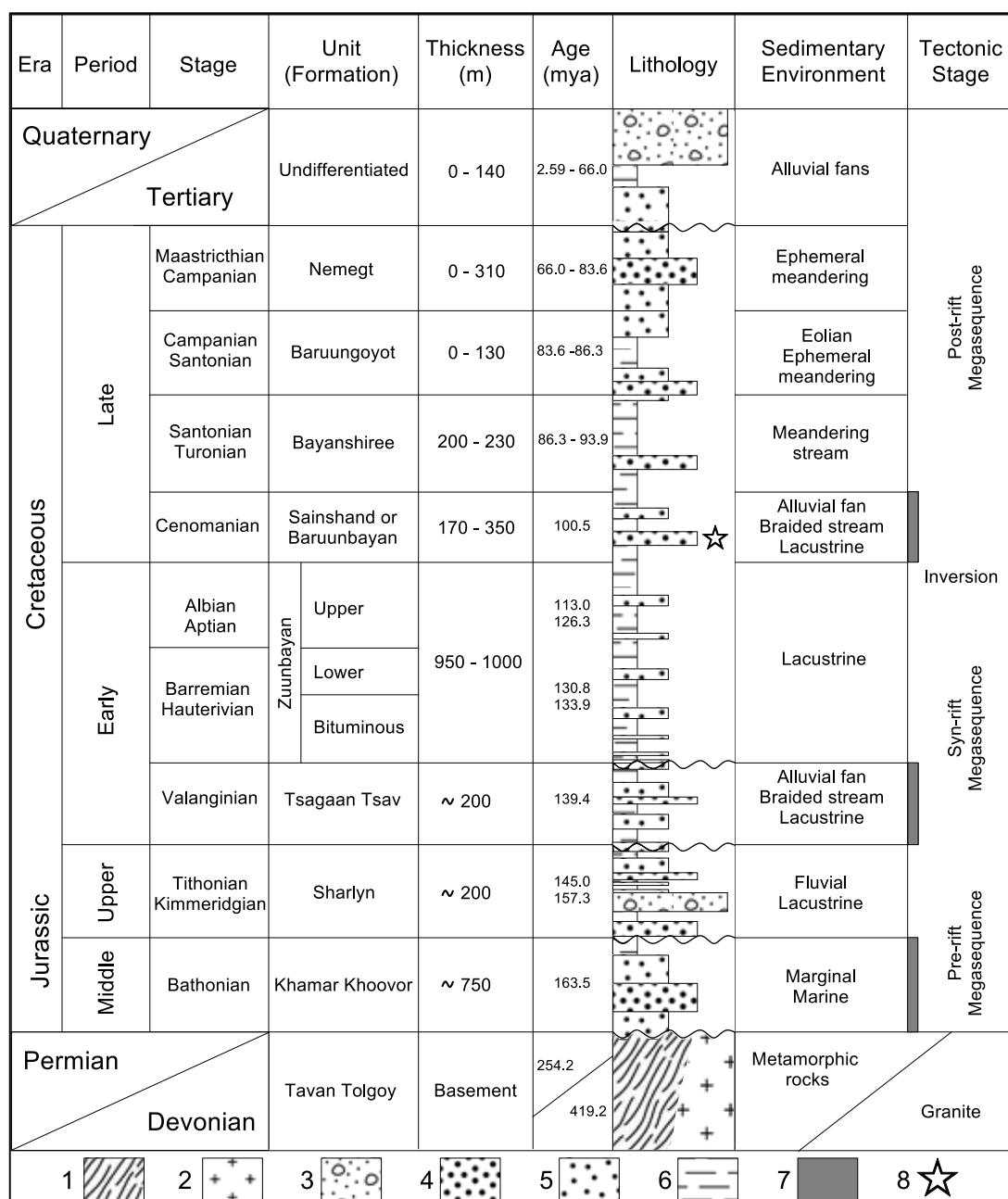


Figure 2

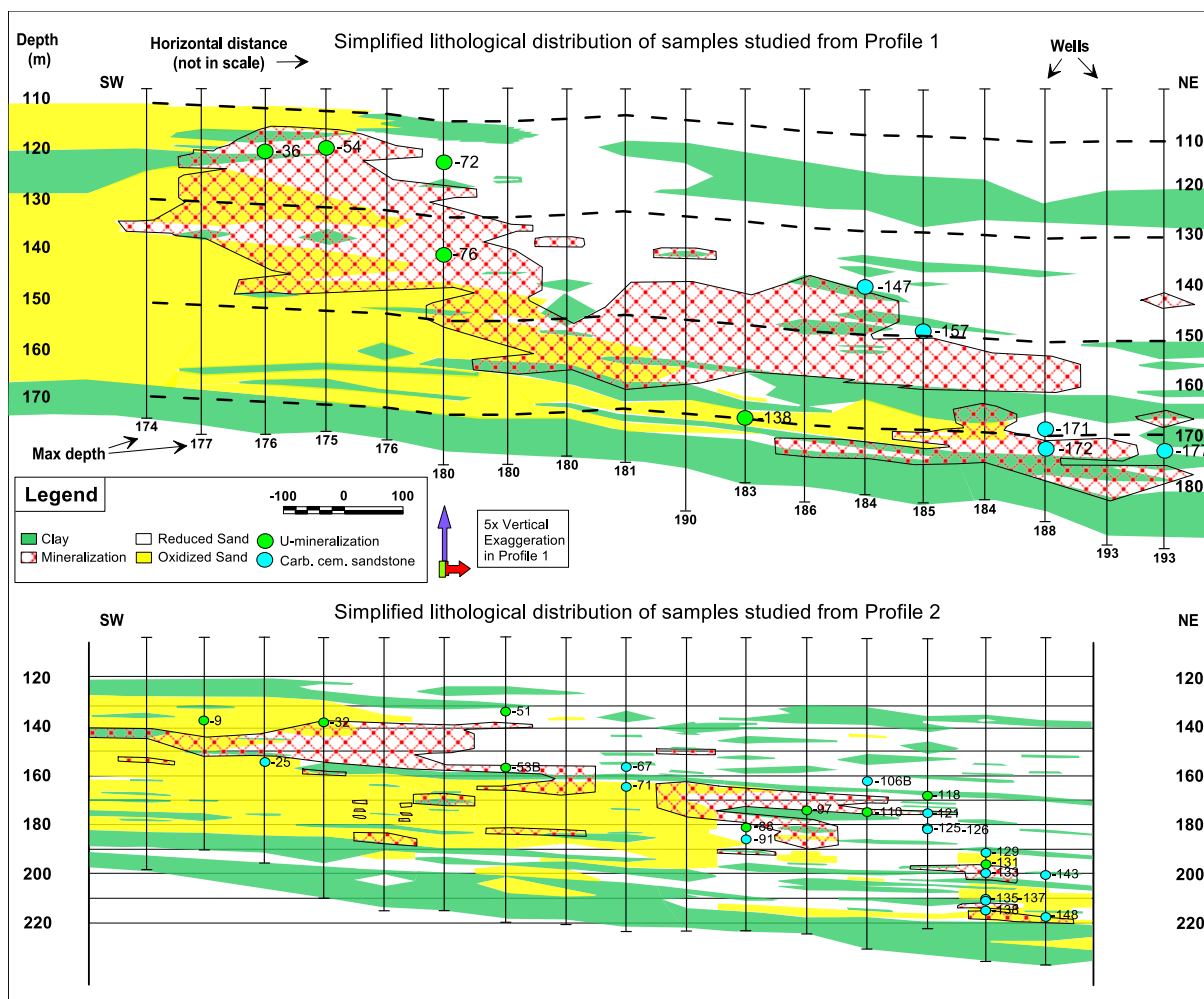


Figure 3

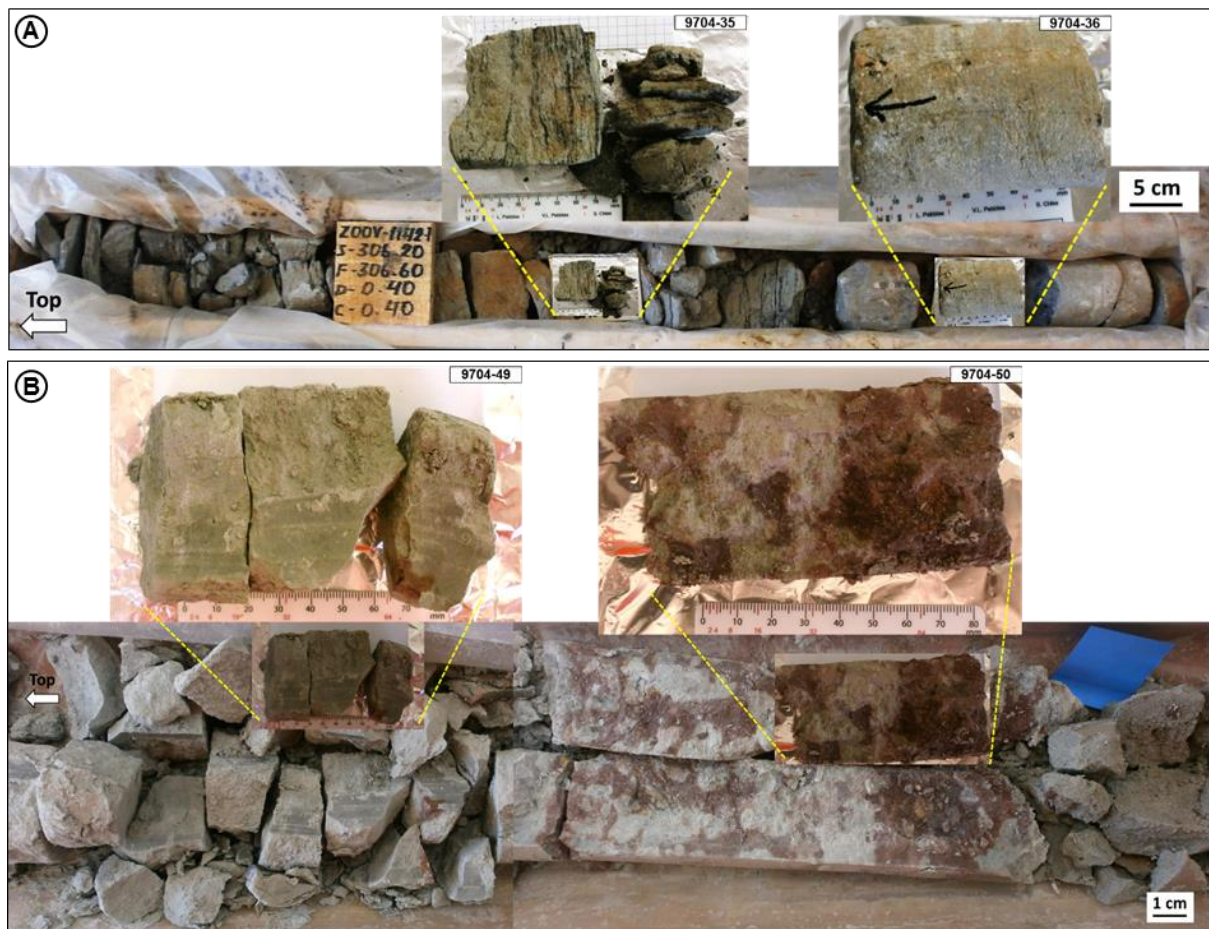


Figure 4

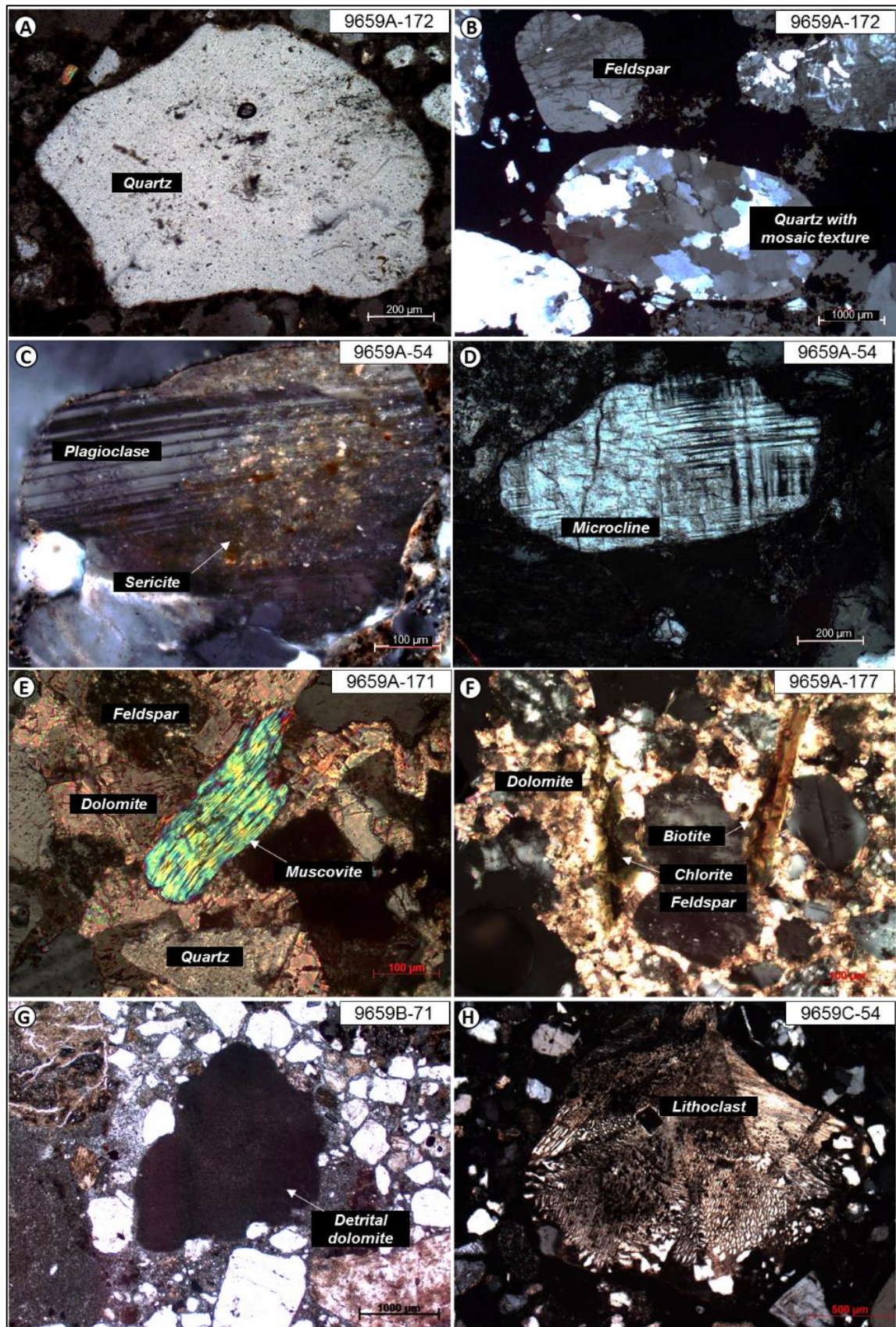


Figure 5

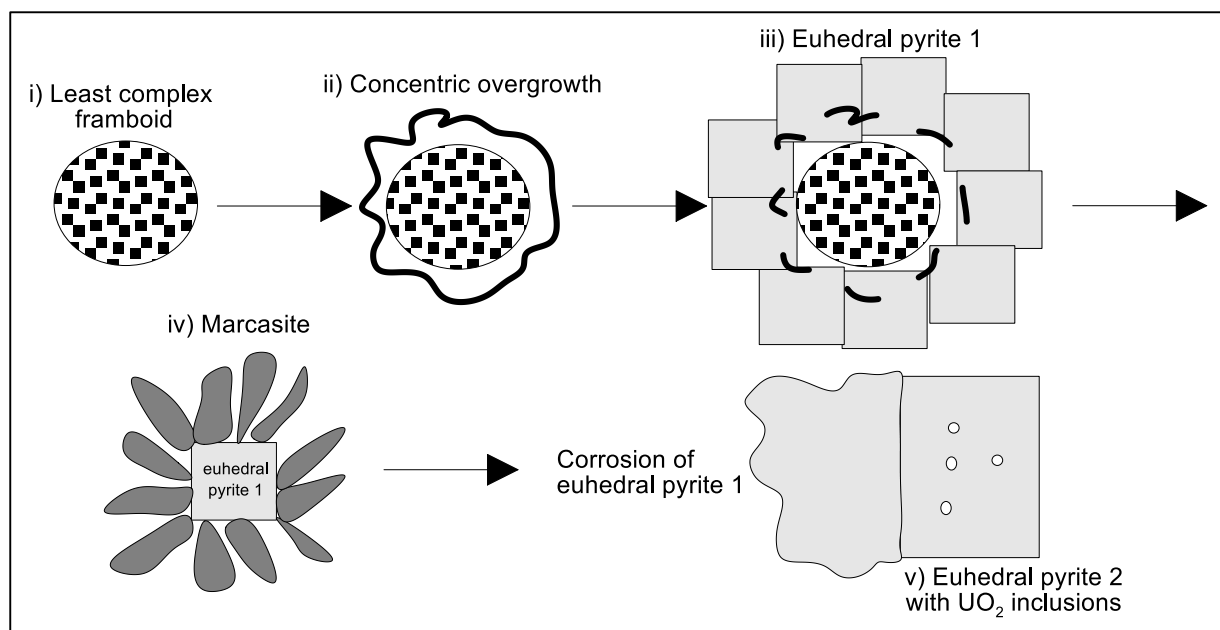


Figure 6

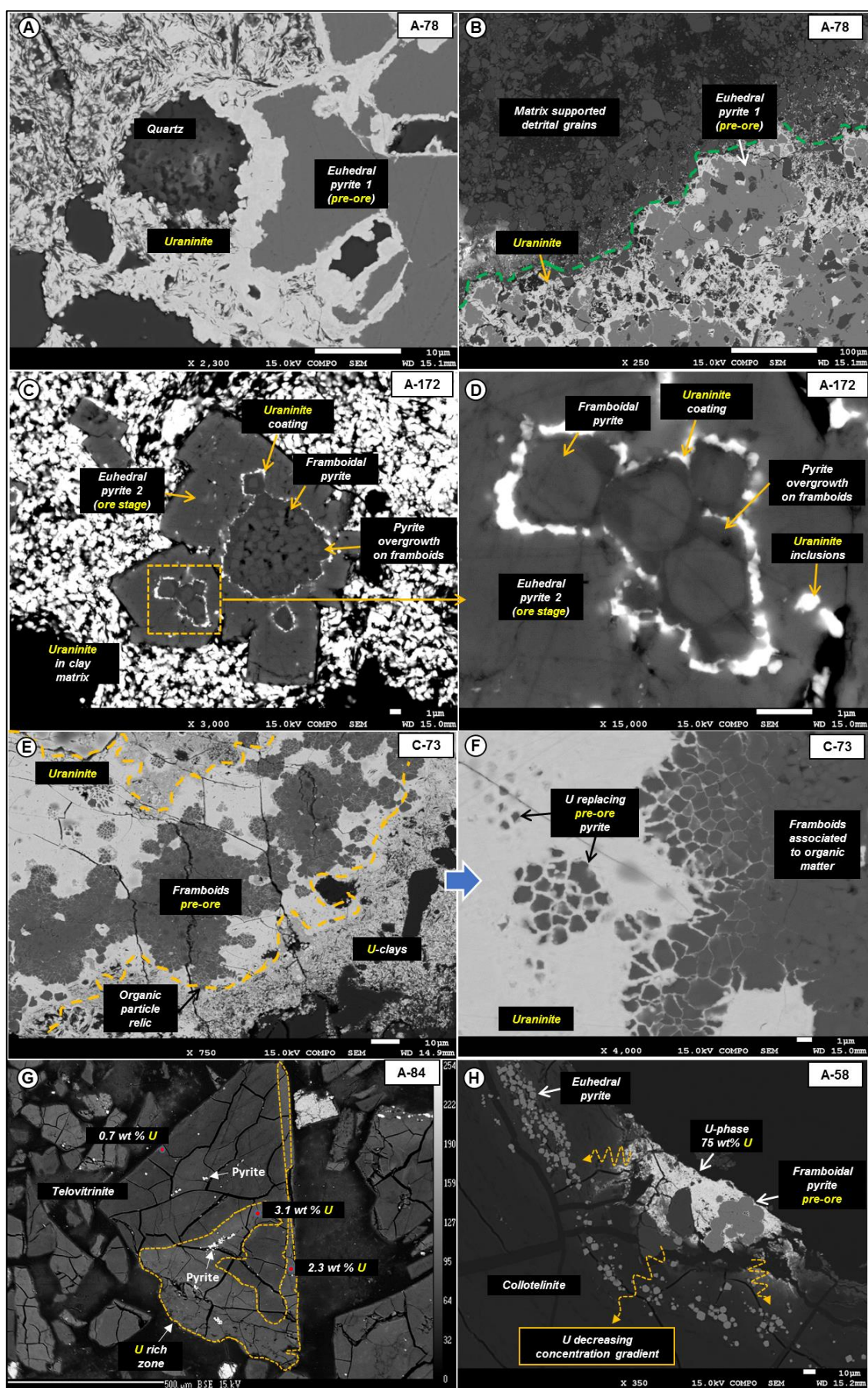


Figure 7

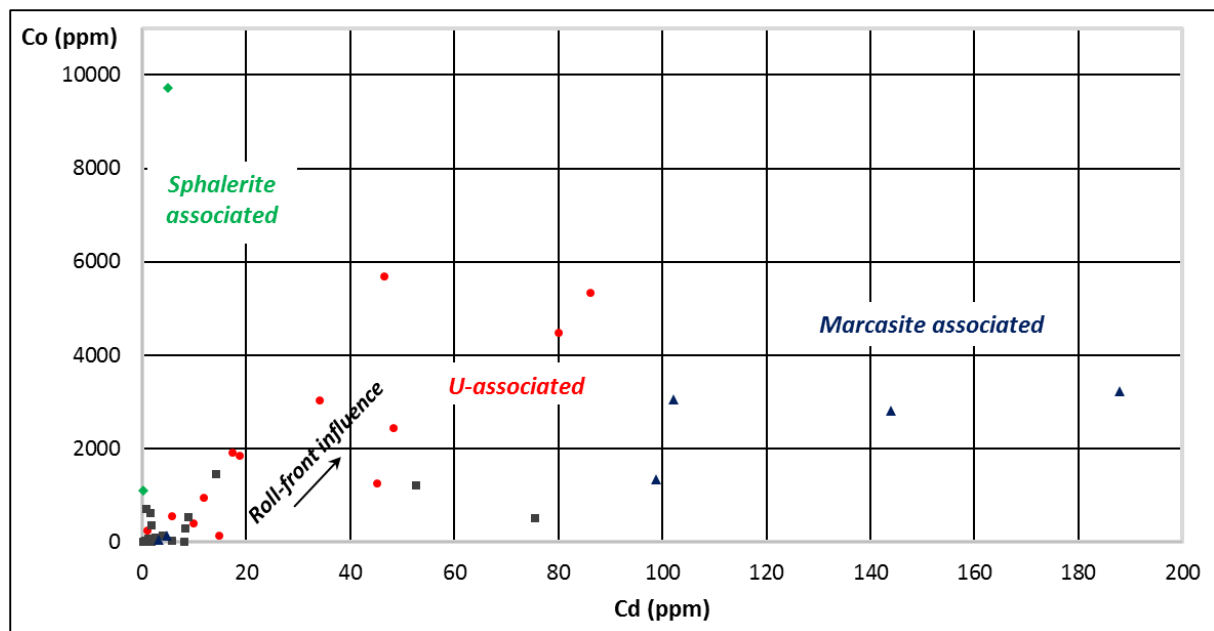


Figure 8

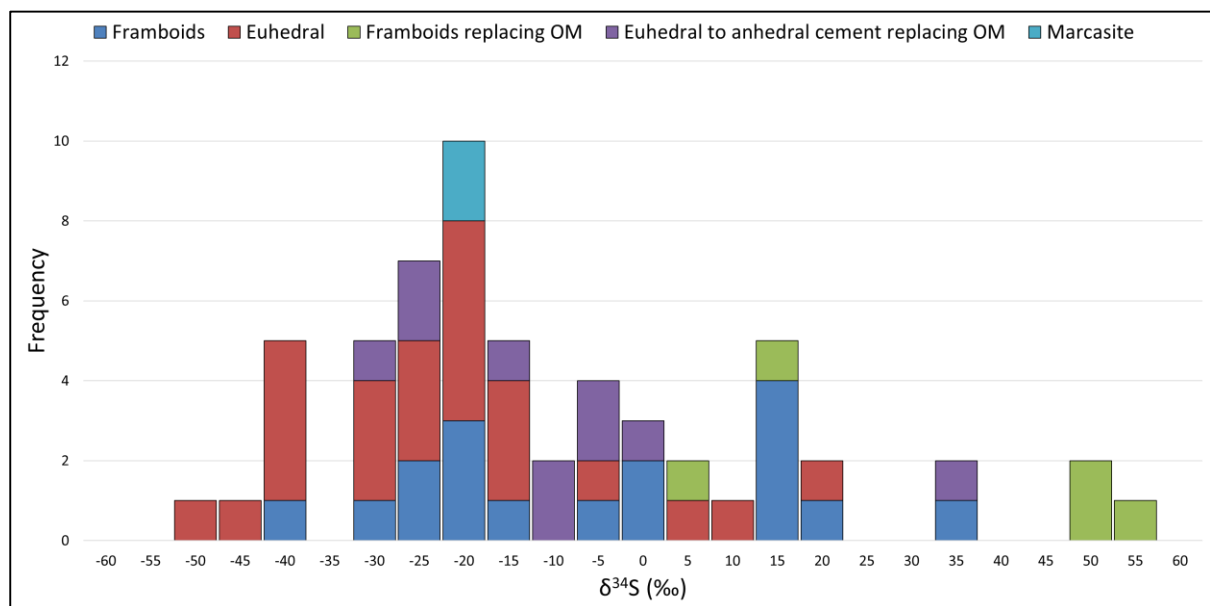


Figure 9

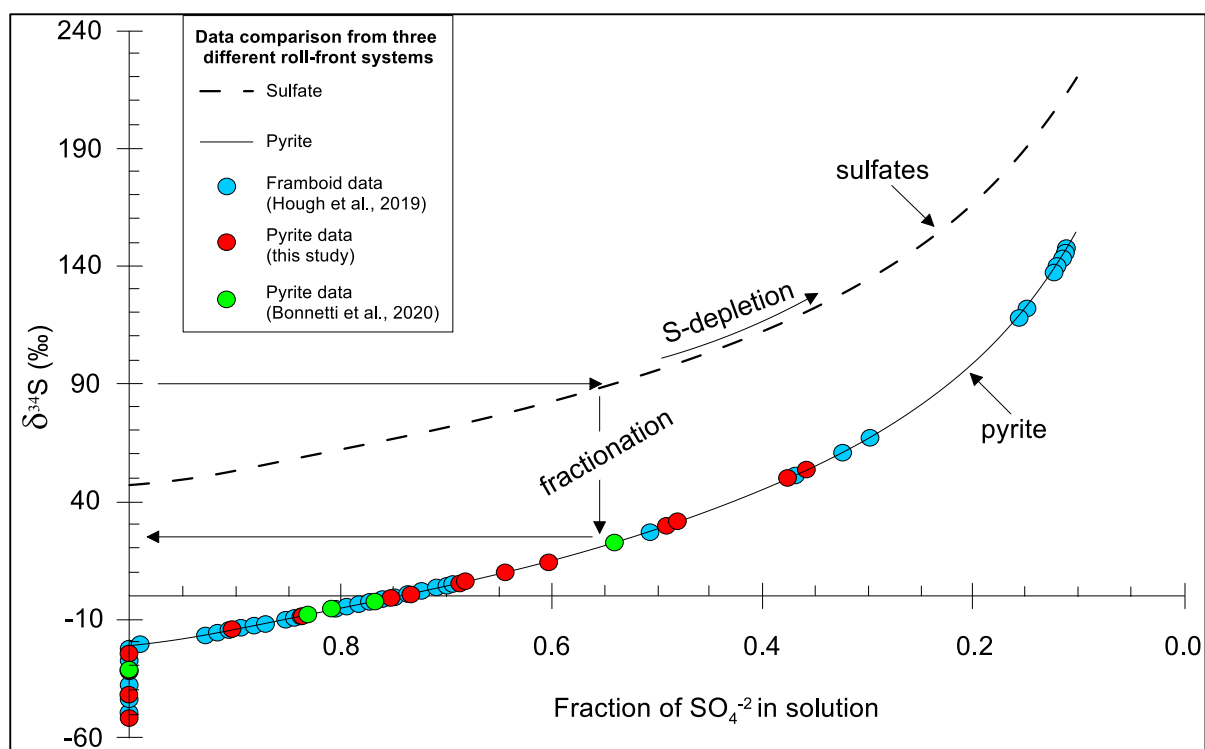


Figure 10

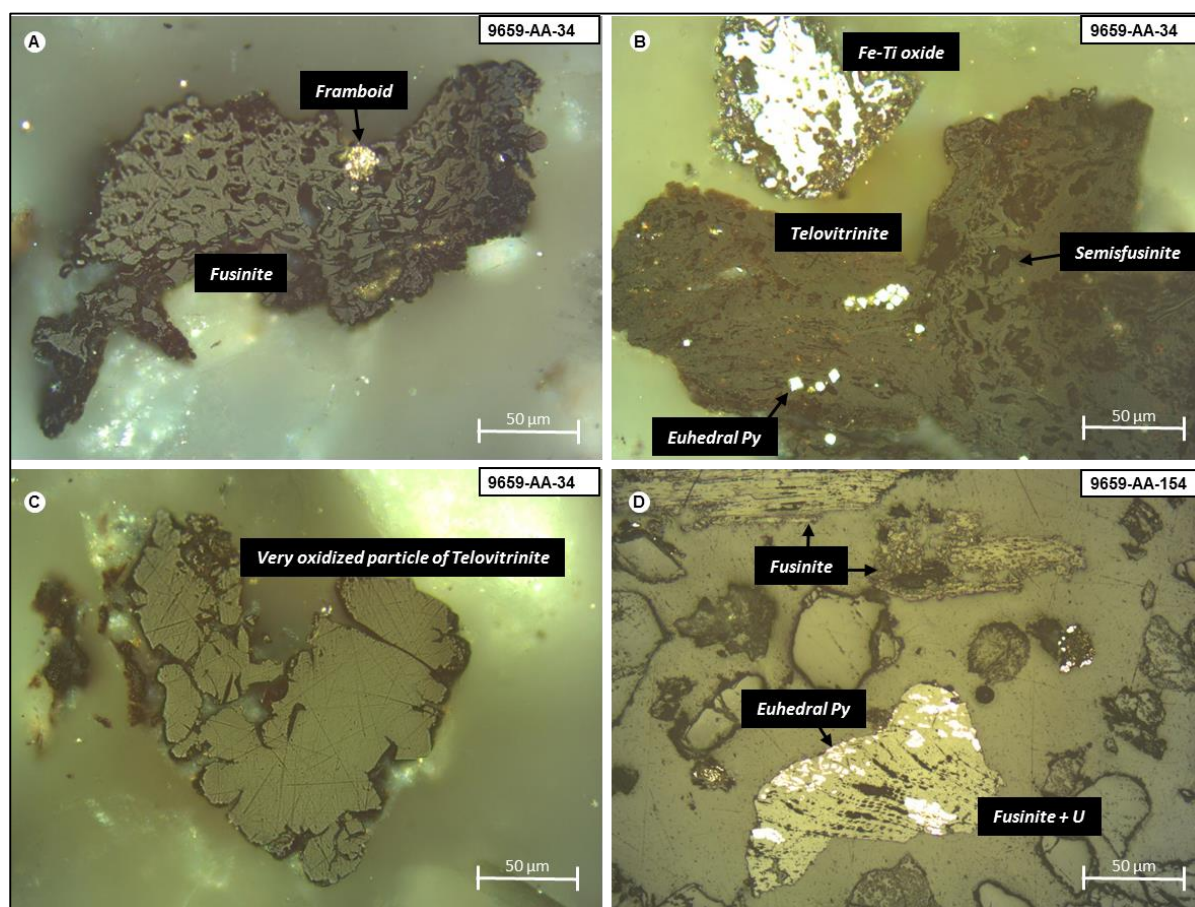


Figure 11

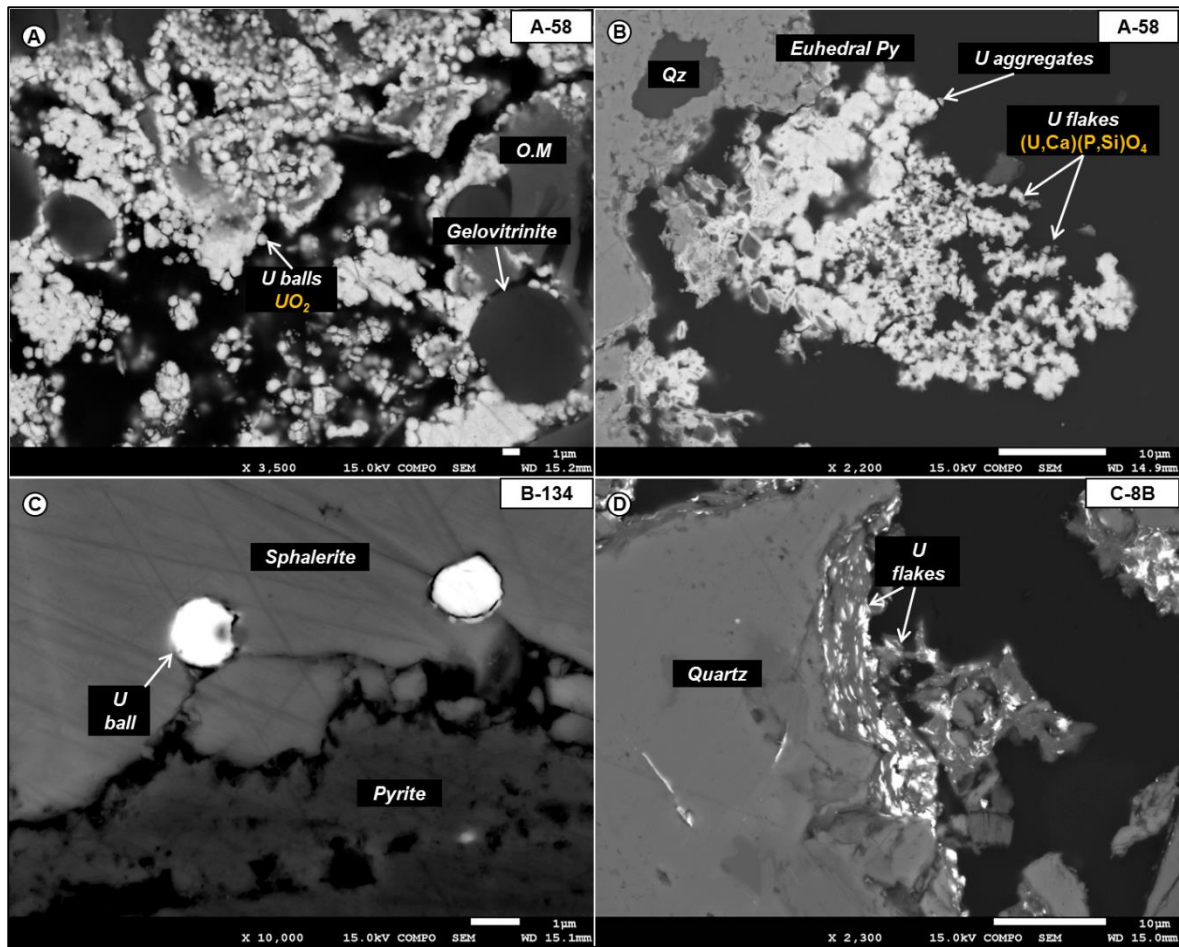


Figure 12

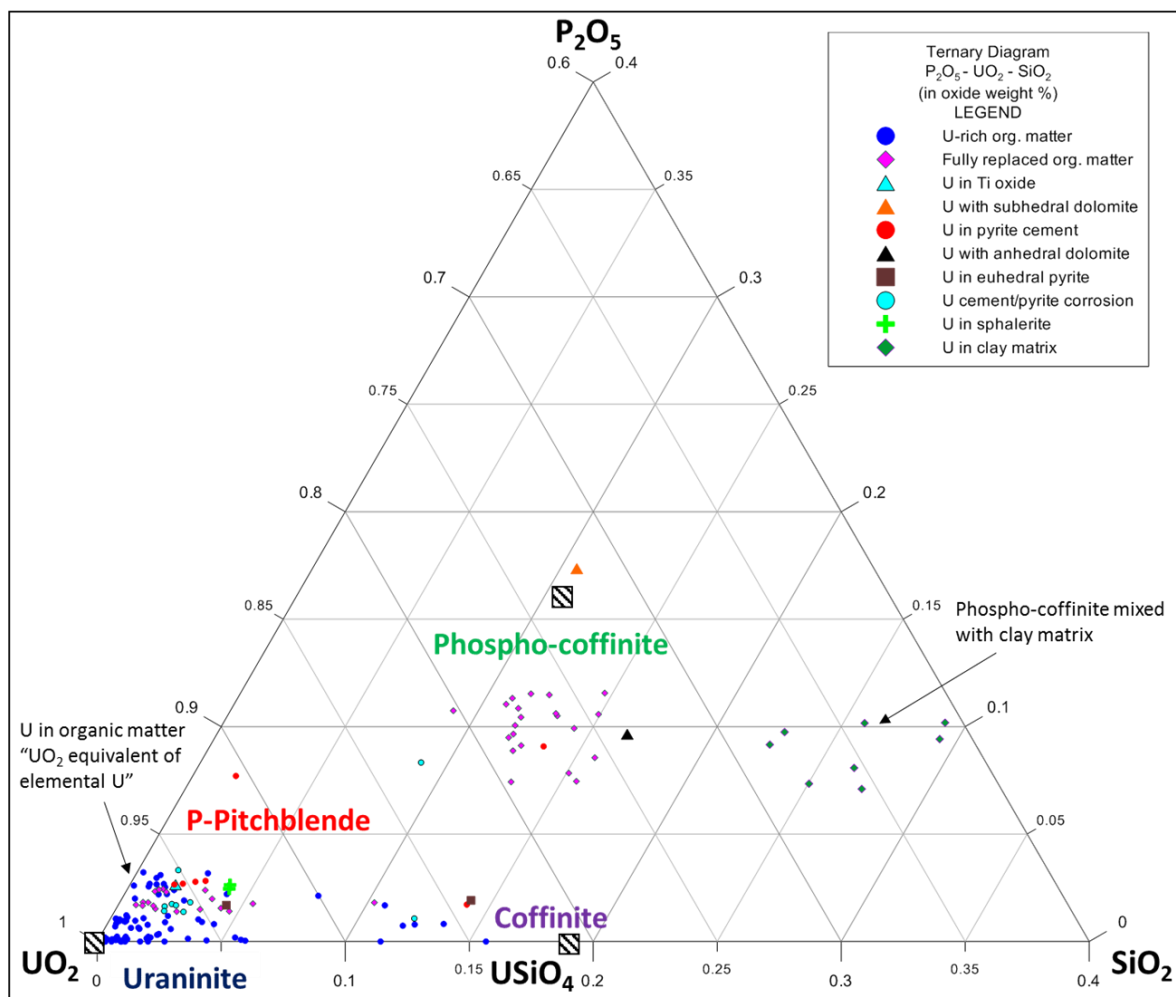


Figure 13

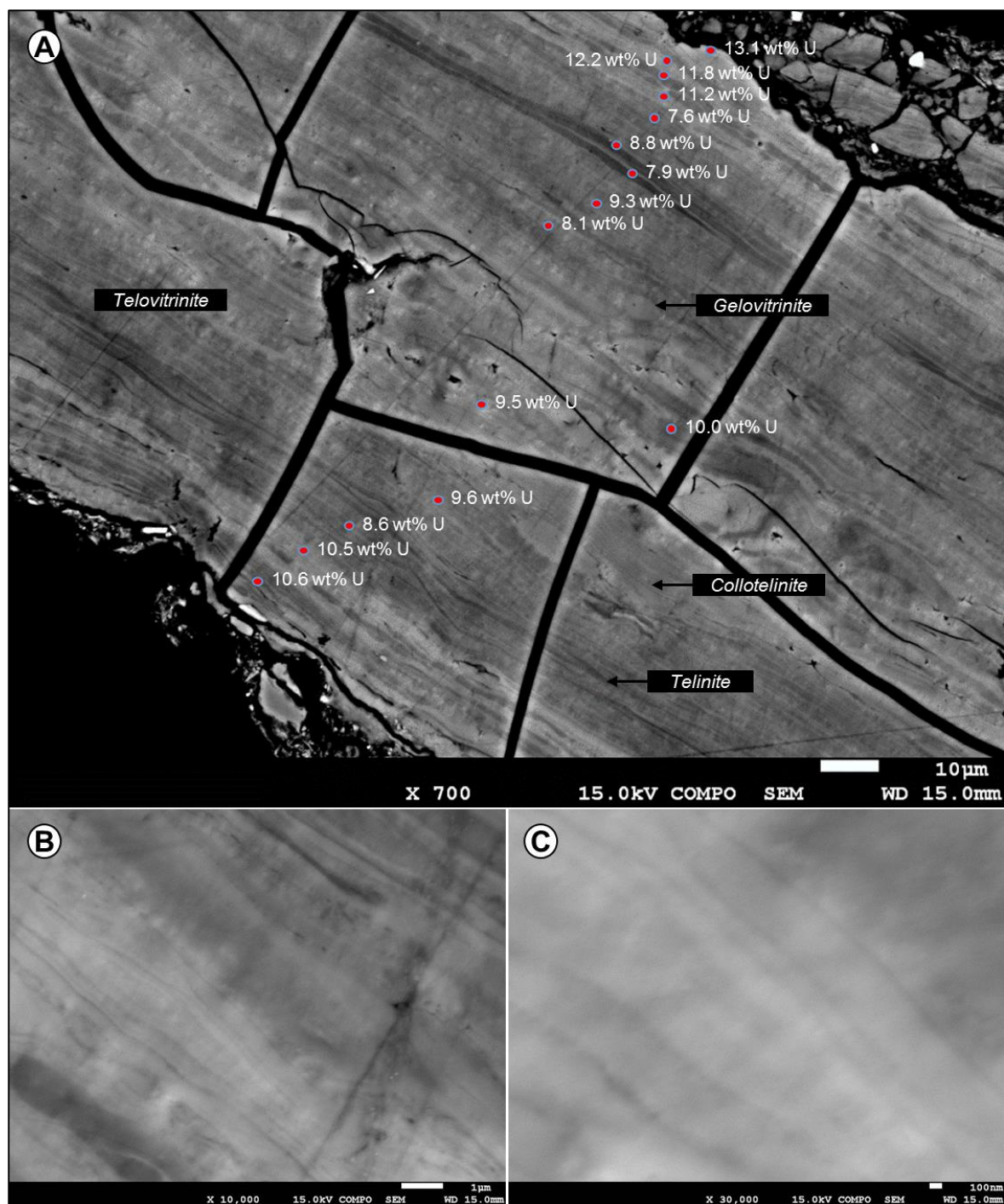


Figure 14

PARAGENETIC EVENT CHART				
Diagenetic events and minerals	Time →			
	Sedimentation / lowermost part of the basin	Early diagenesis	Roll-front	Late diagenesis
- Mg-rich calcite or dolomite precursor	—			
- I Microcrystalline dolomite + siderite	—			
- Framboidal pyrite 1	—			
- Siderite cores	—			
- II Euhedral dolomite + siderite zonations		—		
- Concentric overgrowth of pyrite		—	Partial dissolution of euhedral dolomite	
- II Poecilitic overgrowth of dolomite		—		
- Euhedral pyrite 1		—		
- Marcasite		—		
- Sphalerite 1			—	
- III Subhedral dolomite			—	
- Euhedral pyrite 2			—	
- Sphalerite 2			—	
- Uraninite 1 (spherules)			—	
- Uraninite 2 (massive)		Org. mat. epigenization 1	Corrosion of Euhedral pyrite 1 & Sphalerite 1	—
- Phospho-coffinite		Org. mat. epigenization 2	Corrosion of Euhedral pyrite 1 & Sphalerite 1	—
- Quartz cement				—
- IV Anhydral dolomite				—
- Framboidal pyrite 2 (in Type IV dolomite)				—
- Euhedral pyrite 3 (in Type IV dolomite)				—

Figure 15

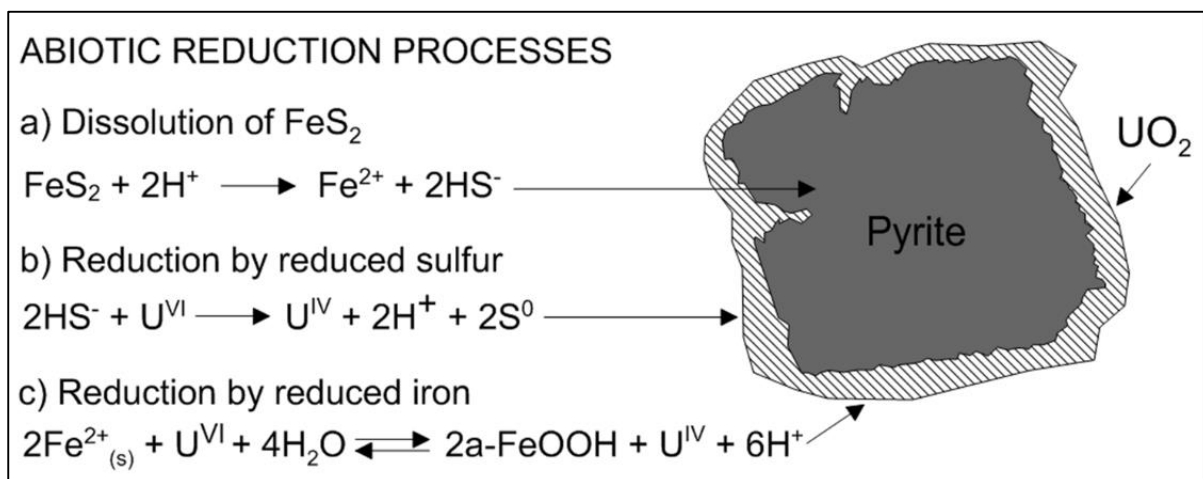


Figure 16

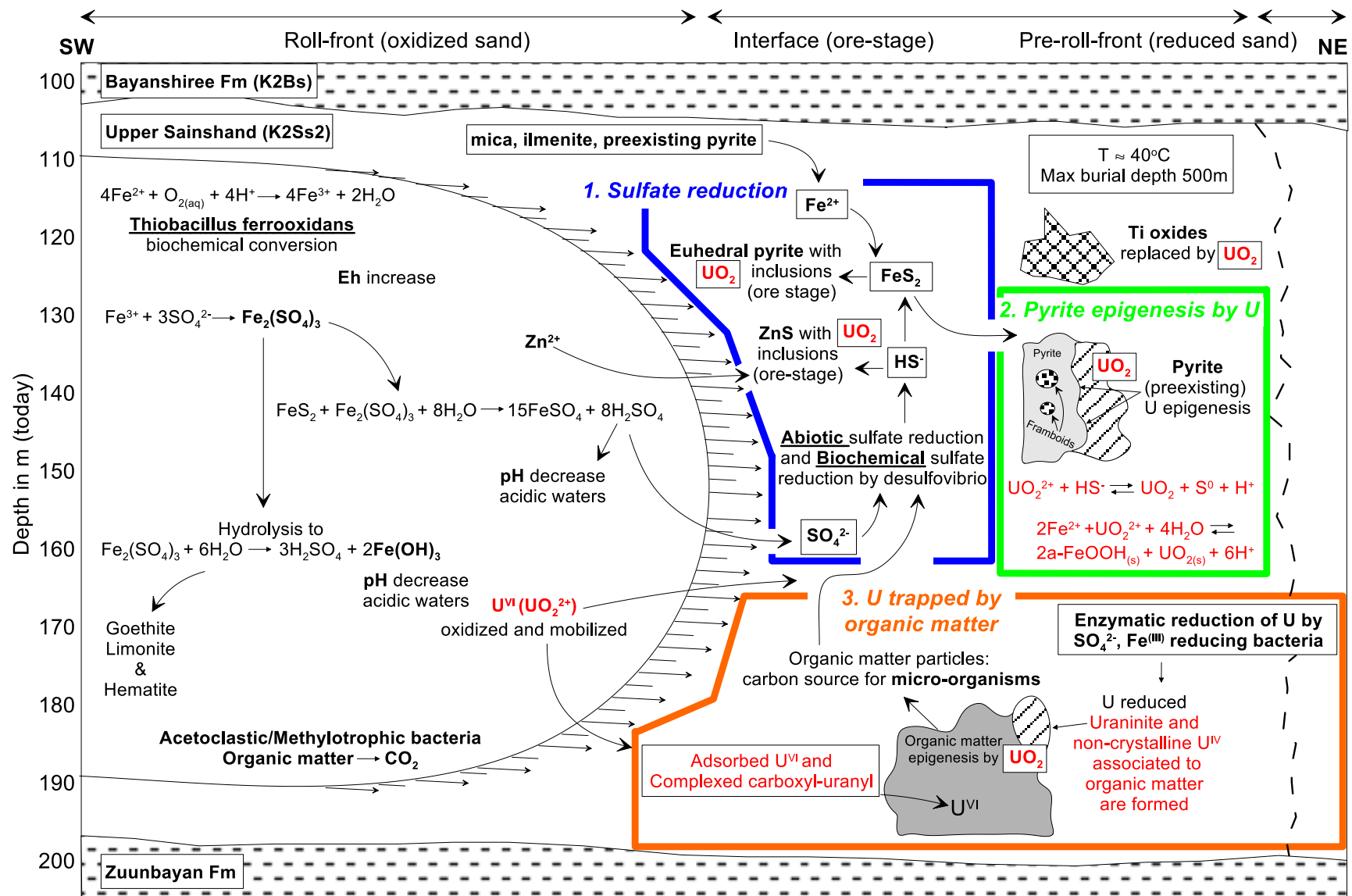


Figure 17

Table 1

Sample	Description	S1 mgHC/g.rock	S2 mgHC/g.rock	TOC(%)	Tmax(°C)	HI	OI	CPS
9704-08	Sand with OM	0.01	0.22	1.56	420	14	163	914
9704-9	Black claystone	0	0.07	0.34	428	21	65	132
9704-11	Black claystone	0	0.11	0.67	430	16	57	70
9704-17	Sand with OM	0.01	0.17	1.08	418	16	152	90
9704-40	Carb-cemented sandstone with OM	0.01	0.44	2.54	423	17	109	97
9704-47		0.01	0.4	1.53	431	26	121	70
9704-150	Black claystone	0.01	1.34	8.01	340	17	163	76
9659A-72	Sand with OM	0.03	0.6	3.07	377	20	122	70
9659A-116	Sand with OM	0.07	0.48	7.29	240	7	220	105
9659A-34	Sand with OM	0.05	0.3	2.18	410	14	101	70
9659A-62	Sand with OM	0.08	0.57	2.41	417	24	134	70
9659A-84	Sand with OM	0.06	0.73	17.57	358	4	172	70
9659A-151	Sand with OM	0.02	0.1	0.38	415	26	97	70
9659A-154	Sand with OM	0.04	0.17	3.25	303	5	171	70

Table 2

Bacteria strains	Chemical reactions
1. Iron reducing bacteria <i>Geobacter metallireducens</i> Lovley et al. (1991)	$\text{CH}_3\text{COO}^- + 8\text{Fe}^{+3} + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8\text{Fe}^{+2} + 4\text{H}^+$
2. Sulfate reducing bacteria <i>Desulfovibrio sulfuricans</i> & <i>sulfosprosinus</i> Lovley et al. (1993) ; Cardenas et al. (2010)	$\text{CH}_3\text{COOH} + \text{SO}_4^{-2} + 4\text{H}^+ \rightarrow \text{HS}^- + 2\text{HCO}_3^- + 3\text{H}^+$
3. Methanogens <i>Methanosarcina</i> Holmes et al. (2018)	$\text{CH}_3\text{COOH} \rightarrow 2\text{CH}_4 + \text{CO}_2$
The same bacteria strains may reduce uranium based on the following reaction	$\text{CH}_3\text{COO}^- + 4\text{U}^{+6} + 4\text{H}_2\text{O} \rightarrow 4\text{U}^{+4} + 2\text{HCO}_3^- + 9\text{H}^+$

Table 1

Sample	Description	S1 mgHC/g.rock	S2 mgHC/g.rock	TOC(%)	Tmax(°C)	HI	OI	CPS
9704-08	Sand with OM	0.01	0.22	1.56	420	14	163	914
9704-9	Black claystone	0	0.07	0.34	428	21	65	132
9704-11	Black claystone	0	0.11	0.67	430	16	57	70
9704-17	Sand with OM	0.01	0.17	1.08	418	16	152	90
9704-40	Carb-cemented sandstone with OM	0.01	0.44	2.54	423	17	109	97
9704-47		0.01	0.4	1.53	431	26	121	70
9704-150	Black claystone	0.01	1.34	8.01	340	17	163	76
9659A-72	Sand with OM	0.03	0.6	3.07	377	20	122	70
9659A-116	Sand with OM	0.07	0.48	7.29	240	7	220	105
9659A-34	Sand with OM	0.05	0.3	2.18	410	14	101	70
9659A-62	Sand with OM	0.08	0.57	2.41	417	24	134	70
9659A-84	Sand with OM	0.06	0.73	17.57	358	4	172	70
9659A-151	Sand with OM	0.02	0.1	0.38	415	26	97	70
9659A-154	Sand with OM	0.04	0.17	3.25	303	5	171	70

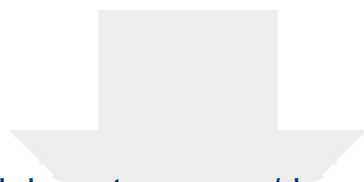
Table 2

Bacteria strains	Chemical reactions
1. Iron reducing bacteria <i>Geobacter metallireducens</i> Lovley et al. (1991)	$\text{CH}_3\text{COO}^- + 8\text{Fe}^{+3} + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8\text{Fe}^{+2} + 4\text{H}^+$
2. Sulfate reducing bacteria <i>Desulfovibrio sulfuricans</i> & <i>sulfosprosinus</i> Lovley et al. (1993) ; Cardenas et al. (2010)	$\text{CH}_3\text{COOH} + \text{SO}_4^{-2} + 4\text{H}^+ \rightarrow \text{HS}^- + 2\text{HCO}_3^- + 3\text{H}^+$
3. Methanogens <i>Methanosarcina</i> Holmes et al. (2018)	$\text{CH}_3\text{COOH} \rightarrow 2\text{CH}_4 + \text{CO}_2$
The same bacteria strains may reduce uranium based on the following reaction	$\text{CH}_3\text{COO}^- + 4\text{U}^{+6} + 4\text{H}_2\text{O} \rightarrow 4\text{U}^{+4} + 2\text{HCO}_3^- + 9\text{H}^+$

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

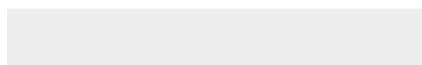
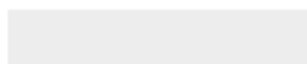
☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

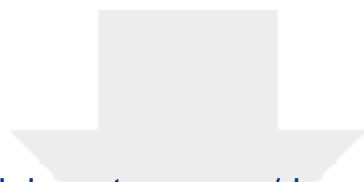


[Click here to access/download](#)

Supplementary Material

Uranium article Appendix images.docx





[Click here to access/download](#)

Supplementary Material

Uranium article Appendix images.docx

