

**DEPOSITIONAL HISTORY OF URANIUM ORES:
ISOTOPIC CONSTRAINTS**

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The elaboration of new and more constrained models for the genesis of uranium deposits has greatly benefited from the application of stable and radiogenic isotope geochemistry during the last two decades. Sulfur isotope and U-Pb geochemistry have been used extensively in the past, but it is only recently that other isotopic systems have been applied (Sm-Nd and Sr isotope geochemistry on pitchblende, K-Ar and $^{39}\text{Ar}/^{40}\text{Ar}$ on clay minerals, $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ on minerals and fluid inclusions). An ideal physico-chemical model for the genesis of a U deposit should incorporate the four following stages: (1) leaching from the source-rock, (2) transportation of the elements by the mineralized fluid, (3) some mechanism of elemental deposition, and (4) preservation of the deposit. When studying a U deposit, detailed data acquisition should not be confined to the deposit nor solely to the U; only an integrated approach including the tectonic framework and explanations for the presence of not only the U but also other elements present in the mineralized zones can provide the necessary information to correctly interpret a deposit. Of course, all elements are not necessarily derived from the same source-rock, nor transported by the same fluid, nor deposited at the same time as the U,

nor expected to behave similarly during alteration. However, isotopic studies are especially well adapted to recognize the different stages of mineralization in a deposit and to provide valuable insight regarding the source, transport, deposition and preservation of U deposits. The purpose of the present review is to discuss the main avenues of research in isotope geochemistry applied to U deposits in sediments, their applicability and their possible development in the near future.

URANIUM ORES IN SEDIMENTARY ENVIRONMENTS

The main types of U ore deposits in surficial and sedimentary environments and their characteristics are presented in table I. For a more detailed treatment on the subject, the reader is encouraged to consult Nash et al. (1981). From an economic point of view, all these types of U deposits do not have the same value. For example, the calcrete deposits are of low grade and located in areas of difficult access whereas the spatially unconformity related deposits have very high grade up to 10% (Cigar Lake, Saskatchewan, Canada) and high tonnage.

A brief review of U geochemistry is given for those not familiar with U metallogeny. In surficial and sedimentary environments, U could occur in solution in three oxidation states: U(IV), U(V) and U(VI). In natural aqueous solutions, U is transported as the uranyl ion (UO_2^{2+}) which form complexes with carbonate, phosphate, chloride, sulfate, ... In many deposits, U is mineralogically present as pitchblende or uraninite where it mainly occurs in the tetravalent state. Therefore, a reduction is necessary for pitchblende or uraninite deposition which could be related to iron, sulfur or organic compounds or hydrogen. In surficial and sedimentary environments, the association with organic matter and the absorption process play an important role in the genesis of a deposit. Furthermore, in some surficial deposits, the U concentration results from deposition of U(VI)-

minerals such as, for example, carnotite in calcrete deposits. In this latter case, no reduction of U is necessary for deposition.

Table 1: Some characteristics of U deposit types in surficial and sedimentary environments, including unconformity type

Deposit type	Host Rocks	U-Mineralogy	Remarks	Example deposits
Quartz-pebble conglomerate	Conglomerate Sandstone	Detrital uraninite, uranothorite, brannerite	Limited to ~2.8 to 2.2 b.y.	Witwatersrand (S. Africa) Blind-River Elliot Lake (Ontario, Canada)
Calcrete	Nonpedogenic calcrete	Carnotite	Young (Tertiary) rich in vanadium	Yeelirrie (Australia)
Black shale	Marine carbonaceous shale	U-organic materials	Disseminated	Ranstad (Sweden)
Phosphorite	Marine phosphorite	Uraniferous carbonate apatite	Reworked pebble phosphorite higher grade (~0.02 %)	Morocco Phosphoria Fm and Bone Valley Fm (USA)
Sandstone tabular			Rich in organics	Ambrosia Lake district (USA) Grants (USA) Müllersbach (RFA)
Sandstone roll	Fluvial sandstone and arkose	Pitchblende coffinite	Zonality in V, Se, U, Mo	Wyoming (USA) Texas (USA)
Sandstone tectono-lithologic			Control by tectonic features and lithology	Akouta (Niger) Lodève (France) Oklo (Gabon)
Breccia pipe	Fluvial sandstone	Pitchblende Coffinite		Arizona (USA)
Spatially unconformity related	Proterozoic metasediments ± unconformably overlying fluvial sandstone	Pitchblende		Cluff Lake, Rabbit Lake, Key Lake, Collins Bay Cigar Lake, Saskatchewan Ranger Jabiluka, Nabarlek, Koongarra (Northern Territory Australia)

SOURCE OF URANIUM

The determination of the source of U that was deposited in many deposits is often extremely difficult to assess other than speculatively. However, the source of U for very young U deposits can be addressed directly by considering the natural $^{234}\text{U}/^{238}\text{U}$ disequilibrium which exists in most waters and rocks (Cherdyntsev, 1971). In addition, an indirect method has been proposed by using U-Th-Pb isotope systematics (Rosholt and Bartel, 1969). Both these methods are considered below.

Uranium Disequilibrium and the U-Th-Pb Method

$^{234}\text{U}/^{238}\text{U}$ ratio in recent U-enriched sediments

Compared to other marine sediments, phosphorites always have high U contents, averaging 120 $\mu\text{g/g}$ (Altschuler et al., 1958).

Since phosphorites forming today are known and the $^{234}\text{U}/^{238}\text{U}$ activity ratio is constant in seawater, if the source of U is seawater it can immediately be recognized. Phosphorite nodules off the coast of Peru, Chile and Namibia are associated with upwelling of organic-rich waters having $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios close to that of modern sea water. However, some $^{234}\text{U}/^{238}\text{U}$ activity ratios obtained on these nodules are slightly higher than that of modern sea water, indicating that at least one other source is present. It has been suggested that these nodules were formed in organic-rich anoxic sediments, so that U derived from pore water rather than from open sea water directly (Veeh and Burnett, 1982). The slightly higher $^{234}\text{U}/^{238}\text{U}$ activity ratios result from the back diffusion of ^{234}U lost from previously formed phosphorite nodules (Veeh and Burnett, 1982) or from recoil. Since a marine setting is the only environment where the $^{234}\text{U}/^{238}\text{U}$ activity ratio is constant, the use of this ratio is very difficult elsewhere.

U-Th-Pb isotope systematics on potential source-rock

There is general agreement that, in the U-Pb system, the two radioactive parents (^{235}U and ^{238}U) and the two radiogenic stable daughters (^{207}Pb and ^{206}Pb) show similar behavior during alteration processes; the equilibrium between ^{232}Th , which is considered immobile, and its radiogenic daughter ^{208}Pb is used as an indicator of U or Pb mobilization. The percentage of U gain or loss is determined by comparing the U content in the sample with the U content calculated from the uranogenic Pb. The age of the disturbance can also be constrained on a concordia diagram based on this technique (Fig. 1). Stuckless (1987) discussed the limitation of this approach. Due to experimental limitations (analytical precision), the use of this approach requires a high initial U to Pb ratio as well as a high radiogenic Pb to common Pb ratio.

A good example for the study of the origin of U is that made by Stuckless and Nkomo (1978) in Wyoming where a volcanic source and/or a granitic source could be considered for the genesis of roll type U deposits. The authors showed that the granite from the Granite Mountains lost large amounts of U during Tertiary times (Fig. 1). As this age is in agreement with the age of ore

deposition at 28-35 Ma (Ludwig, 1978, 1979), this event was interpreted as leaching of U in granite and deposition in sediments. However, the isotopic investigation of tuffaceous strata close to the deposits (Nash et al., 1981) was not achieved in spite of the fact that these tuffs could be an U source as well.

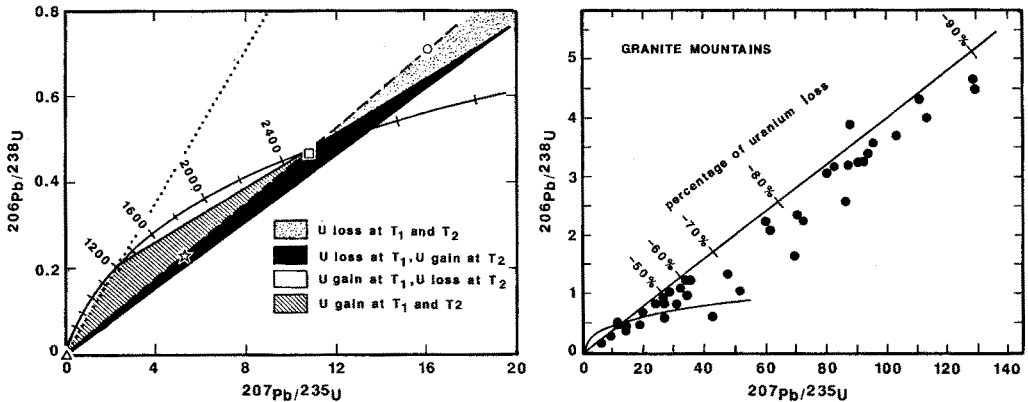


Figure 1: Determination of U loss and gain in a Concordia diagram (after Stuckless, 1987). A: Concordia diagram for a system that formed at 2500 Ma, remained closed until 1250 Ma ago (T₁) and was disturbed again very recently (T₂). Square = sample showing no disturbance; star = sample which lost 50% of its radiogenic Pb or gained 100% U at T₂; triangle = loss of Pb at T₂. B: Concordia diagram for samples of the Lankin Dome granite, Granite Mountains, Wyoming. A reference cord from 0 through the 2600 Ma equilibrium point on the concordia is marked with relative percentage of U loss, assuming closed-system behavior from 2600 Ma until 30 Ma ago

As discussed before, the applicability of U-Th-Pb systematics on potential U source-rocks is favorable when the radiogenic to common Pb ratio is high and the error introduced in the calculation of radiogenic Pb is small. This is especially the case for Precambrian rocks. Although a two event history is the best case, Stuckless and Troeng (1984) have shown that a good set of interpretations could be derived from a three-stage system.

Other Radiogenic Elements (Sr, Nd, Pb, Hf, Os)

The source of other isotopic tracers related to U deposition such as Sr, Nd, Hf, Os or Pb in young deposits or in situations where a precise age correction is possible, is a completely open research field which could have, at least theoretically, great

influence on the discrimination of source-rocks. However, during leaching of the source-rock, differences between the whole-rock and the fluid isotopic ratio could be induced by a mineralogical effect. For example if a mineral such as a plagioclase, which contains Sr without Rb, is leached the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the fluid will be lower than the Rb-rich source-rock (Turpin et al., 1990, Franklyn et al., 1991). The reader should also bear in mind that all the elements present in a deposit do not necessarily have to come from the same source-rock. Presently, the only data of this type, available for sedimentary-related U-deposits, are Sr and Nd isotopic ratios (Maas, 1989; Pagel et al., in press) and initial radiogenic Pb (Ludwig et al., 1985; Lancelot and Vella, 1989) on pitchblende. Ludwig et al. (1985) have shown how to decipher the initial radiogenic Pb isotope ratio in order to determine the age and chemical composition of the source of the initial Pb.

The distribution of REE in pitchblende is homogeneous as it is observed in favorable cases by electron microprobe studies. Although, Nd incorporation during its crystallization is my favor hypothesis. Fryer and Taylor (1984, 1987) and Pagel et al. (1987) have analyzed pitchblendes from many deposits and showed that the REE pattern depends on the type of U deposit. For example, the REE chondrite normalized pattern for pitchblende from unconformity-type deposits from Canada and Australia have a bell-shaped distribution with high contents in intermediate REE. On the other hand, the origin of Sr present in pitchblende is not clear while the Rb/Sr is always very low: from 0.003 to 0.105 in the Cigar Lake (Saskatchewan, Canada) pitchblende (Pagel et al., in press). Zirconium is sometimes present in significant amounts in pitchblende from sedimentary U deposits (Forbes et al., 1984) and Hf is also commonly present.

$^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

Sm-Nd isotopic studies were made on the unconformity-type U deposits of Collins Bay in Saskatchewan (Canada) by Fryer and Taylor (1984) and of Nabarlek and Jabiluka in Northern Territory, Australia by Maas (1989). The important study by Maas (1989) on the Nabarlek, Jabiluka, Koongarra and Ranger deposits (Northern Territory, Australia) shows that, on the basis of the Nd and Sr

data, important constraints can be placed on the genesis of these deposits (Fig. 2). Maas (1989) argued that the covariation of U and REE found in the Alligators Rivers U ores suggests simultaneous transportation by the ore-forming solution. This conclusion is strongly supported by the fact that all the pitchblende crystals from the unconformity-type U deposits have the same REE pattern.

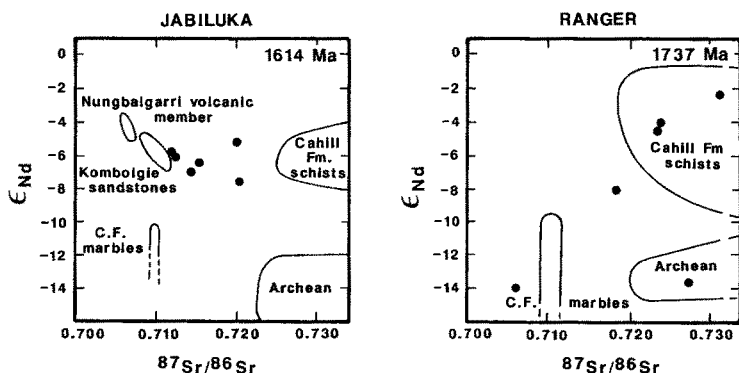


Figure 2: Initial Nd and Sr isotope ratios for primary uraninite from Jabiluka (A) and Ranger (B), Northern Territory, Australia compared with the time-corrected values for potential Nd-Sr source rocks (after Maas, 1989). For Jabiluka, the ore samples lie between the fields of Kombolgie sandstone (and the Nungbalgarri Volcanic Member) and the Cahill Formation schists. For Ranger, five of the six ore samples form a linear array between a carbonate-type and a Cahill schist-type component

A central issue to all these studies on unconformity type U deposits is knowing if the U is derived from the sedimentary cover or if it has been leached from the metamorphic and granitic basement rocks. Late Archean gneisses and the host metamorphic Cahill Formation are the most likely Nd-Sr source-rocks for the Ranger deposit which formed before the deposition of sandstones (1737 ± 20 Ma, Ludwig et al., 1987) if we accept the Rb-Sr age (1648 ± 29 Ma, Page et al, 1980) on syn-Kombolgie Nungbalgarri Volcanics. The Nd and Sr isotope data on the Jabiluka and Nabarlek deposits, formed after the deposition of sandstones, are compatible with the ore fluid acquiring its Nd and Sr isotope signature through mixing of Nd and Sr derived from the Kombolgie sandstones and the metamorphic Cahill Formation (Fig. 2). Despite comparable host-rocks, ore controls and wall-rock alteration from

the Jabiluka and Nabarkek deposits, it is not clear why the Ranger deposit could have a different history.

In Saskatchewan, Pagel et al. (in press) showed that $^{87}\text{Sr}/^{86}\text{Sr}$ in pitchblende is more comparable to that of the Athabasca sandstones, the interbedded volcanics and the upper part of the weathering profile beneath the Athabasca sandstones than to that of the basement at the time of U deposition (Fig. 3).

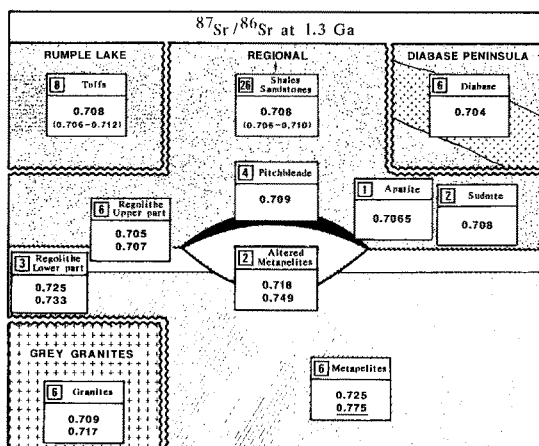


Figure 3: Calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at 1.3 Ga for different fresh or altered rocks, alteration minerals and pitchblende in the Cigar Lake area and its regional environment (after Pagel et al., submitted)

The possible leaching of U preconcentration in the basement has been excluded by Fryer and Taylor (1987) for Saskatchewan and by Maas (1989) for Australia. They have noted that if recycled Nd from protores is considered, much higher $^{143}\text{Nd}/^{144}\text{Nd}$ should be expected. This conclusion is ambiguous because it is conceivable that U was leached from the basement rock and since REE have solubilities much more lower than that of U, the REE content of the fluid is dominated by the U-carrying fluid which is derived from sedimentary formation waters (Pagel et al., 1980).

The above approach is difficult to apply to U deposits in sedimentary environments because the U-minerals are generally very fine-grained. The Akouta deposit (Niger) is, however, an interesting exception because centimetric lenses of pitchblende

are spatially related to the bottom- and for-sets of the sandstone units. The Sm-Nd isotopic data are scattered (Fig. 4) and no age can be derived from the results (Turpin et al., 1991). If the initial Nd ratio is recalculated for the assumed mineralization age, 200 Ma, and if REE patterns are considered, the REE must have been derived either from different sources or from a heterogeneous source without achievement of REE homogeneity in the ore fluid.

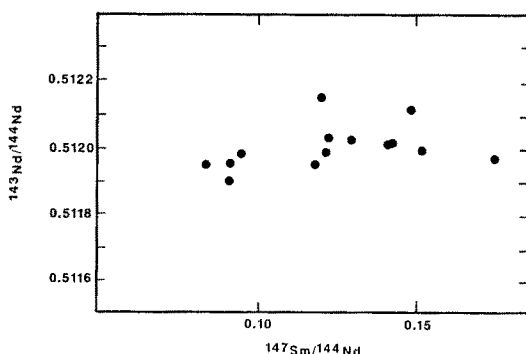


Figure 4: Sm-Nd variation for pitchblende in the Akouta deposit, Niger (after Turpin et al., 1991)

The use of isotopic tracers on minerals associated with pitchblende opens up a wide field of research possibilities; for example, $^{87}\text{Sr}/^{86}\text{Sr}$ in carbonates, barytes, hydrous aluminous phosphate, apatite, and $^{143}\text{Nd}/^{144}\text{Nd}$ in fluorite, clays and other minerals. The development of microanalytical techniques such as the ion microprobe, nuclear microprobe and laser ICP-MS show considerable potential in aiding the deciphering of the multistage development of the formation of a U deposit as well as identifying the possible different sources origin of the elements present in the mineralized zone.

Initial $^{207}\text{Pb}/^{206}\text{Pb}$ in uranium minerals

The existence of a preconcentration event is very difficult to assess in sediment-hosted U deposits, even if the U-Pb data are consistent with the mineralization being epigenetic. If a U preconcentration does exist, the initial $^{207}\text{Pb}/^{206}\text{Pb}$ would be radiogenic and $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ would be significantly higher than the common Pb ratio as well. Such a preconcentration has been observed by Lancelot and Vella (1989) in the Rabejac

deposit (Lodève Basin, France), this was based on an original interpretation presented on figure 5. This deposit has an age of 183 ± 4 Ma but is emplaced in a Permian formation. The initial $^{207}\text{Pb}/^{206}\text{Pb}$ is 0.296 whereas the accepted common Pb ratio determined on galena is 0.8573. These authors modelled the evolution of the U-Pb system assuming a preconcentration event during the Permian, its remobilization at 183 Ma and assuming a galena as sample representative of the regional common Pb of the Permian age. They found μ values ($^{238}\text{U}/^{204}\text{Pb}$)_{present} around 3000 to 4800. This study is a good illustration of how Pb isotopes can be useful in deciphering the complex evolution of U concentrations where fluid circulation occurred on more than a single occasion.

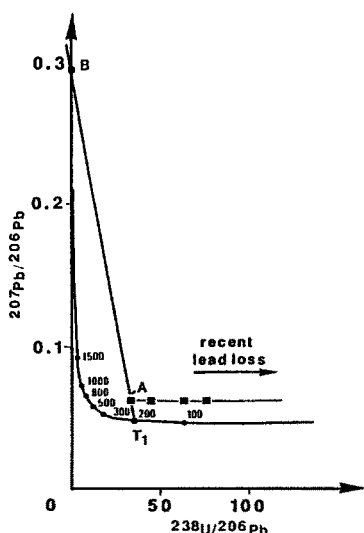


Figure 5: Determination of the initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in pitchblende in a Terra-Wasserburg diagram (after Lancelot and Vella, 1988). Sample A is supposed to have evolved in a closed system since the time of deposition (T_1). The initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratio is determined at point B

Other potential tracers

Among other possible isotopic tracers which could be used are the $^{176}\text{Hf}/^{177}\text{Hf}$, $^{187}\text{Os}/^{186}\text{Os}$, and $^{11}\text{B}/^{10}\text{B}$ ratios, but no data are yet available for U deposits. Despite the presence of significant amounts of Hf in some U minerals, the use of the $^{176}\text{Hf}/^{177}\text{Hf}$ is limited by (1) the difficulty in analysing Hf by mass spectrometry due to a very low ionization yield, however combination of

conventional Hf extraction and SIMS type mass spectrometry has considerably lower the analyzed amount and (2) the small variation of the isotopic ratio. In contrast, the $^{187}\text{O}/^{186}\text{Os}$ ratio varies widely and with improved techniques for chemically extracting Os from rocks and the use of the ion microprobe very small quantities of Os can be detected. The use of stable B isotopes may provide insight into the origin of tourmaline associated with some U ore deposits, especially those which are spatially unconformity-related in Saskatchewan (Canada) and Northern Territory (Australia). It could result from the remobilization of preexisting tourmaline in the basement, related to evaporites or granitic rocks, or it could be related to some dissolved evaporites previously present in the sedimentary cover.

TRACING THE ORIGIN OF MINERALIZING FLUIDS

Stable isotope geochemistry gives valuable answers to questions about the origin of the mineralizing fluid and the processes of U ore deposition. Excellent reviews by Taylor (1974), Ohmoto (1986) and Sheppard (1986) on the general principles of applying stable isotopes to ore genesis are available. D/H and $^{18}\text{O}/^{16}\text{O}$ can potentially be used to determine the type of aqueous solutions: meteoric, connate, formation water, etc. The isotopic composition of a fluid can be determined directly from fluid inclusions or indirectly from the mineral, assuming that the mineral- H_2O D/H and $^{18}\text{O}/^{16}\text{O}$ fractionation factors and temperature are well constrained. Pagel et al. (1980) have directly obtained δD values on fluid inclusions in gangue minerals (quartz and dolomite) from the Rabbit Lake U-deposit. Few data have been published on O isotope ratios in pitchblende and uraninite (eg., Hoekstra and Katz, 1956; Hattori et al., 1978). These minerals are depleted in ^{18}O with $\delta^{18}\text{O}$ as low as -30 per mil (SMOW). However, pitchblende and uraninite crystals have been oxidized after deposition. Therefore, the significance of the O isotope data with respect to deposition is unclear due to the probability of isotopic exchange reactions. If the O isotope fractionation factor

between U dioxide and water calculated by Hattori and Halas (1982) is correct, the $\delta^{18}\text{O}$ of water is negative in most cases. This indicates the involvement of meteoric waters. The determination of C and S isotope compositions of fluids is often difficult because they can more rarely be measured directly on the fluid and isotopic equilibria have not necessarily been established between the fluid species or between the fluid species and the precipitating minerals. Among important processes which can be deciphered by C and S isotopes are the involvement of an organic component in the fluids or the involvement of bacterial or fermentation processes. Under certain conditions, pH and O fugacity can be deduced from isotope geochemistry of the fluid. The major causes for C and S isotopic fractionations in nature are redox reactions involving the isotopic species (e.g. Robinson and Ohmoto, 1973; Ohmoto, 1986), which are very important processes in U ore genesis. Several applications of stable isotope geochemistry are presented below.

Circulation of Sedimentary Formation Waters in Basement Rocks

The formation of U veins in basement rocks is often attributed to the involvement of a fluid derived from sedimentary formations (Turpin, 1984, Turpin et al., 1990; Negga et al., 1986). For the La Lauzière massif (Alps, France), Negga et al. (1986) proposed that U was leached from the basement by meteoric waters and deposition occurred as a response to mixing with more reducing waters from underlying sediments (Fig. 6). The deep sediment-derived waters were confirmed from fluid inclusion data from Mullis and Stalder (1987) who showed that post-Carboniferous sedimentary formation waters can circulate as deep as 1500 m in basement rocks. Some uranium occurrences are known in this context.

In Saskatchewan, the setting is simpler since the relationship between the basement and the cover is nearly unchanged. The δD and $\delta^{18}\text{O}$ data on illite and chlorite from the Athabasca sandstones and from altered basement beneath the sedimentary cover (Wallis et al., 1984; Halter et al., 1985, 1987;

Wilson et al., 1987; Wilson and Kyser, 1987; Bray et al., 1988) show that the illite and chlorite minerals were equilibrated with the same fluid at about 200°C. This means in turn that the sheet-minerals associated with the mineralizing event isotopically did equilibrate with the same fluid. Furthermore, all these illites have indistinguishable K-Ar ages (Clauer et al., 1985; Bray et al., 1987), which suggests that the formation waters from the Athabasca sandstones have penetrated the basement and altered it.

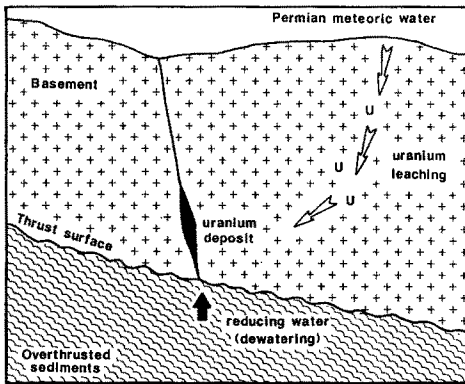


Figure 6: La Lauzière mixing model between Permian oxidized meteoric waters and reducing metamorphic waters (after Negga et al., 1986)

Mineralization Along a Roll Front

Sulfur isotopes have been analyzed in roll-type deposits where negative values become less negative to positive ahead of the roll. Goldhaber et al. (1978) demonstrated a systematic variation of $\delta^{34}\text{S}$ values along the Benavides roll in Texas (Fig. 7) which ranges from -29 per mil to +30 per mil. A two-stage process was proposed: (1) isotopically heavy Fe disulfides ahead of the roll were produced by the introduction of fluids containing dissolved H sulfides derived from underlying oil and gas accumulations and were injected via a fault, (2) invasion by oxygenated U-bearing groundwater creates soluble metastable S by oxidation of S and marcasite precipitation was favored in a low pH zone.

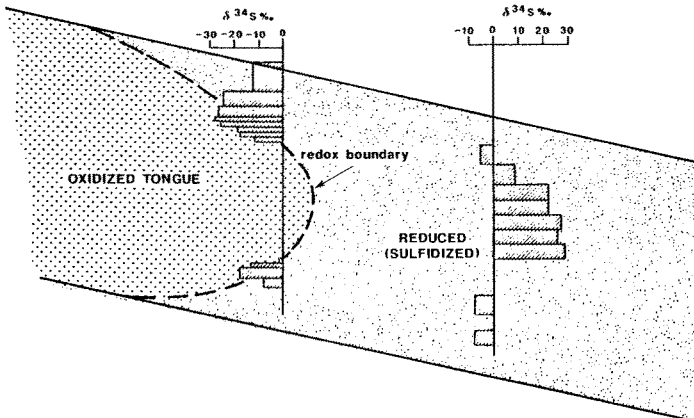


Figure 7: Variation of S isotope ratios along an idealized roll cross-section (after Goldhaber et al., 1978)

Deposition as a Result of Mixtures of Fluids

Goldhaber et al. (1983) have also applied S isotope geochemistry in the Ray Point U-district, south Texas, which is an anomalous area in that it contains FeS_2 minerals in the altered tongue. From S mineralogy and isotope geochemistry, four stages of FeS_2 mineralization are recognized with one pre-ore, another pre-ore to contemporaneous and two post-ore. It is noted that the isotopic composition of the pyrite of stage 3 is similar to that of sour gas in the underlying limestone. The marcasite of stage 4 is related to bacterial activity. Goldhaber et al. (1983) concluded that: "the Ray Point uranium district thus formed and was preserved virtue of its proximity to a zone of interaction of connate brines from depth with shallow meteoric waters".

Involvement of Biogenic Processes

In several deposits of the Grants U Region, isotopically light Fe disulfides suggest that these sulfides were biogenically-derived. During biogenic processes, aqueous sulfide species produced by sulfate-reducing bacteria are enriched in ^{32}S (Thode et al., 1951). For instance, Fishman et al. (1985) have found $\delta^{34}\text{S}$ values between -29 to -42 per mil for ore-stage Fe disulfide

minerals in the Mariano Lake and Ruby 1 deposits, where U is intimately mixed with organics. This favors the introduction of organic matter in sandstones early in the diagenetic history.

DATING THE DEPOSITION AND REMOBILIZATION OF URANIUM DEPOSITS

The age of U deposition can be obtained from radiogenic systems directly if the isotopes considered are present in the U-minerals, or indirectly if they are located in the gangue minerals, whose textural relationships to the U-minerals indicate that they formed at the same time.

In Uranium Minerals

U-Pb and Pb-Pb isotopic ages

Several ways of exploiting the data have been proposed: Concordia diagram ($^{207}\text{Pb}/^{235}\text{U}$ vs. $^{206}\text{Pb}/^{238}\text{U}$ by Wetherill (1956; Fig. 1) or $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ by Tera and Wasserburg (1972; Fig. 5)), U-Pb ($^{235}\text{U}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{238}\text{U}/^{204}\text{Pb}$ vs. $^{236}\text{Pb}/^{204}\text{Pb}$) and Pb-Pb ($^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$) isochrons. In U deposits, different disturbing factors generally have to be taken into account: (a) leaching or diffusion of Pb, (b) presence of common Pb in the mineral structure or as a discrete associated mineral, (c) leakage of intermediate radioisotopes such as Ra or Rn by diffusion or recoil, (d) U leaching in oxidizing environments, (e) an initial disequilibrium in the U-Pb system in young deposits, and (f) recent alteration of pitchblende and formation of a U(VI) mineral. It is generally possible to obtain the age for the formation of a hexavalent mineral (low intercept in a Concordia diagram) and the age of the primary pitchblende (upper intercept in a Concordia diagram). A specific methodology and approach is, therefore, required for U-Pb dating of U minerals

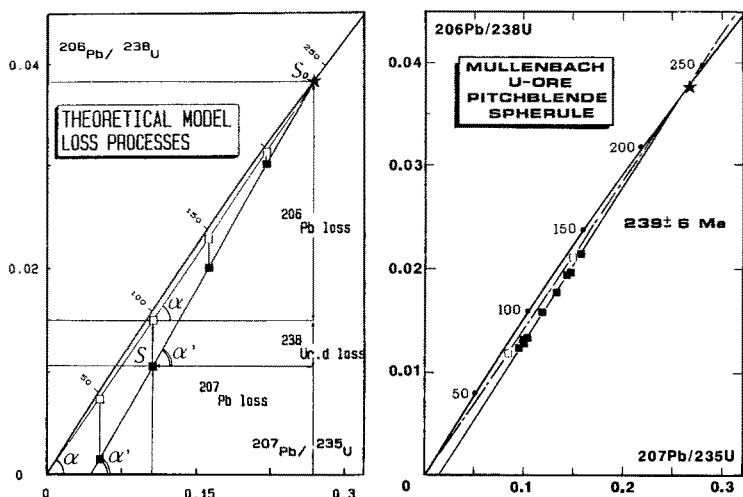


Figure 8: Interpretation of the loss of a ^{238}U radioisotope daughter in a Concordia diagram and its application to the Müllenbach U-deposit (after Holliger et al., 1989). A: Diffusion process in a Concordia diagram for four hypothetical samples. S_0 is the primary age of the U mineralization. The Pb diffusion loss leads to the discordia $0-S_0$. The combined Pb diffusion loss and ^{222}Rn leakage Pb to another isochron at the right. S represents a sample where ^{238}U r.d. loss has occurred. B: Concordia plot for the Müllenbach pitchblende. Nine samples define a best-fit line at $239 \pm 6 \text{ Ma}$. The two other points are located on the line $0-240 \text{ Ma}$

Many specific guide lines are available for these isotopic determinations. In summary: (1) a preliminary investigation by electron microprobe can distinguish the different generations of U minerals which may exist in the same specimen, and in some favorable cases give an idea of the ages. This approach is especially interesting during prospection. Such chemical ages must, however, always be checked by isotopic analyses. (2) The size of the sample is an important parameter to consider. Ludwig et al. (1981) have shown that for the Midnite Mine, Washington, in samples $>10 \text{ cm}$ the system is closed for $^{235}\text{U}/^{207}\text{Pb}$ but not for $^{238}\text{U}/^{206}\text{Pb}$ (leakage of daughter elements), whereas for samples $<1 \text{ mm}$ there is migration of Pb and radioactive daughters of ^{238}U . (3) Until now, dating has been mainly done by thermal ionization mass spectrometry (TIMS) after chemical treatment. But recent development in *in situ* secondary ion mass spectrometry (SIMS) permits U-Pb isotope analysis on a few micron sample (Holliger,

1988). The relative yields of the two elements has been constrained by a well-known, homogeneous and concordant uraninite standard from Zambia. Dating minerals is possible on a single polished section, even if it indicates a multiphase paragenesis. Development of this technique is certainly very important for a better understanding of the mobility of Pb, U and the radioactive daughters of ^{238}U and to select samples with a high $^{206}\text{Pb}/^{204}\text{Pb}$ ratio. (4) The correction for common Pb is one of the most difficult tasks when $^{206}\text{Pb}/^{204}\text{Pb}$ is low because of its effect on the calculated age. Several options exist: (a) to calculate the Pb from the model of Stacey and Kramers (1975), (b) to determine the Pb composition in an associated Pb-bearing U-free mineral (galena, pyrite, K-feldspar), (c) to graphically obtain the value using the Pb-Pb isochron. Wendt (1984) has proposed a three-dimensional discordia plane method to yield the concordia intersection ages in the case of a two-stage evolution history without the necessity for assumptions regarding the isotopic composition of the common Pb present in the samples. (5) The leakage of radioactive daughters of ^{238}U is very important in sediment-hosted U deposits (Fig 8) as demonstrated by Ludwig (1978, 1979), Lancelot et al. (1984) and Holliger et al. (1989). The ^{226}Ra and ^{222}Rn are generally the most frequently lost daughters due to recoil and Ra leaching in reduced environment. A Ra emanation from pitchblende can be very significant and variable (Giletti and Kulp, 1955). An example of leakage of radioactive daughter(s) is presented in figure 8 as illustrated by the Müllenbach U ore (Holliger et al., 1989). (6) The effect of initial disequilibrium has to be taken into account for young U mineralization. Wendt and Carl (1985) have shown that the application of a modified Tera-Wasserburg U/Pb concordia plot could overcome this difficulty.

The U-series ages

From $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios in recent formed U-minerals (<350 ka), it is possible to derive an age, assuming no ^{230}Th was incorporated during mineral formation. This latter assumption is supported by the absence of ^{232}Th in the mineral. The equation is:

$$^{230}\text{Th}/^{234}\text{U} = \frac{1 - e^{-\lambda_{230}t}}{^{234}\text{U}/^{238}\text{U}} + \left(1 - \frac{1}{^{234}\text{U}/^{238}\text{U}}\right) \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left(1 - e^{-(\lambda_{230} - \lambda_{234})t}\right)$$

A data set obtained by Kaufman and Ku (1989) on carnotites from Israel suggests that, under some circumstances, an age can be obtained. Wendt and Carl (1985) have shown that the $^{230}\text{Th}/^{234}\text{U}$ disequilibrium age (132 ± 4 ka) obtained on torbernite from Höhenstein (northern Bavaria) is comparable to the U/Pb age calculated by the modified Tera-Waserburg concordia plot of 137 ± 11 ka. However, if this type of hexavalent U mineral remains in water flow, it acts as a chemically open system, as demonstrated in the Yeeliree deposit (Lively et al., 1979; Airey and Roman, 1981).

Spontaneous fission of ^{238}U

This is an open field of research. Chronologic data can be obtained either by analyzing the fission products, Xe, Kr or Ru for example, or the tracks created in minerals by the fission process. The value of the spontaneous fission decay constant is still under debate, both $8.46 \cdot 10^{-17} \text{ y}^{-1}$ (Galliker et al., 1970) and $7.03 \cdot 10^{-17} \text{ y}^{-1}$ (Roberts et al., 1968) are commonly used.

U-Xe and U-Kr

Xe_s ($^{136}, ^{134}, ^{131}\text{Xe}$) and Kr_s ($^{87}, ^{84}, ^{83}\text{Kr}$) are produced by the spontaneous fission of ^{238}U . The age is given by the following equation:

$$t_{\text{U-Xe}} = \frac{1}{\lambda_{\alpha}} \ln \left(\frac{\text{Xe}_s}{^{238}\text{U}} * \frac{\lambda_{\alpha}}{\lambda_s * \gamma_{\text{Xe}_s}} + 1 \right)$$

where $t_{\text{U-Xe}}$ is the age of the sample, Xe_s is the atomic concentration of Xe produced by spontaneous fission of ^{238}U , ^{238}U is the atomic concentration of ^{238}U , λ_{α} is the decay constant of ^{238}U , λ_s is the spontaneous fission decay constant of ^{238}U , and γ_{Xe_s} is the Xe_s fractional yield produced by spontaneous fission.

Recent developments in mass spectrometry have permitted Eikenberg et al. (1989) to date uraniferous minerals, especially pitchblende, by the U-Xe and U-Kr methods. The preliminary results

show that if pitchblende has recrystallized, the U-Xe and U-Kr systems date the recrystallization event. On the other hand, it has been shown that the U-Xe and U-Kr systems can survive greenschist facies metamorphism. In the Alps, concordant U-Xe and U-Kr ages on coarse pitchblende have been obtained which correspond also to concordant U-Pb ages of around 250 Ma. Fine grained pitchblende have U-Xe and U-Kr ages which agree with the lower intercept age of about 40 Ma on the U-Pb discordia. This method is very promising and could be applied to other U-rich mineral, such as monazite. However, in many cases U-Xe ages establish only lower limits because of natural Xe losses.

Xe₃-Xe_n spectrum technique

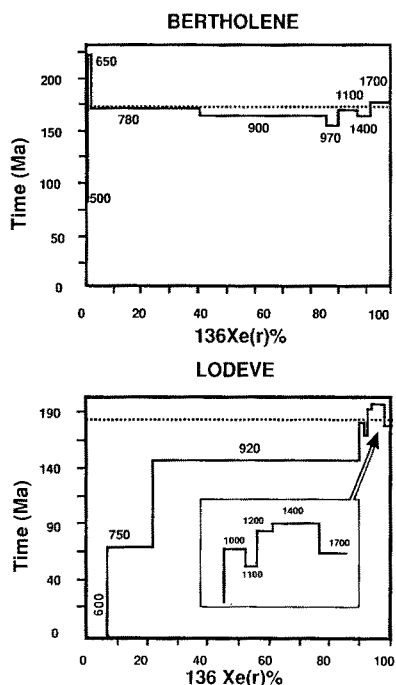


Figure 9: Xe₃-Xe_n spectrum for pitchblende from France (after data from Lévêque and Meshick, 1991). The pattern of apparent age vs. the percentage of radiogenic ¹³⁶Xe is shown, the temperature (in °C) of gas release is indicated and the Pb-Pb values are given by the dotted line. For Bertholène, a plateau is obtained with six heating steps (167 ± 11 Ma), whereas an anomalous Xe₃-Xe_n ratio could be observed at 650°C. For Lodève, the plateau could be drawn with the flat five heating steps, which represent only 10% of the total gas release

To avoid the problem of natural Xe losses, Shukolyukov and Meshick (1987) and L  v  que and Meshick (1991) have applied the very promising Xe_s - Xe_n spectrum technique (Shukolyukov et al., 1974) to pitchblendes, where Xe_s is the atomic concentration of Xe produced by the spontaneous fission of ^{238}U and Xe_n is the atomic concentration of Xe produced in nuclear reactor by induced fission of ^{235}U . In this technique, only the Xe_s/Xe_n ratio is calculated. To overcome the problem of Xe loss, stepwise heating is performed: the Xe_s/Xe_n ratio will increase because of their different origins. At low temperatures, Xe escapes from the most disturbed zones where Xe_s has already escaped from the pitchblende during its geological history whereas the Xe_n escape depends only on the U distribution in the sample. The ratio will stabilize ultimately giving a plateau. The plateau age corresponds to the initial age of the pitchblende when there are distinct peaks of gas release (Fig. 9).

Compared to U-Pb dating by TIMS, Shukolyukov and Meshick (1987) pointed out that the Xe technique is powerful even if the pitchblende is mixed with a common Pb-bearing mineral, such as a sulfide. In this case, the common-Pb correction introduces a large error. The disadvantage of the Xe technique is that it necessitates large grain-size samples, because the range of displacement of fission fragments is about 15 μm . Furthermore, some problems could arise if the sample is not constituted by one generation of pitchblende. It should also be pointed out that not all aspects of the spectrum can be easily explained and that in several cases the Xe age is lower than the U-Pb age, (e.g. Shukolyukov and Meshick, 1987). More work is needed to determine the relation between the escape of Xe and the structure of pitchblende.

U-Ru method

Several Ru isotopes (^{99}Ru , ^{101}Ru , ^{102}Ru , ^{104}Ru) are derived from the spontaneous fission of ^{238}U . It is thus possible to determine an age using an equation similar to the one presented for U-Xe. If it is a closed system, this age is the age of mineral deposition. Preliminary data obtained on deposits from Africa,

Australia, Brazil and Canada show that the ages are higher than the U-lead ages (Maeck et al, 1978).

On Gangue Minerals

The use of spontaneous fission tracks produced by ^{238}U has a high potential for dating U-ore deposition. A pioneer study published by Cunningham et al. (1982) used quartz in contact with pitchblende as an external detector in the Marysville, Utah, volcanic field. This technique could be applied to sediment-hosted U deposits. However, it is time-consuming because it requires a two-stage replica of the etched quartz surface by methyl acetate and Pt-C, a correction for the inclination of the surface with reference to the C axis, and an extrapolation of the fission tracks densities from the interior of the quartz grain to the contact with the pitchblende. Furthermore, it is of limited use in attempts to determine age of mineralization in many, especially old, deposits.

The use of K-Ar systematics on clay minerals associated with U ores has been applied extensively in France (Bonhomme, 1982). Illite concentrates were principally analyzed, but some recent data on corrensite-rich fractions were also successful (Turpin et al., 1991). The application of the K-Ar method requires careful preparation of the samples. It is necessary to obtain a representative fraction of the clay. It is therefore essential to characterize properly the studied fractions. An extensive review of these problems is presented in a companion paper by Clauer and Chaudhuri (this volume). In sedimentary rocks, Brockamp et al. (1987) have shown that individual K-Ar ages of sedimentary clay fractions associated with U deposits are size-dependent and that pure authigenic fractions are only present in the smallest size fractions. The problem is apparently not important in veins, as Bonhomme et al. (1987) did not observe a correlation between the age and size of the analyzed fractions. In several cases where good agreement has been obtained between U-Pb ages and K-Ar ages (Table 2). This implies that despite their small size the clay minerals retain their argon. However, we will see later that this

is not always the case and that strong disturbances of the K-Ar system have been observed in illites from several U deposits (Wilson et al., 1987, Halter et al., 1987). Furthermore, it should be emphasized that in a multistage ore deposit, it is always difficult to correlate the K-Ar age with the mineralization stage.

Table 2: Comparison between Pb-Pb, K-Ar and Xe-Xe ages obtained on the Rabejac (Lodève) and Bertholène deposits (France)

Deposit	Pb-Pb age on pitchblende	K-Ar age on clays	Xe-Xe age on pitchblende
Rabejac	183±4 Ma ¹	182-174 Ma ² illite-chlorite	182±13 Ma ³
Bertholène	173±9 Ma ⁴	170-175 Ma ⁵ illite-smectite	167±11 Ma ³

1 Lancelot and Vella, 1989

2 Bonhomme et al, 1987 (the location of the studied deposit in the Lodève basin is not specified)

3 Levêque et Meshick, 1991

4 Lévêque et al, 1988

5 Schmitt et al, 1984

Dating K-bearing minerals has also been done by laser probe $^{40}\text{Ar}/^{39}\text{Ar}$ method. Illites from the unconformity-type deposits from Saskatchewan (Bell, 1985, Bray et al., 1987) were analyzed. This aspect is also discussed in detail by Clauer and Chauduri elsewhere in this volume. The stepwise-heating technique may also be utilized on U-deposits where secondary K-feldspar is present in the mineralized zone or where several generations of minerals are present.

In the alteration halos of U deposits there are often clay minerals (chlorite, illite,...), which may be appropriate candidates for Rb-Sr dating. If a situation is considered where all the U ore has been remobilized, it is possible that the clay minerals could survive this disturbance of the U-Pb system. Lee and Brookins (1978) and Brookins (1980) have presented Rb-Sr data on clays associated with barren and mineralized samples in the Ambrosia Lake and Smith Lake districts (San Juan basin, New Mexico), which contain peneconcordant ore-bodies with abundant migrated organic material. For ore-stage chlorites, Brookins determined an age of 139 ± 24 Ma. This age is in accordance with

the results of U-Pb data modelling on primary ore which has a minimum age of about 130 Ma (Ludwig et al., 1984). These combined data show that an early deposition of U has occurred in the Morrison formation.

In the unconformity-type U deposits from Australia, the Rb-Sr age of illites associated with U mineralization is 1.7 Ga (Page et al., 1980), whereas the U-Pb ages are significantly lower. The Sm-Nd data (Maas, 1989) prove that the alteration minerals record the age of U deposition, whereas the U-Pb system has been perturbed (Table 4).

The Mo sulfides (molybdenite or jordisite, MoS_2) present in U deposits are rich in Re and contain only radiogenic Os (^{187}Os). If the system remained closed, it is only necessary to analyze ^{187}Re and ^{187}Os to obtain an age (Luck and Allègre, 1982). However, in sediment-hosted U deposits, the Mo sulfide is poorly crystallized (jordisite) and Re may have been leached out. However, Ravizza and Turekian (1989) have successfully determined the depositional age of black shales despite some post depositional mobilization of Re and/or Os on a small spatial scale.

The La-Ba system (Nakai et al., 1986) may be used to date REE-rich minerals, such as monazite and florencite which are sometimes associated with U-minerals.

Comparison of Ages Obtained by Different Techniques

The ages obtained with the various chronometers are not always the same. This could reflect the contrasted geochemical behavior of different chronometric systems during remobilization processes. A comparison among U-Pb and U-Xe and U-Kr data by Einkenberget al. (1989) has shown four possibilities, one of which has not been observed in nature (Table 3). They point out that fission gas ages are necessary to interpret ambiguous discordant U-Pb data from pitchblende, especially if it contains excess radiogenic Pb derived from a former mineralization event. Many data have been obtained by U-Pb, Sm-Nd, Rb-Sr and K-Ar on the

unconformity type deposits from Saskatchewan (Canada) and the Pine Creek Geosyncline (Australia) (Table 4). The U-Pb ages can be, in some cases, significantly younger than the ages obtained by the other methods. The Sm-Nd ages from Nabarlek, Jabiluka II and Kongarra are similar, 1600-1650 Ma, while the U-Pb ages range from 900 to 1437 Ma. In the Cluff D deposit (Carswell structure, Saskatchewan, Canada), the mean K-Ar age on illite is significantly older, 1293 ± 36 Ma, than U-Pb ages obtained on uraninite, 1150 ± 25 Ma, but the reverse is also known. In the Müllenbach U deposit (FRG), the upper intercept in the Concordia diagram yields an age of 239 ± 6 Ma (Holliger et al, 1989) while the K-Ar age on illite is 170 Ma (Brockamp et al., 1987).

Table 3: Systematics between the U-Xe-Kr-Pb system (from Eikenberg et al., 1989)

Case	U/Xe - U/Kr	U-Pb	Significance
1	concordant	concordant	crystallization age
2	concordant	discordant	recrystallization age or mixing age
3	discordant	discordant	loss of daughter products
4	discordant	concordant	not yet observed

These discrepancies between the different chronometers indicate that it is not sufficient to use only one chronometer. More confidence in the results and interpretations can be obtained by using several different systems. Certain trends during remobilization can be defined: (1) U minerals may or may not contain radiogenic Nd and Pb. This will depend on the distance of migration or on geochemical factors, (2) there could be a complete resetting of the U-Pb system without disturbing the K-Ar system in the gangue minerals, especially illite, and (3) a thermal event could reset the K-Ar system without resetting the U-Pb chronometer and the U-Xe and U-Kr systems. For persons who are not familiar with isotopic geochemistry, it should be underlined that it is important to differentiate the given confidence interval on the age, which integrates the analytical error and the natural variation between the analysed samples, with the "geological"

error because it is not straitforward to know what is the geological significance of this age.

Table 4: Ages obtained on the Jabulika, Nabarlek (Australia) and Cluff D (Canada) ore deposits

Deposit	Dating method	Age	Reference
Jabiluka (Australia)	U-Pb on pitchblende, upper intercept	920 Ma	Hills and Richards, 1976
	U-Pb on pitchblende, upper intercept	1280±100 Ma	Gulson and Mizon, 1980
	U-Pb on ores, upper intercept	1437±40 Ma	Ludwig et al, 1987
	Pb isotopes on barren sulfides, out of the ore	1380±110 Ma	Gulson and Mizon, 1980
	Pb isotopes on barren sulfides in ores	1600±150 Ma	Gulson and Mizon, 1980
	Rb-Sr model ages on hydrothermally altered chlorite schists	1600±80 Ma	Page et al, 1980
	Five resetted samples	900-1260 Ma	Page et al, 1980
	Sm-Nd on ores and uraninite	1614±132 Ma	Maas, 1989
Nabarlek (Australia)	U-Pb on pitchblende, upper intercept	≈900 Ma	Hills and Richards, 1976
	K-Ar ages on sericite	1580-1670 Ma	Page et al, 1980
	Mean Sr ages on sericite	1610±40 Ma	Page et al, 1980
	Sm-Nd on ores and uraninite	1616±50 Ma	Maas, 1989
Cluff D	U-Pb on pitchblende, upper intercept	1150±25 Ma	Bellon et al, 1976
	K-Ar ages on illite	1293±36 Ma	Clauer et al, 1985

Uranium Deposits and Geodynamic Processes

All age data obtained on sediment-hosted U deposits in Europe have shown that there are optimum periods for U mineralization (Fig. 10), and that mineralization can also occur in the basement rocks at the same time. This observation was first published by Bonhomme (1982) and subsequently detailed by many workers (Lancelot et al., 1984; Bouladon and de Graciansky, 1985; Philippe et al., 1987; Lévêque et al., 1988; Holliger et al., 1989; Cathelineau et al., 1990; Pagel, 1990). Four major periods (240 Ma, 170-180 Ma, 100-110 Ma, 20-40 Ma) have been identified in sediment-hosted U deposits which, except for the 240 Ma stage, coincide with remobilization events for U deposits in the basement rocks. These latter U deposits formed mainly during a Permo-Stephanian (290-260 Ma) stage which is associated with brittle deformation related to major shear zone movements (Cathelineau et al., 1990). A large amount of U reserves are located in Permian

formations. However, it should be noted that no U deposits located in Permian sedimentary rocks are known to be of Permian age.

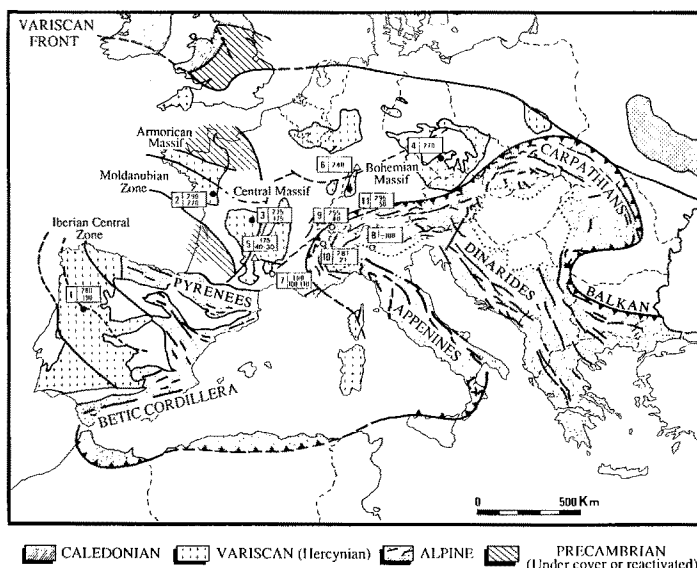


Figure 10: U-Pb and Pb-Pb ages of U deposits in Europe. 1: Urgeirica, Bica and Carrasca, Portugal (Holliger and Pagel, unpublished); 2: Chardon, Escarprière and Commanderie, France (Holliger and Cathelineau, 1986); 3: Margnac, France (Leroy and Holliger, 1984); 4: Příbram, Czechoslovakia (Kolektiv, 1984); 5: Bertholène, France (Lévêque et al., 1988); 6: Müllersbach, Germany (Holliger et al., 1989); 7: Lodève, France (Lancelot et al., 1984; Lancelot and Vella, 1988); 8: Novazza, Italy (Philippe et al., 1987); 9: Valais, Switzerland (Eikenberg et al., 1989); 10: La Lauzière, France (Negga et al., 1986); 11: Krunkelbach, Germany (Hofmann and Eikenberg, 1991)

A late Permian-early Triassic age has been determined by U-Pb for the Müllersbach U deposit (Germany) (Holliger et al., 1989) which is located in Upper Carboniferous sediments underlying sediments of Permian age. Fluid circulation along a vertical redox front (oxidized Permian-reduced Carboniferous) is responsible for the deposition of Zr-bearing pitchblende and associated Cu, V, Se, Ag, Co, Ni, Mo minerals (Pironon, 1986; Pagel and Pironon, 1986).

Jurassic ages have been determined for the Lodève deposits located in Permian formations (Lancelot and Vella, 1989) and the Bertholène deposit (Lévêque et al., 1988) which is spatially

related to an unconformity. The latter is located in an albitized granite underlying the sedimentary cover. Their formation is related to brine circulation during tectonic movements contemporaneous with the opening of the Tethys sea. The Cretaceous age obtained for some Lodève deposits and the Novazza deposit in Italy seems to be a concentrating stage of preexisting U mineralization (Lancelot et al., 1984; Philippe et al., 1987).

The alpine mineralization corresponds to remobilization of pre-existing U mineralization as illustrated by the coffinite in the Bertholène deposit (Lévêque et al., 1988) or small pitchblende spherules admixed to the Permian pitchblende in the Swiss Valais (Eikenberg et al., 1989). Uranium deposits are known in Oligocene sediments, as exemplified by the Coutras deposit (Gironde, France) (Meunier et al., 1990) and the Saint Pierre du Cantal deposit, France, although their ages are not known.

RECONSTRUCTION OF THE THERMAL HISTORY IN MINERALIZED AREAS

The reconstruction of the thermal history in sedimentary basins is often based on organic matter indices, kinetic models, fluid inclusions or clay-crystal chemistry. Pertinent data can also be deduced from fission track annealing in apatite between 70°C and 160°C (Meyer et al., 1989) or from stable isotope geochemistry using equilibrium of coexisting minerals.

The basis of fission track analysis is that, depending on time and temperature, there is an annealing of ^{238}U spontaneous fission tracks. For a degree of annealing, it has been experimentally shown that, for a degree of length reduction, the data could plot on an Arrhenius line and that the activation energy varies, the shortest tracks are more resistant to annealing than the longest ones. Various problems have not been totally overcome to provide an entirely confident application of fission tracks (chemical composition of the mineral, leaching conditions,

rate of dissolution, observation and counting), but this field is extremely promising and, in my opinion, strong efforts must be devoted to this technique. For the study of sedimentary formations, the range of annealing temperatures for apatite is well adapted, whereas for minerals such as sphene or zircon the annealing temperature is higher and is more probably adapted to anchizonal conditions. For example, Koul et al. (1984) have determined a 1420 Ma fission track age on zircon and deduced that the temperature affecting the Kombolgie Formation was at least 175°C. Meyer et al. (1989) presented a study combining fission track, fluid inclusion and organic matter on breccia pipes mineralized in U from Arizona which tend towards 120-140°C.

In U deposits or in their environment, two cogenetic minerals could be found. This allows the possibility of determining a temperature from the stable isotope data. However, uncertainties in the isotopic fractionation factors are quite large for minerals generally occurring in sedimentary environments (illite, chlorite, kaolinite, smectite). Furthermore, the mineral pair of interest must have crystallized in equilibrium with each other which is not always the case in low temperature environments. Also they must have preserved their isotopic composition during subsequent alteration events. Studying the Akouta U deposit, Forbes (1989) has found that the $\delta^{34}\text{S}$ of galena, sphalerite and pyrite have the same values. This is interpreted as resulting from the precipitation of these minerals from a nearly homogeneous fluid without isotopic equilibrium among the minerals at temperatures between 85 and 175°C (from fluid inclusion data) for this deposit.

SPECIFIC BEHAVIOR OF RADIOGENIC AND STABLE ISOTOPES IN AND AROUND URANIUM DEPOSITS

Natural Fission Reactions

Bodu et al. (1972) have identified anomalous isotopic compositions of U in mineralized samples from Oklo (Gabon), and

since, concentration of ^{235}U as low as 0.2% have been found in this area. These anomalies have been explained by natural fission reactions, a process which was confirmed by anomalous isotopic compositions of REE and the presence of isotopes related to fission reactions. Gancarz (1978) has dated the primary U mineralization at Oklo at 2.05 ± 0.03 Ga (upper intercept in the Concordia diagram). This age is comparable, within the limits of uncertainty, to the 1.97 ± 0.06 Ga age determined using fission products (Ruffenach, 1978). Hagemann et al. (1975) determined that the fission reactions have lasted about 600,000 to 800,000 years based on observations of Pu fission systematics and the ^{100}Ru produced by capture from the fission products, ^{99}Tc and ^{99}Ru . It must be stressed that, if all the Oklo zones are considered, the duration is much longer.

The main factors which are necessary for the occurrences of natural fission reactions are: (a) high U content, (b) high concentration of ^{235}U in the U ore at the time required for the process to occur (in the case of Oklo, this concentration was, at 2 Ga, higher than 3% of the total U), (c) presence of water for moderation of the reactions, and (d) absence or scarcity of elements with high neutron capture, such as B or REE.

From O isotope data obtained on chlorite and illite in and around the reactor zones, Gauthier-Lafaye et al. (1989) deduced that there was an increase of temperature from 175°C far from the reactor to $300\text{--}350^\circ\text{C}$ close to the reactor and then a sharp decrease in the reactor to about $125\text{--}150^\circ\text{C}$. They interpret the latter as resulting from the recrystallization of the phyllites during the cooling of the reactor.

Theoretical considerations have shown that such natural fission reactions could have occurred up to 1 Ga (Naudet, 1978) under highly favorable conditions, for example during the formation of the unconformity type U deposits in Saskatchewan (Canada) and Northern Territory (Australia). But search for other natural nuclear fission zones has been unsuccessful. Maas and McCulloch (1990) have shown that there are relatively large Gd and Sm isotopic variations in high-grade ores and uraninites from the

Alligator River Uranium Field. However they conclude that the slow neutron-induced fission of ^{235}U was not adequate for the U ore to become critical. Perhaps this could be due to the high B and/or HREE (high neutron capture cross-sections) contents in these unconformity-type uranium deposits. Some slight $^{235}\text{U}/^{238}\text{U}$ anomalies have been reported on ore from the Colorado Plateau (Cowan and Adler, 1976).

Behavior of Fission Products in Uranium Ores

A lot of research has been devoted to the Oklo U deposit, because it is a long-time-scale for man-made radioactive waste repositories (Loss et al., 1989). It was recognized that several fission products have not been quantitatively retained in the reactors and that some fission-products, such as Mo, Ru, Pd, Ag and Te, have been retained in the peripheral rocks while others, such as Cd, have been totally removed (Curtis et al., 1989; Loss et al., 1989).

The development of accelerator mass spectrometry, which permits the analysis of very small quantities of fission products, has opened up a new field of research which can be applied especially to the study of weathering rates and environmental subjects. Furthermore, these fission products are excellent natural analogue for high-level radioactive waste. ^{129}I is produced in U ores by the spontaneous fission of ^{238}U and the neutron-induced fission of ^{235}U . Fabryka-Martin et al. (1988) have determined $^{129}\text{I}/\text{U}$ in the Koongarra ore (Northern Territory, Australia) and have found that ^{129}I is strongly leached from the ore and that the oxic environment around Kongarra is enriched in ^{129}I . The leakage of ^{129}I from U oxide is the general rule (Boaretto et al., 1990). However, in the case of Yeelirrie (Australia), the present value of the $^{129}\text{I}/^{127}\text{I}$ ratio could be consistent with an age > 1 Ma despite disequilibrium in the ^{238}U series.

^{36}Cl is produced by neutron capture by ^{35}Cl (Kuroda et al., 1957), though $^{36}\text{Cl}/^{35}\text{Cl}$ may monitor the neutron flux in U ores.

Fabryka-Martin et al. (1988) conclude that "in the weathered primary ore body, these flux estimates exceed those predicted for the present day U content of the ore by factors of 2-3, suggesting that the rate of leaching of U in this part of the deposit is rapid relative to the half-life of ^{36}Cl (3.01×10^5 yr)".

Radiation-Related Retrograde Isotope Exchange in Gangue Minerals

As shown previously, stable isotope studies are widely used to characterize the origin of fluids during ore-forming processes and to determine temperatures of isotopic equilibrium. It has been suggested that radiation could induce retrograde isotope exchange (Leventhal and Threlkeld, 1978 ; Dahl et al., 1988) or could favor isotopic exchange (Halter et al., 1987).

Leventhal and Threlkeld's (1978) study of organic matter from the Grants Uranium District, New Mexico and Dahl et al.'s. (1988) study of the Alum shale kerogen demonstrated that the $^{13}\text{C}/^{12}\text{C}$ ratio increases when the U concentration increases. In the Grants, Leventhal and Threlkeld (1978) show that the organic C associated with high grade U ore is heavier ($\delta^{13}\text{C} = -16.9$ to -19.6 per mil) than in the adjacent lower grade samples ($\delta^{13}\text{C} = -22.7$ and -26.4 per mil). The Alum shale results are more surprising because the U content remains under 200 $\mu\text{g/g}$. The $\delta^{13}\text{C}$ varies from -33.5 to -27.4 per mil. This is explained by the generation of isotopically light hydrocarbon gases by irradiation of the organic matter. Some other chemical changes in the kerogen support this hypothesis. However, the decrease of Tmax with increasing U concentration remains unexplained. The variation of $\delta^{13}\text{C}$ with sample age is also puzzling.

In the unconformity-type deposits in Saskatchewan, low δD values have been found chiefly in illite and to a lesser degree in chlorite in the Key Lake, Cluff D and McClean deposits (Wilson et al., 1987 ; Halter et al., 1987 ; Bray et al., 1988). Values as low as -168 per mil have been found while normal values for barren samples are at ~ -50 per mil. Wilson et al. (1987) have proposed that these phyllites exchanged with recent cold meteoric waters.

Halter et al. (1987) obtained data which support this hypothesis, but they proposed that the radiation has facilitated the isotopic exchange and K-Ar exchange of the clays with post-Cretaceous meteoric waters. Halter et al. (1987) and Bray et al. (1988) have found that the δD decreases when the U content increases.

Mineralized bituminens present in U deposits could have low $\delta^{13}C$ values: -43 to -49 per mil at Cluff Lake, Saskatchewan, Canada (Landais and Dereppe, 1985; Leventhal et al., 1987), and -40.8 to -56.5 per mil at Pribram, Czechoslovakia (Kribek, 1989). According to Leventhal et al. (1987), radiation form isotopically light CH_4 . This radiation-induced methane is degraded to solid C which recombine with the solid C and H_2 escape. However, Landais and Dereppe (1985) suggested that these bituminens could be formed by the condensation of light and complex hydrocarbons enriched in ^{12}C isotopes.

CONCLUSION

The study of U deposits in surficial and sedimentary environments has recently opened up a wide field of isotopic research. Isotopic systematics are capable of placing strong constraints on the origin of the U ores. However, the quantification of the chemical processes involved in the deposition of U-ores often requires the use of multiple approaches and techniques involving, for example, fluid inclusions, crystal chemistry, organic matter... However, it seems to me that the lack of data on gangue minerals in ores is a common shortfall of studies. In addition more data on isotopic Sr, Nd, O, H, C are needed to adequately characterize the chemical evolution of the mineralizing fluids. It is hoped that in the near future new technological developments such as the nuclear microprobe, the ion microprobe or the ICP-MS will allow *in-situ* isotopic analyses. More research is needed on fluid inclusions following Changkakoti et al. (1988) who have shown that "radiogenic isotopes in fluid inclusion waters can constitute useful geochronological and

genetic tools when applied in conjunction with geological, geochemical and other geochronological studies". However, in U deposits, minerals suitable for fluid inclusion study and isotopic study are rare, small and consequently difficult to use as generally isotope analyses require the collection of the fluid by crushing or heating. This could be overcome in the future by punctual analyses and by using minerals associated with U.

Specific problems related to the presence of high U content have been documented. These include enhancement of H isotopic exchange in phyllites, increase of heavier C content in organic matter and variation in the isotopic composition of REE, especially Nd. This research merits further investigation to determine the confidence limits of stable and radiogenic isotopes in U metallogeny. Unfortunately, due to the actual low price of U, research on U deposits has slowed down. This tendency should be reversed in the near future because U deposits are good natural analogs to waste disposal.

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