Contrasted behaviour of Au and U in French Hercynian granites at the hydrothermal stage: the Role of fO$_2$ and pH

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Abstract. — The french part of the Hercynian belt in Europe is an important metallogenic province for Au and U. Most of the deposits were discovered in the vicinity of major shear zones, but are located either inside granitic rocks or in the surrounding metamorphic rocks. In spite of numerous similarities (age, presence of peraluminous granites, fluid circulation related to the late Hercynian activity), location of Au deposits in one hand, and U in other hand is distinct. This spatial distinction may be related to differences in the source rock location respective of the two metals. However, potential source rocks of both elements are either observed together in the vicinity of the deposits, or unknown. Thus, the hydrothermal stage was investigated as a key for the understanding of the contrasting behaviour of U and Au.

In most of U deposits, pitchblende is associated with pyrite or hematite + pyrite in the veins whilst the stable mineral assemblage in the host rocks is: quartz-muscovite-feldspar-hematite. Fluids are considered to be mostly aqueous, poorly saline, with a relatively low CO$_2$ content. fO$_2$ is high and higher than that fixed by the hematite - pyrite - magnetite triple point. pH is probably neutral.

In Au (As, Sb) deposits, two types of fluids may be distinguished: a) high temperature (300-400°C) fluids which are in some cases aqueous but more frequently belong to the CO$_2$-H$_2$O-CH$_4$ system; b) lower temperature fluids (150-250°C) which are dominantly aqueous and poorly saline. In most cases, strong K-mica alteration occurred which indicates a strong disequilibrium between fluids and host rocks and a rather low pH. fO$_2$ was low and probably around than that fixed by the Ni-NiO buffer.

Considering the experimental data on U and Au solubility and metal species in fluids, it is clear that under above mentioned conditions U and Au cannot be mobilized and deposited together. U transport requires especially higher fO$_2$ values than those which are necessary for an effective gold solubilization. On the contrary, pH under deposition conditions must be significantly lower in the case of Au than U.

Key words: Uranium, gold, hydrothermal stage, fO$_2$, solubility.

Résumé. — La chaine hercynienne en France présente de nombreux districts métallogéniques (Uranium, Or). La plupart des gisements sont localisés à proximité d'importantes zones de cisaillement, à la fois dans les granites ou dans les roches métamorphiques voisines. En dépit de nombreuses similarités (âge, présence de granites peralumineux, circulation de fluides en relation avec l'activité orogénique tardi-hercynienne), la localisation des gisements d'or d'une part et d'uranium d'autre part est distincte. Cette distinction spatiale ne peut être expliquée de manière simple, par la localisation des roches sources potentielles de ces éléments, qui sont fréquemment situées à proximité des gisements. Le stade hydrothermal constitue certainement un évènement clé pour la compréhension du comportement antagoniste de l'uranium et de l'or.

Dans la plupart des gisements d'uranium, la pechblende est associée à la pyrite ou à l'association hématite + pyrite dans les veines. La paragenèse minéralogique stable dans les roches encaissantes est quartz - feldspath - muscovite - hématite. Les fluides sont aqueux, peu salés; le contenu en CO$_2$ est faible. La fugacité en oxygène est élevée et supérieure à celle qui est fixée par le point triple hématite - pyrite - magnétite. Le pH est proche de la neutralité.

Dans les gisements d'Au (As, Sb), deux types de fluides sont observés:
a) des fluides de haute température (300-400°C) qui sont parfois aqueux mais plus fréquemment appartiennent au système CO$_2$-CH$_4$-H$_2$O; b) des fluides de plus basse temperature (150-250°C), aqueux et peu salés. Dans la plupart des cas, une importante altération à micas potassiques affecte les roches encaissantes et indique un important déséquilibre entre les fluides et roches, à des pH relativement bas. La fugacité en oxygène est basse et probablement de l'ordre de celle qui est fixée par le tampon d'oxydo-réduction Ni-NiO.

Les données expérimentales concernant la solubilité de Au, U dans les fluides montrent que dans les conditions précédemment décrites U et Au ne peuvent être mobilisés et déposés ensemble. Le transport de l'uranium requiert des fugacités en oxygène élevées, supérieures à celles qui sont nécessaires pour une effective solubilisation de l'or. Au contraire, lors du dépôt de l'or, le pH doit être inférieur à celui des fluides

associés à l'uranium.

Introduction

The Hercynian belt in Europe is an important metallogenic province for gold, uranium, tin and tungsten. In the French part of the belt, mineralizations are located in the vicinity of major shear zones (S.Z.) such as the South Armoricain, Limousin, and Marche-Combrailles S.Z. (Fig. 1). Most of the deposits were discovered either within granitic rocks, mostly peraluminous granite, and their surrounding metamorphic series (BURNOL, 1974; DE LA ROCHE et al., 1980; POTY et al., 1986; BACHE, 1980; CROUZET et al., 1979).

In the French metallogenic districts here considered, Au and U deposits present numerous similarities:

— their age range is around 280-315 Ma (LEROY and HOLLIGER, 1984; HOLLIGER and CATHELINEAU, 1986; BOIRON, 1987).

— enclosing rocks are either peraluminous granites (U: FRIEDRICH, 1984; FRIEDRICH et al., 1987), or metamorphic rocks (U: CATHELINEAU, 1982, in Vendée; Au, AHMADZADEH, 1984, at Le Bourneix). In metamorphic rocks, Au ores may be closely associated to granitic rocks as aplitic veins or leucogranitic bodies, as at Le Châtelet and Le Bourneix.

— fluid circulations occurred during the late magmatic stages of the Hercynian activity. At that time, the heat flows necessary to fluid convection were related to late thermal anomalies along the shear zones, as attested by the presence of various subordinate acid-basic intrusions dated around 290-310 Ma (lamprophyric dykes, LEROY and SONET, 1976; HOLLIGER et al., 1986).

In spite of their similarities (age, host rocks, tectonic events, spatial relationships with the same shear-zones,...) hydrothermal U and Au deposits do not exhibit evident genetic and spatial links. Thus, no uranium districts have produced significant amounts of gold and vice versa. In addition, Au and U were never found in the same veins in such districts. In order to explain this feature, it is first necessary to determine the nature and the location of the metal source rocks.

Some authors have tried to explain the specific metallogenic potential of the Hercynian granitic provinces as a consequence of an early specialization of the continental crust (DERRE, 1982). For instance, rock geochemistry has been used to discriminate U and Sn-W specialized granite (DE LA ROCHE et al., 1980; CHATTERJEE et al., 1983). However, in the case of Au and U, most of the potential source rocks for both elements are observed together in the vicinity of the deposits. Furthermore, source rocks are not necessarily host rocks for ores, as shown by Au ores located in granites which may have not been a source, due to their low Au content. Therefore, consideration of the element content in the source rock is not alone sufficient to produce a model which could explain the above mentioned differences.

Ore location is fairly independent on the nature and geochemistry of the host rocks: U veins may crosscut different series (granites, shales, etc.) and gold is observed in both metamorphic rocks and granites or volcanosedimentary series. This indicates that gold and uranium deposition is characterized by high fluid-rock ratios.

Therefore, the hydrothermal stage, e.g. the stages of solubilization, transport and deposition, may offer keys to the understanding of such contrasting features. The purpose of this work is to investigate the role of the physical-chemical conditions (fO_2, fS_2, pH and fluid composition) as factors controlling the ability of hydrothermal fluids to transport and deposit U and Au in granites according to the indications given by DUBESSY et al. (1987) for U and Sn-W.

Geological setting of U and Au deposits

Three different districts have been studied in France: 1) the south Armoricain Massif and Vendée in the western part. 2) the Marche-Combrailles and 3) the Limousin area in Massif Central (Fig. 1).

In the southern Armorican zone, uranium deposits are associated to the Guérande
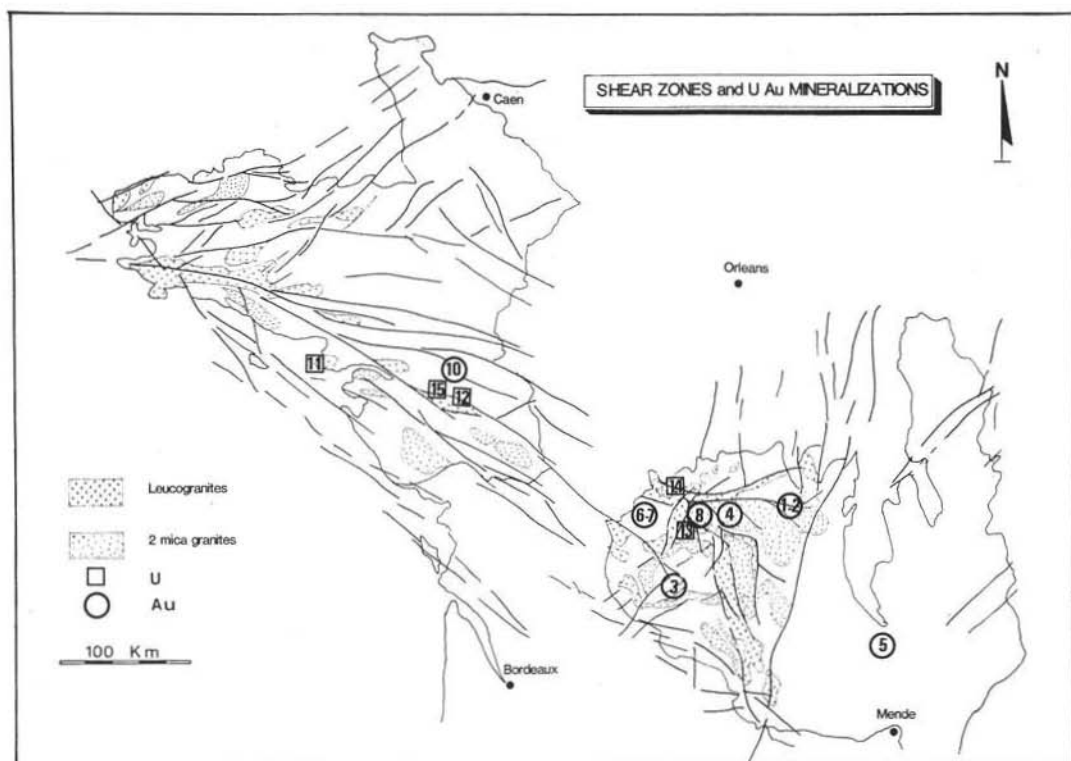
Fig. 1. — Map of U, Au occurences or deposits in French part of Hercynian belt.

leucogranite (Penarran, CATHELINEAU, 1981), and to the Mortagne granite (Chardon, Retail, CATHELINEAU, 1982, 1984). At Mortagne, most deposits are located in the vicinity of the contacts between the granite and the metamorphic rocks. These contacts are mostly shear zones, such as the South Armorican shear zone, which constitutes the northern boundary of the Mortagne batholith. The La Belliere Au-deposit (BACHE, 1980) is located north of the Mortagne batholith in a mica-shist series of the Mauges plateau.

Along the Marche-Combrailles shear zone, uranium deposits occur mostly within the Marche peraluminous granites (Bernardan, LEROY, 1984, and related U-occurrences). Au showings and deposits have been discovered within a band of more than 50 km along the shear zone. Au-veins crosscut either the Hercynian basement (Guéret monzogranite, anatectic biotite-cordierite gneisses (Le Châtelet, ZAPPETTINI, 1983)), the Visean basin (Viges, Villeranges, BOIRON, 1987) and

late intrusive bodies (peraluminous granites (Le Châtelet), lamprophyres).

In the Limousin area, Margnac and Fanay U deposits in the La Crouzille district (LEROY, 1978) are mostly located in the St-Sylvestre peraluminous granite (FRIEDRICH, 1984). U ore occurs in veins crosscutting the granite and lamprophyric dykes, or in alteration pipes («episyenites») resulting from an early subsolidus alteration of the granite, characterized by quartz dissolution, (LEROY, 1978; CATHELINEAU, 1986). Au deposits and showings (Ambazac, Vaulry, Nouic, Janaillac, and the St-Yriex district (AHMADZADEH, 1984) with the Bourneix mine (HUBERT, 1986)) occur mainly within the metamorphic series surrounding the granites. However, Au-veins crosscut frequently sills and dykes of peraluminous granites, as well as altered granites («episyenites») such as at Bourneix.

The presence of early shearing followed by brittle deformation probably play a major role in increasing rock permeability, which in turn

TABLE 1

Synthetic data on vein and wall rock mineralogy of studied U and Au occurrences. po, pyrrhotite; arsp, arsenopyrite; pyr, pyrite; (Au) arsp, gold bearing arsenopyrite; löll, löllingite; stib, stibnite; bert, berthierite, pitch, pitchblende; hem, hematite; BPGC, sphalerite (sph) - pyrite (pyr) - galena (gal) - chalcopyrite (cpy); wolf: wolframite; selen: selenides; sulph: sulphides; carb, carbonate, ank, ankerite; dol, dolomite; Q: quartz; ab, albite; fk, k-feldspar; mu, muscovite; Ill, illite

		OCCURENCES	WALL-ROCK	VEIN MINERALOGY	WALL-ROCK ALTERATION
Au		SINGLE STAGE OF Marche Combrailles	Au DEPOSITION ZONE		
	1	Villeranges BOIRON (1987)	Volcanosedimentary rocks and Gueret granite	1- po-carb 2 -(Au) arsp, pyr,Q-ank 3 -stib, Q	K-mica alteration
	2	Le Châtelet ZAPPETTINI (1983), this work	Peraluminous granite	1- po, (Au) pyr,arsp,Q 2- bert, stib, Q-dol	K-mica alteration
		MULTISTAGE	Au DEPOSITION		
	3	Le Bourneix HUBERT (1986)	Peraluminous granite	1-arsp, native Au,Q, pyr 2-sulfosalt + native Au	K-mica alteration PROUST(1986)
	4	Bennevent BRIL and NENERT (1986)	Gneiss and Gueret Granite	1- po, löll,Q 2-arsp, bert,native Au 3-native Au, sulfosalt, Q-carb 4-BPGC	
	5	Haut Allier BRIL and BEAUFORT (1987)	Metamorphic series	W or Sb ores (± native Au)	Q, Mu, Phengite
	6	Vaulry This work	Gneisses, Bi-granite, and peraluminous granites	1-Q-wolf 2-löll.-Cpy-Nat Au	
	7	Nouic This work	Gneisses	Q-mispickel/nat Au	K-mica alteration
	8	Ambazac This work	granite	(W-Sn)/Q-nat Au	K-mica alteration
	9	Janaillac This work	granite	Q-nat Au-sulph	K-mica alteration
	10	La Bellière This work	Mica-schist series	Q-arsp-sph-nat Au-(gal)	K-mica alteration
U	11	Penarran CATHELINEAU (1981,1984)	Blastomylonites graphitic quartzites	Q1- pitch	Hem stable Q,Ab,Fk,Mu stable ill trapped with Q1
	12	Retail CATHELINEAU (1981)	Bi(Chl)Mu gneisses	1-pitch-pyr 2-pitch-cpy-selen/sulph	
	13	Margnac - Fanay LEROY (1978)	Peraluminous granite episyenite	pitch/ pyr- hem	Phengite Q,Ab,Fk,Mu stable
	14	Le Bernardan LEROY (1984)	Quartz depleted peraluminous granite	pitch	K-micas
	15	Le Chardon CATHELINEAU (1981)	Granite and metamorphic series	pitch- pyr/hem-Q/carb	IS Ill/Sm Q,Ab,Fk stable

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TABLE 2

Microthermometric data on fluid inclusions associated with ore stage from U and Au occurrences
(*: ± NaCl)

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		OCCURENCES	CHEMICAL COMPOSITION	SALINITY wt % NaCl	TEMPERATURE (Th°C)	PRESSURE	REFERENCES
Au	1	Villeranges	H2O-NaCl	2-4 %	150-250	< 1kb	BOIRON (1987)
	2	Le Châtelet	H2O-NaCl	2-4 %	190-210		This work
	3	Le Bourneix	- CO2-H2O (CH4)* - H2O-NaCl	 2-4 %	350-450 200-300	2 kb 0,5 kb	HUBERT (1986)
	4	Bennevent	CO2-H2O*		1- 400 2- 250		BRIL and NENERT(1986)
	5	Haut Allier	CO2 - H2O CO2 -CH4 N2 -H2O	6-8 %	320-420		BRIL and BEAUFORT (1987)
	6	Vaulry	H2O -NaCl	1-6 %	200-240		This work
	7	Nouic	H2O -NaCl	0- 3 %	180-350		This work
	8	Ambazac	H2O -NaCl	4-8 %	280-300		This work
	9	Janaillac	H2O -NaCl	2-4 %	140-180		This work
	10	La Belliere	CO2-H2O (CH4) H2O -NaCl		300-340 180-200		This work
U	11	Penarran	H2O -NaCl	1-2%	340-430		C. THELINEAU (1981)
	12	Retail	H2O -NaCl	1-2%	320-400		CATHELINEAU (1981)
	13	Fanay -132 Margnac-805	CO2-H2O-NaCl H2O -NaCl		300-350 190-250		LEROY (1978) This work
	14	Le Bernardan	no gangue mineral of ore				
	15	Le Chardon	no studiable fluid inclusions				

favours fluid infiltration and hydrothermal leaching of metals, through extensive microfaulting. However, only the brittle deformation occurring during the late reactivation stage of the shear zones has clear genetic relationships with ore deposition.

Methodology

The methodology used consisted in combining mineralogical and geochemical results available on the deposits together with the published experimental and theoretical data on the Au and UO_2 solubilities.

Mineralogical data are derived from previous works (U-deposits) or from the literature (references in Table 1). However, spatial and chronological relationships between ore minerals, and fluids have been carefully checked in different samples from newly studied (Table 1 and 2, noted: this work) Au-localities (Vaurly, Nouic, Ambazac, Janaillac, La Belliere). In the case of the La

Belliere samples, for instance, the study of ore fluids has been carried out on fluid inclusions hosted by recrystallized microfaulted zones in early quartz veins. These sublinear recrystallized zones are the only ones containing the early Au-ore (native Au, sphalerite, arsenopyrite). In other localities, fluid inclusions were studied in the quartz vein hosting the Au - ore without any other discrimination, since relationships between native Au - particles, microcracks and fluids was unclear, such as in many other Au - veins described in the literature (HUBERT, 1986, for instance).

Microthermometry, performed on a Chaix-Meca heating and freezing stage, was used to identify the main components of fluid phases (POTY et al., 1976). Salt concentration, expressed in equivalent NaCl, and fluid density of gas-free fluid inclusions in the ore quartz gangue, were determined by microthermometry (POTTER, 1977, POTTER et al., 1978). In gas-bearing fluid inclusions,

CH_4 was identified by liquid-vapour equilibria below $-81°C$ and CO_2 by melting of a solid below $-56.6°C$. Molar fractions of CO_2, CH_2, H_2S and N_2 were determined in individual inclusions by micro-Raman analysis performed on a DILOR X-Y multichannel modular Raman spectrometer. fO_2 and fS_2 were calculated from the P-V-T-X properties of individual inclusions in the C-O-H-S system (DUBESSY, 1984; RAMBOZ et al., 1985; DUBESSY et al. 1989). Estimation of fO_2, fS_2, pH, was also obtained by considering the sulfide and silicate assemblages together with their relative stability diagrams.

Lastly, mineral solubilities and metal speciation were considered for the determination of the factors controlling the metal transport and deposition, under the conditions deduced from the previous calculations.

Data on fluids and solids

Gold deposits

Gold occurs either as native gold or as a trace element (30 to 5000 ppm) within sulfides. There are different mineral associations involving native gold, but many descriptions have ignored the difficulties in estimating whether gold was deposited together with other minerals or not. For instance, part of native gold may be supergene or very late in the mineralogical sequence, and occurs as a late infilling of cavities or microcracks, difficult to distinguish from gold deposited during the early stages. A second difficulty comes from the relatively great heterogeneity in the mineralogical assemblage of the different deposits. In the Marche-Combrailles zone, BOIRON (1987) demonstrated that gold is only born at a combined state (MARION et al., 1986; CATHELINEAU et al., 1988) in arsenopyrite which crystallized at a specific stage of the hydrothermal sequence, whilst other deposits are characterized by multistage deposition of native gold. Thus a definitive global sequence describing all the occurrences as the result of

a single general process seems unlikely, contrary to the interpretations of PICOT and MARCOUX (1987), and BONNEMAISON and MARCOUX (1987). In spite of these difficulties, different mineral assemblages have been distinguished and are given in Table 1.

Most of the rocks in the vicinity of the gold veins are frequently altered in a quartz + muscovite assemblage, which replaces especially the two feldspars and chlorite (BOIRON, 1987).

Two types of fluids in relations with the ore stage are distinguished:

— fluids of high temperature (300-400°C) have either an aqueous composition, or more frequently a more complex composition in the CO_2-(CH_4)-H_2O system. Such a fluid has been observed at La Belliere (Fig. 2), at le Bourneix deposit (HUBERT, 1986) and in Bennevent l'Abbaye district (BRIL and NENERT, 1987) (Table 2).

— the second type is represented by almost purely aqueous fluids (H_2O-NaCl) of lower temperature (150-200°C), having a low salinity (< 4% wt NaCl). No gas species has been identified either by microthermometry or Raman spectroscopy. This type is the only one observed in the Marche-Combrailles district (Villeranges, Le Châtelet) but it has been identified also in different gold showings in the Limousin area (Vaulry, Ambazac, Janaillac) (Fig. 3). It could correspond to the late type described by HUBERT (1986) at Le Bourneix which is related, according to this author, to the crystallization of economic ores.

The homogenization temperatures mentioned in Table 2, are minimal trapping temperatures, since fluid unmixing was not evidenced. However, pressure in open fault systems such as those of the Marche-Combrailles district, may be considered as hydrostatic and no higher than a few hundred bars. In this case, the temperatures of gold deposition probaby ranged from 200 to 250°C.

In the case of the Le Bourneix deposit, HUBERT (1986) calculated higher pressures around 2 kilobars for the early stage, assuming that the early H_2O (± CO_2, CH_4) fluid from the first stage was trapped at higher pressure than that prevailing during the second stage
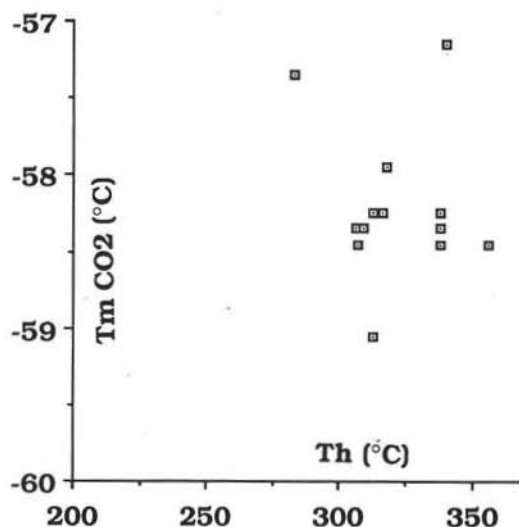
Fig. 2. — Tm CO$_2$-Th plot for fluid inclusions from La Bellière quartz veins. Inclusions are located in recrystallized quartz contemporeneous of gold + sulphides deposition.
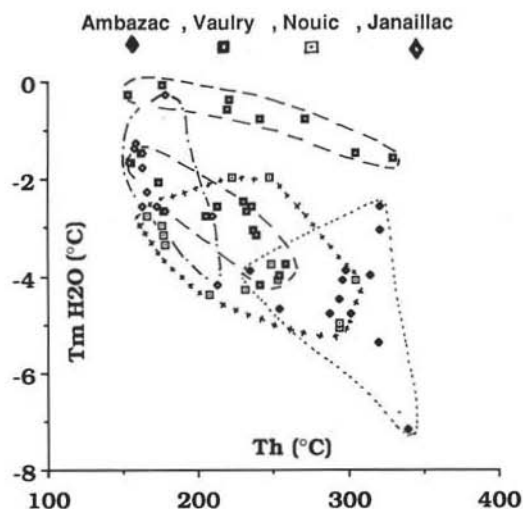
Fig. 3. — Tm H$_2$O-Th plot for fluid inclusions from Ambazac, Vaulry, Nouic and Janaillac gold bearing quartz veins.

(CO$_2$, CH$_4$ rich fluids). Pressure during the second stage was around 0.8 kbar, being related to the boiling pressure of the carbonic fluids.

Uranium deposits

Data are given, at least partially, in many papers (POTY et al., 1986, for instance) and especially in DUBESSY et al. (1987). They are only summarized in the following paragraph.

The most common paragenetic sequence in the Hercynian intragranitic uranium deposit is minor quartz, pitchblende + pyrite, quartz + hematite + pyrite (Table 1). In most veins, pyrite is cogenetic with pitchblende but different occurrences such as Pennaran, La Commanderie and Le Retail in Vendée, (CATHELINEAU, 1982) are characterized by a lack of sulfide crystallization during the ore stage. Hematite may be abundant in the wall rock and is frequently observed in minerals (quartz, carbonate) which crystallized just after pitchblende.

In the wall rocks, the silicate association, quartz - K-feldspar - muscovite remains stable during the ore stage. Authigenic K-mica (phengite, illite, or I/S illite-smectite) may

sometimes have crystallized before and/or during ore deposition (LEROY and CATHELINEAU, 1982; CATHELINEAU, 1983).

Fluids are mostly aqueous, poorly saline with no gas (CO$_2$, CH$_4$) since gas clathrate was not observed during microthermometric studies (Table 2). CO$_2$ was only found in quartz grains from the granite hosting U minéralization at level 132 of Fanay deposit (La Crouzille, LEROY, 1978). However, only low saline fluids were found in quartz combs associated to the pitchblende from Margnac (La Crouzille, LESPINASSE and CATHELINEAU, 1987). Temperature range may be relatively high, around 300-350°C in some cases, but is frequently lower (150-250°C) as attested by the discrete crystallization of illite and I/S illite - smectite which could not have been formed at temperatures higher than 250°C according to illite geothermometry (CATHELINEAU and IZQUIERDO, 1988).

Estimation of pH, fO$_2$, fS$_2$ conditions during gold and uranium deposition

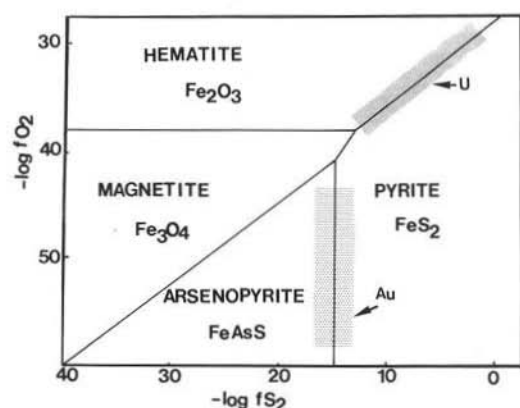At low temperatures (200 ± 50°C), gold may occur as a trace element in closely associated arsenopyrites and pyrites. These

Fig. 4. — Projection of fluids associated with Au and U showings in the log fO_2 - fS_2 plane (T = 200°C, Σ [As]$_{sol}$ = cst).

minerals show that fO_2 was close to that given by the pyrite-arsenopyrite boundary or not very far to that fixed by the pyrite - arsenopyrite - pyrrhotite equilibrium (Fig. 4), as indicated by the stability of pyrrhotite during the first stage of the arsenopyrite deposition.

The data deduced from the P-V-T-X properties of fluid inclusions for Au-deposits of higher temperature (350 ± 50°C) (Fig. 5) are reported in a fO_2 - temperature diagram (Fig. 6). At Le Bourneix (calculation by DUBESSY, TOURAY, 1987) and at La Belliere (this work) fO_2 was around that fixed by the Ni-NiO oxygen buffer.

In uranium deposits, the mineralogy of oxides and sulfides (Table 1) during the ore stage indicates that fO_2 was close to that fixed by the hematite-pyrite boundary, or that fO_2 was compatible with the hematite stability (Figs. 4 and 5). Thus, in both cases of high and low temperature Au deposits, fO_2 was relatively low, and much lower than during U deposition.

The instability of K feldspars and the crystallization of a quartz-muscovite or (illite) assemblage indicates a strong shift towards lower pH during the gold deposition. Such acidity of Au, As, S - bearing solutions in gold deposits is attested by the relatively high content in H^+ of fluid inclusions as demonstrated by the use of nuclear magnetic resonance of the proton on fluid inclusions

hosted by quartz from the Marche-Combrailles deposits (POTY et al., 1987). On the contrary, the stability of quartz, feldspar and muscovite in the wall rocks of most of uranium deposits indicates that pH was probably not very far from the neutrality according to the theoretical data from MONTOYA and HENLEY (1975).

Solubility and speciation data of Au and U in hydrothermal solution in the range 200-400°C

The amount of ore minerals which can be precipitated from the fluid is the result of a change in physico-chemical conditions and depends on: 1) the initial concentration of the metal in the fluid under transport conditions, the maximum concentration being fixed by the solubility of specific ore minerals under these conditions; 2) the solubility of the ore mineral under the precipitation conditions; 3) the amount of fluids which circulate in a given section of the hydrothermal system. Thus, an assessment of the factors affecting solubility may be of great help in understanding the mechanisms leading to metal deposition. The data are summarized in Table 3.
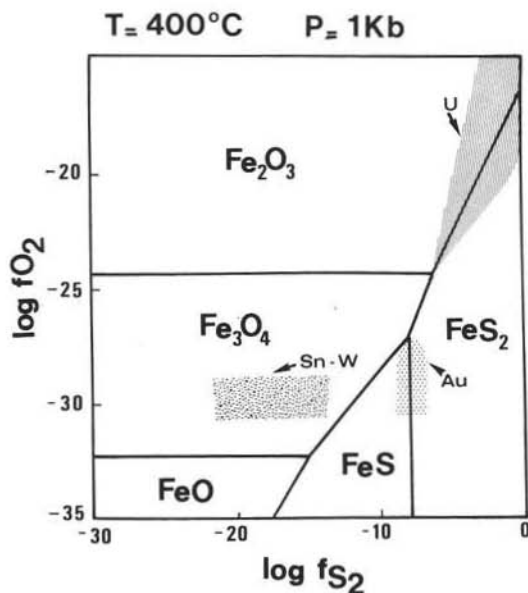

Fig. 5. — Projection of fluids associated with U, Au and Sn-W in the log fO_2 - log fS_2 plane at 400°C and 1 kbar (from BOWERS et al., 1984 and DUBESSY et al., 1987; modified).
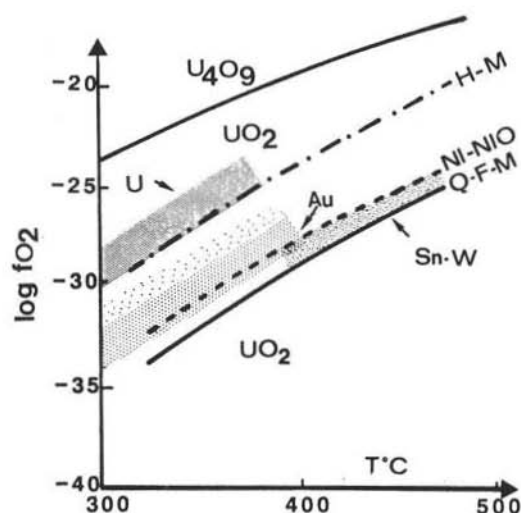
Fig. 6. — Uranium oxide stability field (NGUYEN TRUNG, 1985) and fluids associated with U, Au and Sn-W deposits in a log fO_2 - temperature diagram at 1 kbar (completed from DUBESSY et al., 1987).

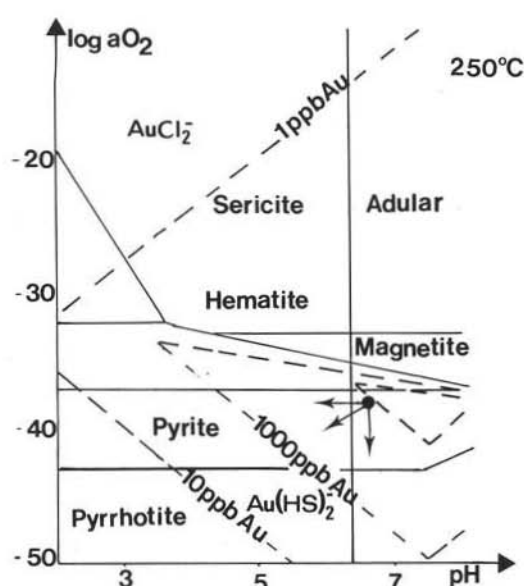
Fig. 7. — fO_2 - pH diagram applied to gold species in solution with indication of stability fields of iron species and silicates (T = 250°C, fCO_2 = 1 atm; from ROMBERGER, 1986, simplified).

Gold

Gold in solution presents valences I and III. However, gold with valence III is probably subordinate to gold with valence I under the hydrothermal conditions of the studied deposits (low fO_2).

Main experimental data concerning gold solubility were obtained by HENLEY (1973) and SEWARD (1973). HENLEY (1973) showed that gold is transported as neutral Au chloride complexes at temperatures from 300 to 500°C, and as $AuCl_2^-$ at low temperature,

under oxidizing conditions. SEWARD (1973) demonstrated that $Au(HS)_2^-$ and $Au_2S(HS)_2^{2-}$ are the main Au species in solution, at fO_2 below hematite - magnetite buffer to stabilize sulfide species in solution, and that gold solubility in bisulfide solutions depends mainly on temperature, pH and sulfide concentration. GRIGORYEVA and SUKNEVA (1981) considered a possible complexation of Au by arsenide complexes in arsenic-rich fluids but stability fields of such Au complexes remain unknown. From the literature data, ROMBERGER (1986) described the possible mechanisms of Au deposition using a fO_2 - pH diagram (Fig. 7) which gives the stability fields of minerals and species in solution. Figure 7 shows that gold is soluble as a chloride complex under acid pH and high fO_2, whilst it is soluble as bisulfide complexes in a large pH range, at low fO_2, in environments where H_2S or HS^- are the main sulfur bearing species.

Considering that the maximum solubility of gold is around neutral to slightly basic pH at low fO_2, three different mechanisms may be proposed for gold deposition: a) fluid

TABLE 3

Estimations of pH, fO_2, fS_2 and temperature for U, Au and Sn-W deposition.

	Au	U	Sn - W
pH	acid	neutral	acid to neutral
fO2	low	high	very low
fS2	high	moderate	
T°C	1) 150-250 2) 300-400	150-300	350-400

oxidation which results in an increase of sulfate to sulfide species in solution; b) decrease in oxygen fugacity; c) decrease in pH; or the combination of the factors b and c.

As no evidence of oxidation was observed in low temperature deposits (T < 250°C) by iron oxide or sulfate crystallization for instance, the first process is fairly unlikely in the studied deposits. On the contrary, evidence of a pH decrease during sulfide crystallization which is almost clearly shown by various occurrences, can be considered as an important factor controlling Au deposition.

The presence of CO_2 and CH_4 in some high temperature (T > 350°C) fluids play an essential role for the control of oxygen fugacity but a more questionable one in metal transport and speciation. On one hand, aqueous solutions probably contain appreciable amounts of bicarbonate ions as shown by the presence of significant quantities of ankerite within the ore bearing quartz. However, although the ankerite crystallization is controlled by fCO_2 (in addition to pH, aFe, aMg), it does not necessarily imply a high fCO_2. On the other hand, the presence of CO_2, observed in very different amounts within fluid inclusions, is actually difficult to consider as a factor controlling gold solubility, at a given fO_2. Thus, the presence of CO_2 and CH_4 is important through their fO_2 control but is probably not a necessary condition for gold transport. Consequently, it cannot be interpreted directly as a metallogenic tool, contrary to the suggestion of SMITH et al. (1984) and WOOD et al. (1986). It may be rather related to the metamorphic origin of the fluid.

Uranium

Most data are given in DUBESSY et al., (1987) and will not be repeated again. In aqueous solutions, three oxidation states (IV, V, VI) are possible for uranium at low temperatures under natural conditions (LANGMUIR, 1978) and at high temperatures (NGUYEN TRUNG, 1985). In the H_2O - UO_2 system, at fixed temperature, the UO_2 solubility depends on pH and fO_2. Under

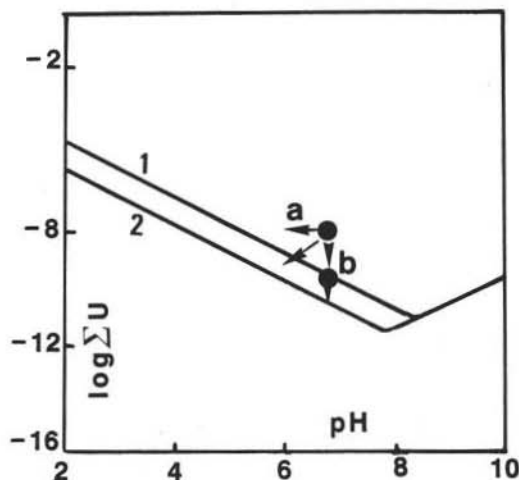Fig. 8. — UO_2 solubility in H_2O, LiOH and NaOH as a function of pH, T: 200°C, saturation vapor pressure (from NGUYEN TRUNG, 1985), for fO_2 buffered by 1) H-M; 2) Ni-NiO. Arrays refer to solubility decrease due a) pH decrease; b) destabilization of (carbonate, phosphate) complexes, or a fO_2 drop.

fO_2 conditions fixed by the hematite-magnetite (H-M) or Ni-NiO oxygen buffer, minimum solubility is near pH neutral (NGUYEN TRUNG, 1985) but U solubility increases when fO_2 increases from that fixed by the Ni-NiO to H-M oxygen buffer (Fig. 8). In addition, uranium concentration is enhanced when complexation by inorganic ligands (chloride, carbonate and phospate) occurs.

Experimental work and calculations (NGUYEN TRUNG, 1985) demonstrate that under the above mentioned conditions (neutral pH, high fO_2, moderate fS_2: Table 3), uranium may be transported as carbonate or phosphate complexes. Taking into account these data, the possible changes in the physico-chemical conditions yielding uranium deposition are shown in Figure 8. Considering that U is probably mobilized at relatively neutral pH, and that the minimum of U solubility is around 7-8, two major mechanisms can be considered for uranium deposition: 1) a decrease in oxygen fugacity, or a decrease in the ligand concentration at nearly constant neutral pH; 2) a decrease in pH, which is less probable, as no mineralogical evidence of such a process has been found

Conclusions

This study demonstrated that:

1 - the distribution of gold and uranium mineralizations is mainly controlled by the hydrothermal stage and especially by the fluids chemistry characterized by fO_2, fS_2, and pH.

2 - The main factors controlling mobilization, transport and deposition of Au and U are typical of each metal (Table 3). The experimental data on U and Au solubility and metal species in fluids clearly indicate that under the above mentioned conditions U and Au cannot be mobilized and deposited together. U transport requires high fO_2 values ($fO_2 >$ H-M) which are incompatible with an effective gold solubilization under the form of HS- bearing complexes. On the contrary pH under deposition conditions must be significantly lower with respect to uranium.

3 - The data show that the conditions required for Au transport are intermediate between those mentioned (DUBESSY et al., 1987) for U and Sn-W. This may explain why discrete Au-mineralizations are associated in some cases with U (VANHANEN, 1987, for instance) but more frequently with Sn-W deposits (Portugal, ALMEIDA and NORONHA, 1988; Haut Allier, BRIL and BEAUFORT, 1987; La Belliere, La Lucette,...). This relation between some Au and Sn-W mineralizations is not suprising, since the mineralogy (K-mica alteration) and fluid composition (high temperature carbonic fluids) in both cases indicate rather similar conditions in which acid pH and low fO_2 prevailed.

4 - The results obtained from the mineral and fluid studies are in good agreement with experimental data and theoretical predictions on U and Au solubilities. This is of considerable importance for metallogenic studies, and confirms the need for multidisciplinary approach to the processes. The use of data from both mineralogy and fluids is especially useful for a correct estimation of the physical and chemical conditions. These results stimulate a more extensive study of physical-chemical conditions in Au and U deposits, since the rate of Au or U solubilization depends probably much more on the water-rock ratio and solution chemistry during fluid circulation than on the element content available in the source rocks. Such study could confirm whether the results found in the French Au and U deposits may be generalized or not.

REFERENCES

AHMADZADEH H. (1984) - *Le district aurifère de Saint - Yrieix (Haute-Vienne): Etude des minéralisations auro-antimonifères dans leur cadre géologique*. Unpubl. Thesis, Clermont Ferrand, 98 p.

ALMEIDA A., NORONHA F. (1987) - *Fluids associated with W and Au-Ag deposits of the Mirandela area, NE Portugal: An example of peri-granitic zoning*. Bull. Mineral., III, 3-4, pp. 331-342.

BACHE J.J. (1980) - *Les gisements d'or dans le monde. Essai de typologie quantitative*. Mem. B.R.G.M., n° 18, 102 p.

BOIRON M.C. (1987) - *Minéralisations à Au, As, Sb, altérations hydrothermales et fluides associés dans le bassin de Villeranges (Combrailles, Massif Central français)*. Geol. Geochim. Uranium, Mem. Nancy, 15, 310 p.

BONNEMAISON M., MARCOUX E. (1987) - *Les zones de cisaillement aurifères du socle hercynien français*. Chron. Rech. Min., 478, pp. 29-42.

BOWERS T.S., JACKSON K.J., HELGESON H.C. (1984) - *Equilibrium activity diagrams for coexisting minerals and aqueous solutions at pressures and temperatures up to 5 kb and 600°C*. Springer Verlag, 397 p.

BRIL H., BEAUFORT D. (1987) - *Alterations hydrothermales et circulations de fluides liées aux minéralisations filoniennes à W + Au et Sb + Au du Haut Allier (Massif Central, France)*. Colloque SFMC «Minéraux argileux et géothermie», Paris, Nov. 1987.

BRIL H., NENERT S. (1987) - *Le distric auro-antimonifère de Bénévent l'Abbaye (Limousin, Massif Central français): paragenèses et inclusions fluides, résultats préliminaires*. IX Symposium on fluid inclusions, Porto, p. 135.

BURNOL L. (1974) - *Different types of leucogranites and classification of the types of mineralization associated with acid magmatism in the north-western part of the French Central Massif*. In «Metallization associated with acid magmatism», M. Stemprock, L. Burnol and C. Tischendorf, ed. vol. 3, Prague, pp. 191-204.

CATHELINEAU M. (1981) - *Les gisements uranifères de la presqu'ile Guérandaise (Sud Bretagne); Approche structurale et métallogénique*. Mineralium Deposita, 16, 2, pp. 227-240.

CATHELINEAU M. (1982) - *Les gisements d'uranium liés spatialement aux leucogranites sud armoricains et à leur encaissant métamorphique*. Mem. Sci. Terre, Nancy, 42, 375 p.

CATHELINEAU M. (1983) - *Les minéraux dans les gisements hydrothermaux d'uranium: II. Distribution et évolution cristallochimique des illites, interstratifiés, smectites et chlorites*. Bull. Mineral., 106, pp. 553-559.

CATHELINEAU M. (1984) - *Uranium veins in western*

France: *Mineralogy and geochemistry of uranium deposition*. Proceedings of The Second International Congress on Applied Mineraloy in the Mineral Industry, Los Angeles, California, February 22-25.

CATHELINEAU M. (1986) - *The hydrothermal alkali metasomatism effects on granitic rocks: quartz dissolution and related subsolidus changes*. Journal of Petrology, 27, 4, pp. 945-965.

CATHELINEAU M., IZQUIERDO G. (1988) - *Temperature - composition of authigenic micaceous minerals, in the Los Azufres geothermal system*. Contrib. Mineral. Petrol., 102.

CATHELINEAU M., BOIRON M.C., HOLLIGER P., MARION P. (1988) - *Gold-rich arsenopyritres: Crystal chemistry, gold location and state, physical and chemical conditions of crystallization*. Extended Abstract, Gold 88, Melbourne, May 1988, pp. 235-240.

CHATTERJEE A.K., STRONG D.F., MUECKE G.K. (1983) - *A multivariate approach to geochemical distinction between tin-specialized and uranium-specialized granites of the southern Nova Scotia*. Can. J. Earth Sci., 20, pp. 420-430.

CROUZET J., RECOING M., TOLLON F. (1979) - *Les gisements aurifères du Massif Central français*. Chron. rech, Min., 452, pp. 5-38.

DE LA ROCHE H., STUSSI J.M., CHAURIS L. (1980) - *Les granites à deux micas hercyniens français. Essais de cartographie et de correlations géochimiques appuyés sur une banque de données. Implications pétrologiques et métallogéniques*. Sci. de la Terre, Nancy, 24, 1, pp. 5-221.

DERRE C. (1982) - *Caractéristiques de la distribution des gisements à étain et tungstène dans l'ouest de l'Europe*. Min. Deposita, 17, pp. 55-77.

DUBESSY J. (1984) - *Simulation des équilibres chimiques dans le système C-O-H. Conséquences méthologiques pour les inclusions fluides*. Bull. Mineral., 107, pp. 157-168.

DUBESSY J., RAMBOZ C., NGUYEN TRUNG C., CATHELINEAU M., CHAROY B., CUNEY M., LEROY J., POTY B., WEISBROD A. (1987) - *Physical and chemical controls (fO2, T, pH) of the opposite behaviour of U and Sn-W as exemplified by hydrothermal deposits in France and Great Britain, and solubility data*. Bull. Mineral., 110, pp. 261-281.

DUBESSY J., POTY B., RAMBOZ C. (1989) - *Advances in fluid chemistry based on micro Raman spectrometric analysis of fluid inclusion*. European Journal of Mineraloy, 1, (in press).

FRIEDRICH M. (1984) - *Le complexe granitique hyperalumineux de Saint-Sylvestre, Nord Ouest du Massif Central Français*. Geol. Geochim. Uranium, 5, 342 p.

FRIEDRICH M., CUNEY M., POTY B. (1987) - *Uranium geochemistry in peraluminous leucogranites*. Uranium vol. 3, 2-4, pp. 358-386.

GRIGORYEVA T.A., SUKNEVA L.S. (1981) - *Effect of sulfur and of antimony and arsenic sulfides on the solubility of gold*. Geochem. Intern., V, pp. 152-158.

HENLEY R.W. (1973) - *Solubility of gold in hydrothermal chloride solutions*. Chem. Geol., 11, pp. 73-87.

HOLLIGER P., CATHELINEAU M. (1986) - *Le chronomètre U-Pb en milieu uranifère: application aux gisements hydrothermaux d'uranium liés spatialement au batholithe*

de Mortagne (Vendée, France). Chron. Rech. Min., 485, pp. 33-43.

HOLLIGER P., CUNEY M., FRIEDRICH M., TURPIN L. (1986) - *Age carbonifère de l'unité de Brame du complexe granitique alumineux de Saint-Sylvestre (NO du Massif Central) par les données isotopiques du zircon et monazite*. C.R. Acad Sci., t. 303, serie II, 14, pp. 1309-1314.

HUBERT P. (1986) - *Textures et inclusions fluides des quartz aurifères. Application au gîte de Cros Gallet (Haute Vienne, France) et au prospect de Sanoukou (District de Kinieba, Mali)*. Document du B.R.G.M., 114, 350 p.

LANGMUIR D. (1978) - *Uranium solution mineral equilibria at low temperatures with applications to sedimentary ore deposits*. Geoch. Cosmochim. Acta, 42, pp. 547-569.

LEROY J. (1978) - *The Margnac and Fanay uranium deposits of the La Crouzille district (Western Massif Central, France): geologic and fluid inclusions studies*. Econ. Geol., 73. pp. 1611-1634.

LEROY J. (1984) - *Episyénitisation dans le gisement d'uranium du Bernardan (Marche). Comparaison avec des gisements similaires du Nord Ouest du Massif Central français*. Mineralium Deposita, 19, pp. 26-35.

LEROY J., SONET J. (1976) - *Contribution à l'étude géochronologique des filons de lamprophyres recoupant la granite à deux micas de Saint Sylvestre (Limousin, Massif Central français)*. C.R. Acad. Sc., 283, pp. 1477-1480.

LEROY J., CATHELINEAU M. (1982) - *Les minéraux phylliteux dans les gisements hydrothermaux d'uranium. Cristallochimie des micas hérités et néoformés*. Bull. Mineral., 105, pp. 99-109.

LEROY J., HOLLIGER P. (1984) - *Mineralogical, chemical and isotopic (U-Pb method) studies of hercynian uraniferous mineralizations (Margnac and Fanay mines, Limousin, France)*. Chem. Geol., 45, pp. 121-134.

LESPINASSE M., CATHELINEAU M. (1987) - *Relations between microfissuration, fluid circulation, and rock alteration in granitic environment: a tool for paleostress field chronology*. Abstract S 05-10, EUG IV, Terra Cognita, 7, 2-3, p. 27.

MARION P., REGNARD J.R., WAGNER F.E. (1986) - *Etude de l'état chimique de l'or dans des sulfures aurifères par spectroscopie Mössbauer de 197Au: premiers résultats*. C.R. Acad. Sc., Paris, 302, II, 8, 571-574.

MONTOYA J.W., HENLEY J.J. (1975) - *Activity relations and stabilities in alkali feldspar and mica alteration reactions*. Econ. Geol., 70, pp. 577-582.

NGUYEN TRUNG C. (1985) - *Geochimie théorique et expérimentale des oxydes d'uranium dans les solutions aqueuses de 25 à 700°C sous une pression de 1 à 6000 bars. Synthèse hydrothermale de certains mineraux d'uranium VI et IV. Geologie et geochimie de l'uranium*. Unpub. thesis, INPL, Nancy, 479 p.

PICOT P., MARCOUX E. (1987) - *Nouvelles données sur la métallogénie de l'or*. C.R. Acad. Sc., t. 304, serie II, 6, 221-226.

POTTER R.W. (1977) - *Pressure corrections for fluid inclusion homogenization temperatures based on the volumetric properties of the systems NaCl-H2O*. J. res. U.S. Geol. Survey, 6, pp. 245-257.

POTTER R.W., CLIME M.A., BROWN D.L. (1978) - *Freezing point depression of aqueous sodium chloride*

solution. Econ Geol., 73, pp. 283-283.

POTY B., LEROY J., JACHIMOWICZ L. (1976) - Un nouvel appareil pour la mesure des températures sous microscope: l'installation de microthermométrie Chaix-Meca. Bull. Soc. Fr. Mineral. Cristallogr., 99, pp. 182-186.

POTY B., LEROY J., CATHELINEAU M., CUNEY M., FRIEDRICH M., LESPINASSE M., TURPIN L. (1986) - Uranium deposits spatially related to granites in french part of the Hercynian orogen. IAES, TECTDOC, in «Vein type uranium deposits», pp. 215-246.

POTY B., DEREPPE J.M., LANDAIS P., PIRONON J. (1987) - Use of ¹H NMR for discrimination of solutions having different proton concentrations. Application to fluid inclusions. IX Symposium of fluid inclusions, Porto, pp. 101-102.

PROUST D. (1986) - Altérations hydrothermales du gisement aurifère de Cros Gallet, Le Bourneix, District de Saint Yriex, (Haute-Vienne). Coll. PIRSEM, Montpellier, p. 79.

RAMBOZ C., SCHNAPPER D., DUBESSY J. (1985) - The P-V-T-X-fO_2 evolution of H_2O-CO_2-CH_2 bearing fluid in a wolframite vein: reconstruction from fluid inclusion studies. Geochim. Cosmochim. Acta, 49, pp. 205-219.

ROMBERGER S.B. (1986) - The solution chemistry of gold applied to the origin of hydrothermal deposits. Proceedings of the symposium «Gold in the western field», Can. Inst. of Min. Met., vol. 38, pp. 168-186.

SEWARD T.M. (1973) - Thiocomplexes of gold and the transport of gold in hydrothermal ore solutions. Geochim. Cosmochim. Acta, 37, pp. 379-399.

SMITH T.J., CLOKE P.L., KESSLER S.E. (1984) - Geochemistry of fluid inclusions from the McIntyre Holliger gold deposit, Timmins, Ontario, Canada. Econ. Geol., 79, pp. 1265-1285.

TOURAY J.C. (1987) - Transport et dépot de l'or dans les fluides de la croûte continentale, l'apport des études d'inclusions fluides. Chron. Rech. Min., 488, pp. 43-54.

VANHANEN E. (1987) - The uraniferous mineralizations in the Kusamo schist belt, Northeastern Finland. Proceedings of the «International workshop on metallogenesis of Uranium deposits», IAEA Vienna, March 1987, (in press).

WOOD P.C., BURROW D.R., THOMAS A.V., SPOONER E.T.C. (1986) - The Hollinger Mc-Intyre Au quartz vein system, Timmins, Ontario, Canada; geologic characteristics, fluid properties and light stable isotope geochemistry. Proceedings of gold '86 symposium, Toronto, pp. 56-80.

ZAPPETTINI E.O. (1983) - Le gisement d'or du Châtelet (Creuse, Massif Central français). Cadre geologique régional. Etude métallogenique. Unpublished Thesis, Limoges, 151 p.