Contrasted behaviour of Au and U in French Hercynian granites at the hydrothermal stage: the Role of fO2 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 CO2 content. fO2 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 CO2·H2O·CH4 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. fO2 was low and probably around 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 fO2 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, fO2, solubility.
associés à l'uranium.

Mots clés: Uranium, Or, Stade hydrothermal, fO$_2$, Solubilité.

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 Armorican, 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; BACIE, 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 Armorican 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
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 gneiss (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, Noutic, 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

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<tr>
<th>OCCURRENCES</th>
<th>WALL-ROCK</th>
<th>VEIN MINERALOGY</th>
<th>WALL-ROCK ALTERATION</th>
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<tr>
<td>Au</td>
<td>SINGLE STAGE OF</td>
<td>Au DEPOSITION ZONE</td>
<td>1- po-carb</td>
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<tr>
<td>Marche Combrailles</td>
<td>Villeranges BOIRON (1987)</td>
<td>Volcanosedimentary rocks and Gueret granite</td>
<td>2-(Au) arsp, pyr, Q-ank</td>
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<td></td>
<td>Le Châtelet</td>
<td>Peraluminous granite</td>
<td>1- po, (Au) pyr, arsp, Q</td>
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<td>ZAPPETTINI (1983), this work</td>
<td>Au DEPOSITION</td>
<td>2- bert, stib, Q-dol</td>
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<tr>
<td>MULTISTAGE</td>
<td>Le Boursiné HUBERT (1986)</td>
<td>Peraluminous granite</td>
<td>1- arsp, native Au, Q, pyr</td>
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<td></td>
<td>Bennevent BRIL and NENERT (1986)</td>
<td>Gneiss and Gueret Granite</td>
<td>2-sulfosalts + native Au</td>
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<td>Haut Allier BRIL and BEAUFORT (1987)</td>
<td>Metamorphic series</td>
<td>1- po, löll, Q</td>
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<td>Vaultry This work</td>
<td>Gneisses, Bi-granite, and peraluminous granites</td>
<td>2- löll, Cpy-Nat Au</td>
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<td>Nouic This work</td>
<td>Gneisses</td>
<td>Q-mispickel/nat Au</td>
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<td>Ambazac This work</td>
<td>granite</td>
<td>(W-Sn)/Q-nat Au</td>
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<td>Janaillac This work</td>
<td>granite</td>
<td>Q-nat Au-sulph</td>
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<td>La Bélière This work</td>
<td>Mica-schist series</td>
<td>Q-arps-sph-nat Au (gal)</td>
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<tr>
<td>U</td>
<td>Penarren CATHELINEAU (1981,1984)</td>
<td>Blastomylonites graphitic quartzites</td>
<td>Q1- pitch</td>
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<td>Retail CATHELINEAU (1981)</td>
<td>Bi(Chl)Mu gneisses</td>
<td>1-pitch-pyr</td>
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<tr>
<td></td>
<td>Margnac - Fanay LEROY (1978)</td>
<td>Peraluminous granite episyenite</td>
<td>2-pitch-cpy-selen/sulph</td>
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<tr>
<td></td>
<td>Le Bernardan LEROY (1984)</td>
<td>Quartz depleted peraluminous granite</td>
<td>pitch</td>
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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 UO₂ 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 $-81^\circ$C and CO$_2$ by melting of a solid below $-56.6^\circ$C. Molar fractions of CO$_2$, CH$_2$, H$_2$S 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; CATHELNEAU 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 BONNEMAZON 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$_2$O 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$_2$O-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, Janallac) (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 probably 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$_2$O (± CO$_2$, CH$_4$) fluid from the first stage was trapped at higher pressure than that prevailing during the second stage.
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Fig. 2. — Tm CO₂-Th plot for fluid inclusions from La Bellière quartz veins. Inclusions are located in recrystallized quartz contemporaneous of gold + sulphides deposition.

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Fig. 3. — Tm H₂O-Th plot for fluid inclusions from Ambazac, Vaulry, Nouic and Janaillac gold bearing quartz veins.

(CO₂, CH₄ 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 co-genetic 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 (CO₂, CH₄) since gas clathrate was not observed during microthermometric studies (Table 2). CO₂ was only found in quartz grains from the granite hosting U mineralization 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, fO₂, fS₂ 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
minerals show that \( f_0^2 \) 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 \( f_0^2 \)-temperature diagram (Fig. 6). At Le Bourneix (calculation by Dubessy, Touray, 1987) and at La Bèllièvre (this work) \( f_0^2 \) 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 \( f_0^2 \) was close to that fixed by the hematite-pyrite boundary, or that \( f_0^2 \) was compatible with the hematite stability (Figs. 4 and 5). Thus, in both cases of high and low temperature Au deposits, \( f_0^2 \) 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.

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**Fig. 4.** Projection of fluids associated with Au and U showings in the log \( f_0^2 \)-\( f_2 \) plane (\( T = 200°C \), \( \Sigma [As]_{tot} = \text{cst} \)).

**Fig. 5.** Projection of fluids associated with U, Au and Sn-W in the log \( f_0^2 \)-log \( f_2 \) plane at 400°C and 1 kbar (from Bowers et al., 1984 and Dubessy et al., 1987; modified).
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Fig. 6. — Uranium oxide stability field (NGUYEN TRUNG, 1985) and fluids associated with U, Au and Sn-W deposits in a log $f_{O_2}$ - temperature diagram at 1 kbar (completed from DUBESSY et al., 1987).

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 $f_{O_2}$).

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 $\text{AuCl}_2^-$ at low temperature, under oxidizing conditions. SEWARD (1973) demonstrated that $\text{Au(HS)}_2^-$ and $\text{Au}_2\text{S(HS)}_2^-$ are the main Au species in solution, at $f_{O_2}$ 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 $f_{O_2}$ - 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 $f_{O_2}$, whilst it is soluble as bisulfide complexes in a large pH range, at low $f_{O_2}$, in environments where $\text{H}_2\text{S}$ or $\text{HS}^-$ are the main sulfur bearing species.

Considering that the maximum solubility of gold is around neutral to slightly basic pH at low $f_{O_2}$, three different mechanisms may be proposed for gold deposition: a) fluid

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<th>Au</th>
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<tr>
<td>acid</td>
<td>neutral</td>
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<tr>
<td>low</td>
<td>high</td>
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<td>high</td>
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<tr>
<td>$f_{O_2}$</td>
<td>1) 150-250</td>
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<td>$f_{S_2}$</td>
<td>2) 300-400</td>
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<td>$T^\circ C$</td>
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Fig. 7. — $f_{O_2}$ - pH diagram applied to gold species in solution with indication of stability fields of iron species and silicates ($T = 250^\circ C$, $f_{CO_2} = 1$ atm; from ROMBERGER, 1986, simplified).
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 CO₂ and CH₄ 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 fCO₂ (in addition to pH, aFe, aMg), it does not necessarily imply a high fCO₂. On the other hand, the presence of CO₂ observed in very different amounts within fluid inclusions, is actually difficult to consider as a factor controlling gold solubility, at a given fO₂. Thus, the presence of CO₂ and CH₄ is important through their fO₂ 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 H₂O - UO₂ system, at fixed temperature, the UO₂ solubility depends on pH and fO₂. Under fO₂ 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 fO₂ 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 phosphate) occurs.

Experimental work and calculations (Nguyen Trung, 1985) demonstrate that under the above mentioned conditions (neutral pH, high fO₂, moderate fS₂; 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 fO2, fS2, 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 fO2 values (fO2 > 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 Bélière, La Lucette, ...). This relation between some Au and Sn-W mineralizations is not surprising, 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 fO2 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 metallocenic 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.

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