Fluid flows and metal deposition near basement/cover unconformity: lessons and analogies from Pb-Zn-F-Ba systems for the understanding of Proterozoic U deposits

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Fluid flows and metal deposition near basement / cover unconformity: Lessons and analogies from Pb-Zn-F-Ba systems for the understanding of Proterozoic U deposits

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ABSTRACT

Fluid circulation at the basement / cover unconformities is of first importance for mass transfer and especially Pb-Zn, F, Ba, and U–deposits. This is typically the case for world-class Proterozoic U deposits (Athabasca, Canada, Kombolgie, Australia, Franceville,Gabon) basins, which show many similarities with younger Pb-Zn-F-Ba systems, where fluid mixing near the basement/cover unconformity is one of the key factors for the ore formation. Data have been compiled in order to compare a series of parameters (time gap between basin formation and metal deposit, origin and nature of the ore fluid, temperature of fluid end members in the case of mixing, style of migration). Pb-Zn Irish Paleozoic deposits, F-Pb-Zn-Ba deposits related to extensional tectonics from Spain, western France and Silesia and fluid movements related to a continental rifting on the example of the Rhine graben, have been considered.

Results show great similarities in all fluid systems: i) a wide range of fluid salinity indicating the lack of homogeneity of fluid chemistry at the scale of the reservoirs, ii) the deep penetration of brines through faults and dense networks of microfractures within the basement below the unconformity, iii) local fluid-rock interaction yielding to porosity increase and significant fluid chemistry changes, iv) a pulsatory fluid regime during fluid trapping, v) anisothermal fluid mixing revealed by a systematic temperature gap between the brines and the recharge fluids, vi) major stages of fluid movements facilitated by discontinuity opening in relation with later tectonic / telogenetic stages linked to major geodynamic events without relationships with sedimentation and burial, at the exception of a few cases characterized by the synchronous production, penetration of surface brines and ore genesis. The conditions of burial, penetration of brines in the Archean basement, suggest the need of thermal convection for the brine movements which could be linked to extensional tectonics.

Key words : fluid movement, brines, metal, unconformity, extensional tectonic

INTRODUCTION

Fluid circulation at the sedimentary cover basement unconformity is of first importance for mass transfer and especially Pb-Zn, F, Ba, Ag and U – ore deposits. In most cases, either the present day depth of the unconformity occurs at a few hundred metres or a few kilometres at maximum and indicating the loss of significant part of the sedimentary formations, or it is no more present. Such a loss of information on the overlying basin complicates largely the interpretation of the fluid and mass transfer processes including the most critical stages of ore formation. This is typically the case of the major U world – class deposits hosted by the Proterozoïc basins. Such deposits occur close to the unconformity (U/C) between a Proterozoic sandstone cover and an Archean to Lower Proterozoic metamorphic basement. Main host basins are located in Saskatchewan (Athabasca Basin, Canada), Northern Territories, Australia (McArthur Basin, Alligator River Uranium Field), Oklo (Gabon). In all cases, only a minor part of the basin is preserved, as more than 5 to 7 kilometres above the unconformity are now eroded.

Although the nature of the ore process has been investigated since more than 30 years several aspects of the ore genesis remain not fully understood (references in Kyser & Cuney, 2008). Genetic models invoke large-scale circulation of basinal fluids and U uptake either from monazite-zircon paleoplacers in mid-Proterozoic sandstones, or from the basement, this yielding to two contrasted models: i) direct penetration of basinal fluids into the basement with U reduction at the contact with reducing lithologies and /or reducing fluids (Hoeve & Sibbald, 1978), ii) penetration of brines into the basement, U uptake in the basement itself and U deposition favoured by fluid mixing at the vicinity of major faults (Richard *et al.* 2010) There are several uncertainties on the genetic model of deposition, in particular on the relative timing and relationships between U deposition and geodynamic processes, the extension of the fluid movements, the relative role of water rock interaction versus fluid mixing for the uranium deposition.

The nature of the fluids, in particular high salinity Na-Ca brines with variable Na/Ca ratios (Derome *et al.* 2003, 2005, 2007, Richard *et al.* 2010), the evidence of brine mixing, the penetration of the sedimentary brines in the basement, the localisation of the fluid migration near the unconformity display however, similarities with fluid movements such as those reported in MVT like deposits (Leach *et al.* 2005) or more generally carbonate hosted Pb-Zn ores and F-Ba deposits at the vicinity of the unconformity. Although such an analogy was not proposed in the past for such deposits, the similarities between rather old, Mid-Proterozoic U deposits and more recent fluid-rock systems in particular Mesozoic Pb-Zn-F-Ba deposits from western Europe have encouraged us to develop a comparative study between the two families of deposits.

The understanding of the Pb-Zn-F-Ba deposits was largely improved by the direct study of paleofluid chemistry, and the consideration of the time relationships between burial, diagenesis, fluid circulation related to metal deposition and the geodynamic context. These data, generally dispersed in the literature, or gathered together only for specific types of deposits, have been thus compiled and compared on the example of major examples from western Europe: Pb-Zn Irish Paleozoic deposits, F-Pb-Zn-Ba deposits related to extensional tectonics, associated with the Atlantic ocean and Gascogne rifting, in Spain, western France and Silesia). In addition, an intracontinental rift, the Rhine graben where Trias formations and the basement were affected from Oligocene to present day times by large-scale fluid flow, was also considered (Table 1). Besides, major accounts to the understanding of fluid mixing were also considered from the literature in this comparative work. The geodynamic context and style of fluid movement, although largely submitted to discussions in the past 15 years, are much better known than in Proterozoic systems and appears better constrained. The main goal of this paper is thus an attempt to compare Proterozoic basins, hosting giant U-deposits, (the Alligator River Uranium Field in Australia, the Athabasca basin in Canada and the Oklo deposit in Gabon) with the reference Pb-Zn-F-Ba ore deposits for which the geodynamic context, and style of fluid movement are better known than in Proterozoic systems. The objective

was to get key information and models on ore fluid movements in the upper lithosphere and to evaluate their applicability to U deposits.

GIANT U DEPOSITS RELATED TO THE UNCONFORMITY BETWEEN PROTEROZOIC BASINS AND THEIR ARCHEAN BASEMENT

The discovery in the 1980-1990's of several giant U deposits near the unconformity between Proterozoic basins and their basement, in particular in the Athabasca Basin, Saskatchewan, (Canada) and in Alligator River Uranium Field (ARUF), McArthur Basin, Northern Territories, (Australia), has encouraged a rather systematic evaluation of the nature of the ore fluids and of their origin. Such deposits occur close to the unconformity between a Mid-Proterozoic sandstone cover and an Archean to Lower Proterozoic metamorphic basement (see references in the synthesis by Kyser & Cuney, 2008). Genetic models invoke large-scale circulation of basinal Na-Ca rich fluids (Pagel, 1975; Pagel & Jaffrezic, 1977; Pagel *et al.* 1980; Derome *et al.* 2003, 2005, 2007, Richard *et al.* 2010).

There are several uncertainties on the general model of deposition, in particular on the timing of U deposition. Between the 1.7-1.8 Ga, the ages for the sedimentation and the Grenville orogen, a few geodynamic events have occurred but without clear effects on the basin which is located away from the major deformations. Since the 80's for instance, ages of the U-ores for Proterozoic basins, have been successively made older from 1.1 Ga up to 1.6 Ga due to the improvement of analytical techniques which made possible the analysis of smaller and smaller amount of ore considered as devoid of Pb loss due to coffinite alteration or uraninite recrystallisation (Alexandre *et al.* 2009). Thus, in Canada, depending on the age of the U-deposit, the Grenville, Berthoud (Sims & Stein, 2003), or Mazatzal (Amato *et al.* 2008) orogens have been successively considered as the cause of fluid movements or more recently as the cause of recrystallization of primary ores (Alexandre *et al.* 2009). Difficulties to relate precisely a fluid event to a geodynamic

event characterized by a specific fluid signature and migration style complicate the proposition of a metallogenic model.

Alligator River Uranium Field (Australia)

The Kombolgie sub-basin (northern Territory, Australia) overlies a basement consisting of Archean and Early Proterozoic granito-gneisses (Nanambu Complex), the Kakadu Group gneisses and quartzites, and the metasediments of the epicontinental Cahill Formation. All these rocks underwent the Barramundi and the Top End orogenies between 1870 and 1800 Ma (Page & Williams, 1988). A thick (up to 1800 m presently preserved) unmetamorphosed detrital sequence composed of fluvial and aeolian sandstones (the "Kombolgie Sub-Group") unconformably overlies the crystalline and metamorphic basement and is dated 1822 and 1720 Ma (Sweet *et al.* 1999). The youngest members of the Kombolgie Sub-group were deposited in marine conditions, as suggested by the occurrence of glauconite and halite crystal casts (Kyser *et al.* 2000), and by stromatolitic and evaporitic dolostone-sandstone occurring in the McKay formation (Rawlings 1999). All uranium deposits are located in basement rocks and ages are comprised between 1600 and 1650 Ma for the Jabiluka, Nabarlek and Koongarra deposits (Maas 1989; Sm-Nd, Rb-Sr data on uraninites, references in Kyser & Cuney, 2008).

The Kombolgie basin and its basement are characterized by hydraulic breccias developed frequently along faults. Breccias consist of angular blocks of sandstones cemented by nice euhedral drusy quartz crystals of rather exceptional size up to 10 cm at their base. Two brines and a low salinity fluid showing clear evidence of mixing with the brines (Derome *et al.* 2003) are observed in the drusy quartz crystals from sealed faults (Table 2). The two brines consist of: i) a Na-rich fluid with Tm ice ranging from -15 to -35°C (mode around -25°C) yielding to chlorinity close to 5 moles/kg H_2O and a Th between 90 and 160°C (mode: 135°C). Na/Ca ratios determined by Laser Induced Breakdown Spectroscopy (LIBS) are around 8; ii) a Ca-rich fluid characterized by Tm ice ranging from -35 to -52 °C (mode at -42°C and chlorinity between 5.6 and 6 moles/kg H_2O) and Th between 100 to 140°C (mode 110°C). Na/Ca ratios are closed to 0.1. The low to moderate salinity fluid display Tm ice in the range of -0.3 to - 10°C (mode at -2.5°C) and Th between 115 and 155°C with a mode at 140°C. Na/Ca ratio are variable in the range of 1 to 10.

The Athabasca uranium deposits

The Athabasca basin lies on Archean to Paleoproterozoic basement which consists of gneisses, metapelites and mafic to felsic intrusions affected by the Thelon –Talston (1.9 to 1.8 Ga) and Trans–Hudson (1.9 to 2.0 Ga) orogenies. The sedimentary sequence is now around 1500 meters at maximum but is though to have reach 5 km based on pressure-temperature estimation from fluid inclusion studies (Pagel 1975, Derome *et al.* 2005). The sandstones as well as the basement display local quartz dissolution and precipitation and a major Mg-silicate alteration assemblage (Mg-rich di-octahedral chlorite (sudoite), Mg tourmaline (dravite) and Mg-illite). Ages proposed for the mineralization has been estimated in the range of 1510 to 1540 Ma (Cummings & Krstic, 1992, Alexandre *et al.* 2009). In quartz and carbonate veins, two to three phase inclusions are observed and consist in two brines: a sodium rich brine (Tm ice from -15 to -30°C) and a calcium rich brine (Tm ice from –30 to –55°C) which have circulated and mixed at the base of the basin and within the basement at the time of the formation of the uranium mineralisations at temperature close to 150 ± 30 °C (Table 2). The calcium rich brines were formed by interaction of the sodium-rich fluid interacting with the basement rocks. Both brines were originated from evaporated seawater as shown by the low Cl/Br ratios from Mc Arthur River, the Cl concentrations and other recent isotopic data including ^{37}Cl (Derome *et al.* 2005, Richard *et al.* 2009) (Fig. 1).

Oklo natural reaction zones (Gabon)

The Francevillian sedimentary series unconformably overly the Archean crystalline basement represented by the north Gabon massif in the north and the Chaillu massif in the west (Gauthier-Lafaye, 1986, Gauthier-Lafaye & Weber, 1989). U/Pb, Rb/Sr and K/Ar age determinations of the granitoids (K-rich plutonites and diorites) from the Chaillu massif yield ages ranging from 2.88 to 2.4 Ga (Bonhomme *et al.* 1982). The Francevillian series is a 1 to 4 km thick, unmetamorphosed sequence of clastic and volcanoclastic sediments. The lithostratigraphic succession from the bottom to the top consists of: i) conglomerates and fine to coarse sandstones deposited in a fluvial to deltaic environment, ii) fine-grained marine sediments, mainly pelites and black shales, iii) massive dolomite and cherts

interbedded with black shales, iv) ignimbrites and epiclastic sandstones with interbedded shales (Fig. 2).

Numerous quartz veins, often associated with wall-rock alteration, attest to significant fluid movements along fractures during diagenesis of the Franceville basin. Diagenesis of these formations resulted in a silicification of detrital quartz grains and formation of authigenic illite and chlorite in the matrix (Gauthier-Lafaye, 1986, Gauthier-Lafaye & Weber, 1989). Fluids were related to the formation of diagenetic minerals, generation of U ore deposits and the migration of hydrocarbons. The extensional fractures in the Archean basement and the sandstones are filled by a quartz- chlorite – calcite – sulphide and a U mineral assemblage (Mathieu *et al.* 2000). Mineralisations are dated around 1960 to 2050 Ma (Holliger, 1988).

Fluid circulating during the quartz - chlorite - calcite - sulphide and U mineral stage can be divided in three major types with the following characteristics (Mathieu et al., 2000): i) high salinity Ca-Na rich brines displaying large Tm ice variations but showing two groups from -63 to – 46°C (Ca dominated fluid and Na/Ca ratio around 0.5) and from -36 to -27°C (Na dominated fluid and Na/Ca from 2 to 9) (Table 2). Th ranges from 95 to 155°C. The highest salinity fluid displays the lowest Th; ii) moderate salinity fluids with Tm ice in the range of -24 to -14°C and Th in between 90 to 160°C. These fluids are Na dominated fluids with Na/ Ca ratio from 2 to 5.5. iii) low salinity fluids having Tm ice in the range of –1.3 to -5.5°C and Th between 100 to 175°C. Na is the major cation found in these fluids using LIBS, Ca being detected in some inclusions yielding to Na/Ca around 25.

BRINE MIGRATION IN RELATION WITH OCEANIC RIFTING

The Poitou High and Pb-F-Ba occurrences of the North-Western Massif Central

Significant fracture and porosity sealing characterizes the sedimentary cover-basement interface in the north-western margin of the Aquitaine basin (France) close to the north-western part of the French Massif Central. The Poitou High area is located at the north-western border of the French Massif Central, corresponding to the northern edge of the Aquitaine Basin. Below a ca. 150 m thick sedimentary cover consisting of marine Lias and Dogger formations, the basement lithology is

dominated by plutonic rocks from the “Tonalitic Lineament” of the Limousin (Peiffer 1986; Shaw *et al.* 1993) containing multiple intrusions of medium-K calc-alkaline tonalites and granodiorites dated around 350-360 ± 5 Ma (U-Pb on zircons; Bertrand *et al.* 2001). Dolomite, calcite, fluorite, barite and quartz constitute most of the fracture fillings attesting fluid circulation either in the sediments or in the basement (Fourcade *et al.* 2002, Boiron *et al.* 2002, Cathelineau *et al.* 2004). These processes (Fig. 3) are large scale as shown by the similarities of mineral sequences, fluid types and general features of most of the F-Ba-Pb-Zn deposits located at the basement-sedimentary cover interface all along the margins of the French Massif Central, (Munoz *et al.* 1995, 1999, Ziserman 1980) as well as U reworking at Le Bernardan, (Patrier *et al.* 1997).

Microthermometry and Raman microprobe investigations show the existence of a single dominant fluid type (H_2O-NaCl-KCl-$CaCl_2$ ± $MgCl_2$) in all primary two-phase fluid inclusions from all the minerals of the infilling sequence. They show a range of final ice melting temperatures from -3.8°C to -30.2°C (ice ± hydrohalite melting) (Table 2). The highest measured chlorinity is around 5.2 moles/kg. The fluids are Na-dominated with a Ca contribution as indicated by the Na/ Ca ratio around 4 ± 1 measured by LIBS. Homogenization temperatures are between 65°C and 130°C for quartz and slightly lower for dolomite (90-115°), barite (85-115°C), fluorite (85-100°C) and calcite (65-100°C) (Boiron *et al.* 2002).

Albigeois fluorite deposits

The most important fluorite district in France is considered to have formed during Mesozoic times (150 Ma, Bonhomme *et al.* 1987) in relation with a third stage of extensional tectonics occurring much after the main rifting period of the Atlantic ocean, and before the Gascogne gulf rifting considered as coeval of the Aptian-Albian ages. Munoz *et al.* (1999) put forward a model of continental brine circulation (salinity: 20-26 wt % eq. NaCl, Ca-(Mg)-Na brines and Th between 85 and 170°C) (Table 2), deeply in the basement and the formation of ores along faults where the fluorite deposited as a consequence of temperature drop. Although the main ores

precipitate from waters having a $\delta^{18}O$ of around 0 to 3.2 ‰ and D/H in the range of –15 to –63 ‰, authors considered that isotopic features are derived from meteoric waters having underwent an isotopic shift by interaction with host rocks. This is the main argument in favour of the continental origin of the brines. It can be also noted that recent paleogeographic reconstruction and fission track data tend to indicate that the French Massif Central was in great part covered by the sea during Lias and Dogger times.

The Malines Pb deposit

The Malines Pb deposit in Cevennes (South-eastern part of the french Massif Central) is an interesting example of a rather complex history, subject of several controversies because hosted in old series (Cambrian in age) but affected by a series of thermal - diagenetic - hydrothermal events that were difficult to date. Most dates are relative and do not concern strictly the ores. Ambiguous textural relationships attributed either as primary early diagenetic textures (karts infilling below the inconformity) or to epigenetic replacement, clay ages (Clauer & Chaudhuri, 1995) are interpreted as synchronous of the main fluid stage and considered as general diagenetic stages without direct relationships with the ore deposition (Leach *et al.* 2001). The remagnetization ages (60-50 Ma) are presented as related to chemical process in direct link with the ore stage (Rouvier *et al.* 2001) but as indicated by Muchez *et al.* (2005) no definitive argument of a direct genetic link with the deposit of great mass of the Pb ores is given. The best relative chronological indicators are based on geology (crosscutting relationships between ores and sedimentary formation) and tectonics and put forward a post-Triassic age at minimum, the most probable being an early Jurassic age (Macquar & Lagny, 1981, Macquar *et al.* 1990, probably post-Hettangian, (Lotharingian to Bathonian) following Charef & Sheppard, 1988) for the main ore stage and probably Kimmeridgian as sulphide rich layers (sedex) are observed locally (Ming An et al. 1995). This does not preclude an earlier pre-concentration stage. The main ore stage is characterized by the mixing of a metal-rich brine (150°C), considered as a connate water related to the dewatering of the basin by Charef & Sheppard (1988), but which could be also linked to fluid-rock interaction within the anhydrite-gypsum Triassic series overlying the mineralized Cambrian formations, and a cooler dilute fluid (Table 3). As in many other occurrences from the southern Massif Central, the thickness of the sedimentary

overburden cannot explain entirely the reached temperatures, and Charef & Sheppard (1988) conclude to the existence of localized thermal anomalies, in part caused by the fluid movements from deeper parts of the Rhône basin which thickness reached up to 8 km.

Mesozoic Fluorite veins (Spain)

Fluorite veins developed in the Catalan costal range in faults affecting a basement dominated by a series of calkalcaline granodiorite - monzogranite overlained by Triassic sediments including Keuper evaporites. Piqué *et al.* (2008) conclude to the deep circulation of brines issued from the leaching of Mesozoic halite and gypsum series by seawater and/or meteoric waters, within the basement where brines uptook metals and gained K, Ca, Sr and Ba. Resulting Na-Ca-Cl (K-Mg) brines are thought to have circulated during a late Jurassic-Early Cretaceous rifting stage (dated 137 Ma) related toextensional tectonic and to the opening of the Atlantic ocean (Piqué *et al.* 2008). The authors mention that this period is characterized by elevated crustal temperatures during Mesozoic which can explain localized convection (Juez-Larré & Andriessen, 2006). Although rich in metals, ore fluids deposited fluorite, probably in relation with fluid mixing owing the large range of salinities, but were not able to deposit metals due to the S content of the fluids following Piqué *et al.* (2008).

The fluorite deposits in Asturias (Northern Spain) are hosted by Permo-Triassic and Paleozoic rocks. Mineralisations occur in breccias and fractures and consist of fluorite, barite, calcite, dolomite and quartz and small amounts of sulphides. Mineralisations result of fluid mixing between deep brines with surficial waters. Fluid movements and fluorite deposition occurred between late Triassic and late Jurassic times (Sm-Nd age on fluorite at 185±28 Ma, Sanchez *et al.* 2010) in relation with rifting events associated with the Atlantic Ocean opening. Downward penetration of brines into the basement, infiltration of surficial fluids and upwards brine migration into the Mesozoic basin margins are the major processes to explain the fluorite deposition in areas of fluid mixing (Sanchez *et al.* 2009).

The Pb-Zn deposit in Spain (Catalan coastal range and Basque Cantabrian area)

In the Maestrat basin, Zn-Pb deposits occurred in dolomitized Aptian limestones in the margins of the half–graben shape Penyagolosa sub-basin. Metal deposit is thought to be the result of the mixing between low temperature – low salinity (although it reaches up to 15 wt % eq NaCl) resident fluids enriched in sulphur may be migrated from below and issued from thermochemical sulphate reduction, and a high salinity brine of around 80-130°C supposed to be an evaporated seawater issued from the sabkha-like environments from Late Cretaceous/Early Paleocene, as suggested by the age of 62 ± 0.7 Ma for the mineralization process (Grandia *et al.* 2000, 2003a). The small thickness of the series at that time would imply large thermal discrepancies between the entering of fluids and the series, and probably larger convecting cells than those suggested by the authors in their sketch drawings, may be more than 4 km from the surface to reach temperatures of 130°C. In that case, the penetration and ascending migration of brines would be synchronous of the rifting stage (Fig. 4).

In sediment hosted Zn-Pb deposits of the Basque Cantabrian basin in Northern Spain, fluid mixing have been demonstrated based on microthermometric data and Na-K-Li-Cl-Br systematics on fluid inclusions (Grandia *et al.* 2003b). Fluids of different origins were involved in the mineralizing process: i) brines (25 wt % eq. NaCl) issued from seawater evaporation, ii) brines dissolving halite closed to salt domes, iii) low salinity fluids (seawater or fresh water) considered as diluted fluids.

The carbonate hosted Zn-Pb in Upper Silesia

Zn-Pb mineralizations occur on both sides of a Permian graben in Devonian to Jurassic rocks, especially in an early diagenetic/epigenetic dolosparite. More than 90% of the ores are hosted by the dolomitized series from Muschelkalk, but the age of the process is considered to be at less older than the upper Triassic, and from the lower Cretaceous as suggested by the age of 135 ± 4 Ma obtained on sphalerite. Ores form from highly saline Na-Ca brines (20-23 wt. % eq. NaCl, Table 2). Brines are thought to be evaporated seawater from Permian-Trias age which penetrated deeply in the Carboniferous units from the basement where they uptook metals and resulted through albitisation in Ca enriched brines. The expulsion from the basement would be much later during their extensional stages contemporaneous of the opening

of the Northern Atlantic ocean (Fig. 5). Following Heijlen *et al.* (2003), brines (70-160°C) are not considered to have migrated through a gravity driven flow model as originally suggested by Leach *et al.* (1996) but expelled along deep seated faults affecting both basement rocks and their overlying sedimentary basins, in relation with extension through a dilatational pump mechanism following the seismic model of Muir Wood & King (1993).

THE IRISH Pb-Zn DEPOSITS

Irish deposits, which include Navan the largest Zn resource in Europe, are considered to have been formed by the penetration of evaporated seawater, the acquisition of metals by water rock interaction deeply in the continental crust down to 5 to 10 km (Russel 1978), and the mixing of this ascending brine with surficial brines rich in H_2S issued from bacterial activity within the lower carboniferous limestones overlying the lower paleozoic basement, in fractured zones (Blakeman *et al.* 2002, Wilkinson *et al.* 2005). This model emphasizes the role of rift zones and local extensional tectonics and considers the topographic flow models proposed by Hitzmann & Beaty (1996) as unsuitable for the Irish deposits. It puts forward also the role of thermo-haline density driven convection as the main engine for the fluid movement (Fig. 6). The age (350 Ma, in Wilkinson *et al.* 2005) of these deposits is in favour of a model of brine circulation nearly coeval with their formation as Mississipian evaporites which are present in the sedimentary sequence, a feature at variance of most other deposits presented in our comparative study. The relationships between the process of seawater evaporation and the heating mechanism of the surface brine is however not fully elucidated in terms of paleogeography, the extension of the Mississipian sea controlling the area and volume of evaporated seawater formed at that time and able to penetrate form the surface, and depth-temperature relationships controlling the possible temperatures reached near the marine sediment – seawater interface.

INTRACONTINENTAL RIFTING: THE SOULTZ-SOUS-FORÊTS GEOTHERMAL AREA, RHINE GRABBEN (EASTERN FRANCE)

The Soultz-sous-Forêts geothermal plant is located in the Rhine Graben which constitutes part of the continental rift extending from Frankfurt (Germany) to Basel (Switzerland). It formed during the Oligocene by large-scale extension related to

mantle upwelling (Rousset *et al.* 1993). The north-western part of the Rhine Graben is filled by an asymmetric sedimentary cover ranging from Triassic to Oligocene overlying an Hercynian fractured granitic basement. The sedimentary cover is composed of thick Tertiary series, mainly represented by marls and clays. It overlies Triassic sediments which are subdivided into the three classical lithofacies: Keuper, Muschelkalk and about 300 m of Buntsandstein sandstones (Fig. 7). The main granite body is an Hercynian monzogranite dated at 331±9 Ma (U-Pb method, Alexandrov *et al.* 2001) with no equivalent at the surface.

At Soultz-sous-Forêts, past to recent fluid movements are recorded by series of healed or sealed micro- to macrostructures, which provide evidence of a rather continuous self-sealing of the open space (Dubois *et al.* 1996, Smith *et al.* 1998, Cathelineau & Boiron, 2009). This circulation is believed to be at the origin of drastic changes in heat transfer in this area, explaining that the present day temperature gradient decreases from 0.09-0.10°C.m-1 in the sedimentary cover to unexpected values of 0.04-0.01°C.m-1 in the upper part of the fractured granites (Clauser & Villinger, 1990, Person & Garven, 1992). In drill holes, the sedimentary cover and the granite display altered zones characterized by dense network of veins, and alteration of the host rocks (Ledésert *et al.* 1999, Sausse, 2002, Sausse *et al.* 2006). Veins are filled by quartz or barite and healed microfissures reveal a successive self-sealing of the rocks.

Previous studies of paleofluid circulation in EPS-1 (Exploration Puits Soultz) drill hole have shown the circulation of moderate to highly saline fluids either in the sedimentary cover and in the basement down to 2200 m depth (Dubois *et al.* 1996, 2000) and in the GPK2 (Géothermie Puits Kutzenhausen) deep drilling in the basement up to 5057 m (Cathelineau & Boiron, 2009). In the two studied zones either in sandstones and granite closed to the unconformity or in the deep granite samples, fluids show a large range of Tm ice: -31.6 to -0.2°C in the shallowest levels and from -24.6°C to -0.1 in the deep granite. These data indicate a probable fluid mixing between two end-members: a brine enriched in divalent cations and a rather dilute fluid. All inclusions homogenized to the liquid phase between 100°C and 184°C. The measured Th range between 100°C and 165°C for the shallow studied zone and from 150°C and 185°C at 5057m. The Tm ice - Th diagrams (Fig. 8) show that the fluid inclusions with the highest salinity (i.e. the lowest Tm ice) have the lowest homogenization temperatures, and the low salinities correspond to the highest

Th. The mixing trend found at 5057 m is sub-parallel to the mixing trend found for samples from a depth ranging from 1430 m to 2207 m. The two extreme salinities are similar in both cases, but a difference in Th of approximately 35-40°C is found between the two sets of samples.

Although not precisely dated, a series of F-Ba showings are observed on both sides of the Rhine graben (Vosges and Schwartzwald) in the basement and the margins of Mesozoic basins. A part of them have been considered on the basis of structural relationships as Tertiary to recent and linked to the graben activity (Lüders 1994, Franzke & Lüders, 1993), or linked to earlier rifting stages during Mesozoic. In Schwartzwald district, fluorite-barite-quartz vein formation are related to the circulation of seawater derived fluids having strongly interacted with the basement where they gained chlorine and calcium (21-26 wt % eq. NaCl) and mixed along faults with surface-derived meteoric dilute fluids at temperature in the range of 100-180°C (Lüders & Franzke, 1993, Baatartsogt *et al.* 2007).

PALEOFLUID COMPOSITIONS AND ORIGIN

A great part of the data was already published in each case study (references below) but these data are homogenized to illustrate the main differences or similarities between main fluid types, in order to compare to literature data on reference deposits. Microthermometric data, cation and halogen rations are compared and presented in figures 8 to 12 and table 2.

Chlorinity and Tm ice ranges

A remarkable feature of a part of the study cases, eg the Oklo and Northern territories U deposits, the F-Ba deposits from Massif central, and the Rhine graben examples is the nearly continuous trend of chlorinity between two end-members (Fig. 8 and 9): a dilute end-member with the highest Tm ice values close to 0°C, and a brine end-member. Fluid inclusions with variable Tm ice within a same quartz overgrowth, or set of fluid inclusion planes (FIP), were found and considered as nearly coeval, or corresponding to the same fluid event. This indicates that at each increment of sealing or trapping within a same vein, fluids trapped reflect the compositional inhomogeneity of the migrating fluids. Such variations are particularly well shown by the Soultz veinlets and deep granite sample FIP, formed within a

relatively short period after Oligocene under nearly constant temperature conditions but characterized by inclusions with almost all chlorinities from brines to dilute fluids. In the western Massif Central and at Soultz, the lowest Tm ice values are around –32°C, as fluids are NaCl dominated brines. The high chlorinity brine with low Na/Ca ratios were mostly found in Proterozoic basins. In the later, two contrasted cases were observed: i) the Athabasca basin where brines with similar chlorinity and large variation in Na/Ca ratio resulting in a large Tm ice range (-6 to -30°C) do not show dilution evidences and ii) the Northern Territories U deposits (Australia) and Oklo where mixing of two brines is also accompained by a dilution.

Na/Ca-Na/K ratios

One of the most striking features of the inclusion fluids from the studied U-Pb-Zn- F-Ba deposits is their low Na/K and Na/Ca ratios. Brines with low Na/Ca ratio were also reported in more recent systems such as waters from the KTB (Möller *et al.* 2005) but with much lower chlorinities (Fig. 10).

Both ratios reach values near 1 in most of evolved brines, and a large part of the paleofluids have Na/K ratio below 20 with mean values lower than 10 and Na/Ca ranging from 1 to 10. The low Na/K ratio are much lower than those predicted by Na-K geothermometers or found in hydrothermal systems for a temperature range of 90 –150°C, e.g. values ranging from 50 to 150 (Verma & Santoyo, 1997).

Halogen ratios

In most studied cases, a part of the Cl/Br ratios are mostly lower than that of seawater and may correspond to brines having passed the halite saturation, and in some instances the epsomite saturation (Fig. 11). It can be noted that data points were calculated for mean values as the bulk leachates mix all fluid inclusions, but that the chlorinity range is larger in individual samples. Low Cl/Br ratios are typical of primary brines, e.g. brines issued from seawater evaporation. In Mid-Proterozoic basins such as those from Northern Territories, Mc Arthur (Canada), Cl/Br values are low whatever the chlorinity, in the range of 100 to 400, and not scattered. In other Athabasca deposits, a rather wide range of values from 200 up to 800 have been measured (Richard, 2009). At Soultz or in the NW Massif Central, Cl/Br ratio are more scattered, indicating either a mixing of primary brines having a large range of

Cl/Br ratios, a rather improbable hypothesis or a mixing of primary brines with secondary brines as data points are significantly above the mixing lines between seawater (or dilute fluids such as meteoric recharge fluids) and an evaporite brine having passed the epsomite saturation. The existence of secondary brines with higher Cl/Br ratio is easily conceivable as dilute fluids or seawater entering the fluid system may have interacted with the evaporite formations as described elsewhere (Hanor & Mcintosh, 2007). Ranges and values of Cl/Br ratios found in ore fluid inclusions in all studied sites is in favour of an evaporitic source for chlorine and of partial to significant mixing of primary and secondary brines. In a few cases, secondary brines predominate (Fig. 12) (Spanish Pb-Zn-F deposits Catalan and Cantabrian coastal range, Grandia *et al.* 2003 a and b, Piqué *et al.* 2008, Sanchez *et al.* 2009).

Homogenisation temperatures and distribution of Tm-Th pairs

Figures 8 and 9 are a comparison of Tm-Th pairs for a series of studied cases. The common feature to all FI populations is the Tm-Th trend between two end-members: a brine with a Th around 100°C and a dilute fluid end-member with a higher Th, around 30 to 40°C higher than the Th of the brine.

A scattering of Th for a given Tm ice is observed for some FI populations, this being attributed to several reasons: i) unavoidable effects of streching, ii) the presence in U deposits of radiolytic gases such as H_2 which cause generally an increase in Th, a rather common observation in most U deposits, iii) superimposition of non-synchronous fluid populations at different temperatures, iv) fluctuation in fluid pressure above the hydrostatic pressure, a process which can be mostly considered in a deep seated fluid system when the unconformity reaches a depth of 4-5 km.

It can noted that fluid pressure may be estimated from the consideration of the depth of the unconformity at the time of the deposition, assuming the nature of the pressure (hydrostatic or lithostatic). The depth is generally inferred from temperature estimates, considering geothermal gradients and assuming the nature of the fluid pressure. For depths lower than 5 km, the pressure is likely to be hydrostatic, but at lower depths, intermediate or fluctuating pressures could be recorded. This uncertainty of the nature of the fluid pressure makes more difficult the interpretation of Th values. In the case of all trends characterized by a large and continuous range of Tm ice correlated with Th (Soultz, Oklo), it is highly probable that pressures can be

interpreted as hydrostatic. Alternatively, rather large scattering in Th for a given fluid salinity can be interpreted as the result of alternating changes in fluid pressure above the hydrostatic pressure assuming that the temperature was constant. This is the case of Athabasca U deposits.

DISCUSSION

The evolution of the fluid system responsible for the formation of carbonate hosted deposits in the sedimentary basins, and metal deposition in the basement near the unconformity is summarized in the figure 13 and table 3. Main stages are discussed below.

Brine origin

High chlorinities reaching 4 to 6 moles/kg, Cl/Br ratios much lower than the seawater ratio (Cl/Br< 600 molar ratio), indicate a probable primary origin of the brines, e.g., brine issued from the evaporation of seawater. In the case of ores found within an outcropping basement, or in the case of sedimentary basin only known by a thin remaining sequence at the top of the basement, evaporitic brines are mostly suspected on a geochemical basis. Almost no evidence of evaporite or localized relics of such formations is found at present, this being due either to the dissolution of salt since the basin formation, or to the erosion and complete loss of these formations. Secondary brines are also suspected in a number of cases explaining the difficulty to find the pristine evaporite formations. In the case of old systems, such as mid-Proterozoic basins, a great part of the basins is now eroded (more than 3 kilometers following P-T reconstructions, see Derome et al. 2003, 2005), and evaporite formations only found sporadically, frequently at great distances of the mineralized areas. In Australian Mid-Proterozoic basins, a few occurrences are described away from the studied zones such as the evaporitic dolostones in the MacKay formation in the south-eastern part of the McArthur basin (northern territories, Rawlings 1999). In addition, evaporites are very sensitive to leaching, resulting in secondary brines, and these evaporites may not be visible anymore.

In most other cases considered in this paper, evaporites were found or supposed close to the basement (Fig 1 to 7): Hettangian series at the unconformity in the NW Massif Central (Poitou High), Trias evaporites near the unconformity in the Rhine graben, Silesia, most Spanish examples. In the Poitou High, evidences of

evaporites are found at a certain distance or for relics of evaporite layers such as boxworks of gypsum in the case of the Infra-Liassic series, the Hettangian evaporite layers being found at more than 100 km to the south in the Angouleme region, and Trias evaporite even at higher distances. In the Rhine graben, although salt layers are easily identified within the Trias series from Alsace, drill holes did not crosscut salt formations at Soultz. In other occurrences cited, at the exception of the Irish deposits, evaporites from Trias are lying above the basement and can be considered as a key factor of the process. These observations are in favour of a rather wide brine migration away from their “mother” formation.

Why deep penetration of brines within the basement is so important?

Brines – basement rocks interactions: The penetration of basinal fluids within the basement has been previously discussed (Yardley et al, 2000, Cathles & Adams 2005), and described in southern Norway (Munz *et al.* 1995, Gleeson *et al.* 2003), in Spain (Piqué *et al.* 2008), and in various places in Europe (Bouch *et al.* 2006, and see review in Muchez et al. 2005). The depth reached by the brines remains in a great number of cases rather hypothetic as the style of migration. Recent detailed studies of granitoids from Athabasca, and deep samples from the Soultz granite provide some keys for the understanding of the process of brine migration. The deep penetration of brines within the basement through faults is thus asscociated with an intimate fluid invading through the matrix permeability. Dense networks of opened and interconnected microfractures are revealed by the healed brine inclusion plane networks within the basement (granites or granitoïds). Microfracturing such as at Soultz is observed in the whole granite down to 5 km depth (Cathelineau & Boiron 2009), and allow brines to interact deeply with the host rocks. FIP from deep samples are dominated by recent reservoir fluids and fluid salinities depict the full range of mixing between the sedimentary brine and the hot dilute fluids. Thus, either sets of micro-fissures were formed and healed at depth since the Oligocene or the inherited FIP from earlier stages were reopened and healed by the main reservoir fluids.

Such a microfracturing is also found in basement rocks from Saskatchewan (Athabasca basin, Mercadier 2008, Mercadier *et al.* 2009). There, the early microfractures, from the late Hudsonian retrograde metamorphism were reopened and healed by evaporitic brines, indicating a fully pervasive brine infiltration through

rocks. The efficiency of the process needs the formation, or re-opening of microfissures at the time of the brine movements, the healing of the cracks which ensured the trapping of the paleobrines indicating that fissures formed probably during repeated microsismic events. This penetration of the brine in the microfractured pathways is one of the key factors for metal extraction. The studies of brines within the basement rock microfractures are however scarce and would merit further development to generalize such a process.

Metal extraction: The presence of an eroded basement with regolith or weathered surface generally found down to a few tens of meters below the unconformity is the second key factor of the metal extraction: after peneplanation, within the weathered part of the outcropping basement, supergene alteration affects most feldspars and phyllosilicates and their deep alteration is a major cause of element release. Pb and Ba are released from feldspars, F and probably Zn from biotite, U from uraninite in biotite and monazite, and subsequent sorbed onto clays and Fe-Ti oxides and hydroxides. In Western Europe, the main metal reservoir is thus the weathered Hercynian terranes, “peneplaned” at Trias and affected by supergene alteration. The latter produced a thick weathered and oxidized zone, well exposed in basement quarries showing the unconformity (Mauzé-Toarçais for instance, for the Poitou High). Metal can be easily extracted by brines later on, once most of the metal bearers are deeply altered. It can be noted that In the case of Ag and Ni-Co-As deposits from Morocco, the metals are extracted from weathered ultramafic rocks (middle Precambrian) and transported later on by brines during late Trias or early Lias (Essarraj *et al.* 1998, 2005) near the unconformity following the same process. Brines penetrating the weathered basement have all the features (temperature, chloride content) required for an optimal metal solubilisation and complexation, as shown by the increased metal concentrations in fluids at increasing chlorinity and temperature (Yardley, 2005). The high metal concentrations (Cu, Pb, Zn, Fe, Mn, …) of sedimentary brines was reported in most carbonate hosted base metal deposits (Heijlen *et al.* 2008, Piqué *et al.* 2008, Wilkinson *et al.* 2009).

In the case of uranium, Hecht & Cuney (2000) have documented the dissolution of accessory minerals (zircons and monazite) in the presence of brines which constitute an additional source of U at the time of brine circulation. LA-ICPMS analyses have shown that brines from the Athabasca basin could transport significant amounts of U which range from 10 to some hundred of ppm (Richard *et al.* 2010).

When interacting with the basement, chemical features of the sodium dominated brine may drastically evolve towards Ca-K-(Mg) rich brines. High Ca/Na ratios are generally interpreted as the result of a Ca/ Na exchange through mineral–fluid interaction such as albitisation, or Na-metasomatism at greater depth (review in Kharaka & Hanor, 2004). The complete conversion of a Na dominated evaporitic brine into a Ca dominated brine is however still difficult to interpret. Such Ca rich fluids were found either in the present day waters sampled in the basements (KTB for instance, Möller *et al.* 2005), or in the Saskatchewan deposits where they are considered as the main brine responsible for U extraction and deposition.

Fluid mixing

***Mixing of two or more fluids in the major fluid pathways*:** Two major fluid types are generally found in cemented pathways: i) one or more brines frequently identified as primary brines issued from evaporated seawater having passed halite saturation and expelled during compaction stages or tectonic stages linked to major geodynamic events. ii) dilute fluids corresponding to recharge meteoric (or marine) fluids or local resident fluids issued from multiple evolution. In all studied cases, brines display a large range of composition, and in most cases a large range of chlorinity indicative of mixing between brines and dilute fluid end-members. The variety of salinity-temperature pairs indicates that at each stage of fluid circulation and healing of the micro-fissures, a distinct rate of mixing between the two fluids is registered. These different rates of mixing show also that the reservoir fluids were not fully homogenized at the time of healing of the micro-fissures. The dilute end-member of the mixing trends is likely considered as a recharge fluid of meteoric origin. Pristine features of surface fluids are however generally lost, as the $\delta^{18}O$ of the fluid estimated from the $\delta^{18}O$ values of quartz are in general typical of fluids buffered by sediment mineral assemblages. $\delta^{18}O$ values are in most cases, ranging from 0 to 4 ‰ (Table 2). Exceptions concern fluid flow in large drainage faults, such as those described by Smith et al. (1998) at Soultz. Very similar Th-Tm ice trends with nearly complete series of chlorinities between the two end-members were found in a part of the studied basins as already presented in the preceding paragraph and indicate that the mixing process occurred in most of the studied locations. In some of the listed examples, e.g. the Asturias F district (Sanchez et al. 2009), the Maestrat

basin, (Grandia et al. 2003a), authors do not report clear trend of mixing between a dilute end member and a brine but series of trapping of fluids covering a large range of chlorinities. It can be noted that in other unconformity deposits such as those from Saskatchewan (Athabasaca basin), the dilute fluid end-member is almost lacking and fluid mixing concerns only the two brines end-members, the Na-dominated and the Ca-dominated (Derome et al. 2005, Richard *et al.* 2010). The lack of chemical homogenization of the circulating fluids seems however to characterize most of the basins considered in our comparative study.

Cold fluids and hot ascending fluids in thermal disequilibrium with host formations? In a part of the study cases, a systematic temperature gap is recorded between the two fluid end-members, generally a few tens of degree cooler than the recharge fluids. The presence of slightly colder brines indicates that downward penetration of sedimentary brines tends to cool the deep reservoir fluids. The 35-40°C gap between the estimated temperature for brines that record the hotter dilute fluids, may correspond to more than one kilometer difference in depth, assuming a mean thermal gradient of about 30°C /km, if the two fluids are in thermal equilibrium with the host rocks in their respective reservoirs. The temperature difference between the brine and the hotter dilute fluid in a given zone, e.g. the area of fracture sealing is indicative of an anisothermal mixing. At Soultz, the anisothermal mixing is found in all parts of the granite reservoir, as shown by the variety of salinity-temperature pairs and the Tm-Th trend which are typical of each depth interval (Cathelineau & Boiron, 2009).

In a part of the Proterozoic basins (northern territories, Australia, Athabasca basin, Canada and Oklo, Gabon), the range of homogenization temperatures is rather similar to those recorded at Soultz in the upper parts of the reservoir (2 km) or in the north Massif Central. Temperatures can therefore be either converted into depths of 4-5 km assuming regular thermal gradients, or can be considered as temperatures representative of abnormal thermal gradients at much shallower depths of 1-3 km such as those recorded in the Rhine graben.

Significant exceptions are: i) data obtained on Maestrat basin where brines at 130°C (23 wt% eq. NaCl) mixed with a cooler and more dilute fluid (Grandia *et al.* 2003a), ii) Asturias where no definite mixing trends were obtained (Sanchez et al.,

2009), and Malines where the dilute fluid is cooler (70°C) than the brines (150°C) (Charef & Sheppard, 1988).

Brine-host rock interactions in the deposit area (mineral dissolution, silicification, dolomitization, and Mg alterations)*:* Two main cases may be distinguished: i) alteration within sedimentary formation which are generally dominated by dolomitization. In the sedimentary cover, in limestones especially, dolomitization and calcite dissolution creating porosity were observed in a great number of cases. The main driving force for this process is linked to the high Mg concentration of the evaporated seawater which is the main cause of the calcite dissolution and the replacement by dolomite. The resulting fluid is depleted in Mg and enriched in Ca. ii) Mg-silicate alteration within the basement. It is worth noting that Mg rich evaporite fluids are responsible for the intense Mg-metasomatism which affects the basement. Mg alteration from U deposits is characterized either by the crystallization of chlorites (Oklo, Northern territories, Australia), or by a sudoite-Mg illite assemblage in Athabasca (Kister *et al.* 2006, Mercadier *et al.* 2009). These alteration display similar mineral assemblage than the main talc deposits such as the Trimouns deposit in Pyrenees which results from the circulation of evaporitic brine during the Gascogne gulf extension (Boulvais *et al.* 2006, Boiron *et al.* 2007). As Ca-Mg brines are generally enriched also in potassium, K-alteration (adularisation) may also occur at the top of the basement near the unconformity in the Poitou high.

Large silicification characterizes the main ascending pathways and is generally favoured by the cooling and mixing of hot fluids with lower temperature dilute fluids. The main driving force at the origin of massive quartz precipitation is thus the decrease of the quartz solubility at decreasing temperature (Crerar & Anderson, 1971). Thus, little amount of quartz is precipitated in Canada unconformity deposits, where no hot dilute recharge fluids were found, compared to Australian deposits where large amounts of quartz formed by dilution and cooling of recharge fluids in faults, above the unconformity U deposits. Rather significant silicification are found at Soultz (quartz filled faults, Smith *et al.* 1998) and some deposits from the Poitou High (quartz-galena infillings from Melle, La Charbonière and Chatenet quartz-fluorite veins, Boiron *et al.* 2002). Silicification is thus a major indicator of temperature change, sometimes coupled with dilution in pathways favouring the convection of external fluids.

Anisothermal mixing of brines with dilute fluids favours the precipitation of different mineral assemblages depending on the availability of metals, and the presence of not of sulphur. Dilution process provokes the destabilisation of metal complexes, especially U and Pb chlorides. The availability of sulphur is however a key parameter and two main sources may be invoked: the bioreduction of sulfates (BSR) which is invoked for instance in Irish deposits for the S enrichment of one of the two mixed brines, the colder and most superficial one responsible of the Zn deposit (Wilkinson et al., 2005), and the thermal reduction of sulphates (Machel 2001) which can produced H_2S and be therefore one of the factor controlling metal deposition when some sedimentary formation reached the oil window (case of the Maestrat basin, Grandia *et al.* 2003 a and b). In cases where one fluid involved in the mixing was not sufficiently rich in sulfur, mixing caused mainly the precipitation of fluorite and carbonate, the spent fluid remaining enriched in metals. Such fluids may have kept their potential for a metal deposition in more favourable environments. Metal deposits may be found, therefore, away from the fluorite deposits, as suspected by Piqué *et al.* (2008) for the central Catalan coastal range deposits.

Geodynamic context

The cause of fluid migration remains frequently unknown due to difficulties in dating precisely the ore events and to relate precisely the origin of the fluid migration to specific geodynamic events. These relationships are almost impossible to prove to have occurred on great distances once the basin or the belt is eroded. Extensional versus compressional tectonic movements were thus largely discussed in the literature to explain MVT deposits. The debate on gravity driven fluid movements proposed by Leach *et al.* (2005) for a series of deposits is in part linked to the weakness of the method used for dating the process. Thus, in the case of Cevennes Pb deposits, after a few decades of models favouring a rather old karst infilling, the deposits were alternately considered as linked to compressional tectonics related to the Pyrenean orogeny (60 Ma) on the basis of remagnetization (Rouvier *et al.* 2001), or linked to previous extensional stages during Malm (see discussion, In Muchez et al. 2005). In most cases where rather young ages were proposed (135 Ma in Silesia, 185 Ma in Asturias, 60 Ma in Cevennes) it has been impossible to link precisely the remagnetization of minerals to the ore formation. Models were therefore hardly discussed : Heijlen *et al.* 2003, for Silesia, Wilkinson *et al.* 2005, for Irish deposits,

Muchez *et al.* 2005 for a variety of deposits hosted by Mesozoic formation over Europe including Cevennes, put forward the many arguments in favour of reliable ages (Sm-Nd on fluorite for instance) and robustness of models invoking the link between extensional tectonics and ore formation rather than younger stages related to orogeny (pyrenean, or alpine events for Mesozoic deposits).

The origin of hot fluids can be found in localized abnormal heat flows, and convection cells favoured by faults crosscutting both the basement and the sedimentary cover. In the Poitou region, up to now, such convection cells were mostly inferred for the lower Lias formation, where metal deposits were considered as syn-sedimentary. In that case, hydrothermalism was considered as synchronous with the Atlantic ocean opening. New geochronological data tend to indicate that these convection cells were active after the main stage of lower Lias sedimentation e.g. around 140-155 Ma (Fourcade *et al.* 2010). The major stages of fluid movements in relation with porosity increase due to localized mineral dissolution, or discontinuity opening are thus not related with early diagenesis or main stages of compaction, but correspond to later events linked to major geodynamic events. Most fluid events described in this paper occur in between 50 and 200 Ma later after the sedimentation.

Style of migration: deep downward penetration and convective cells

The main driving forces for the convection of brines are: i) the role of “relief “ area as already proposed for MVT deposits (Leach *et al.* 2001) and ii) abnormal heat flow which characterizes rifting tectonics. The patterns of palaeofluid circulation are shown in Figures 1 to 7: i) a major system of laterally migrating brines at the basement - sedimentary cover interface where both sandstones and the upper part of the basement had a high permeability, acquired for the basement by weathering during the emersion period, ii) local convective cells rooted at least at more than 5 km depth, involving low salinity fluids (presumably surface derived, likely migrating, through basement from structural highs) generally centered on horst fault systems, or faults (reverse in the case of the unconformity U deposits), iii) deep downward penetration of brines which accounts for the introduction of large amounts of chlorine in the basement microfractures. In the western Massif Central, brines are considered to have migrated along the unconformity below an impermeable cover formation, and then mixed locally with recharge fluids in fault systems.

Numerical hydrological modelling of basins aquifers by Evans *et al.* (1991) shows that: i) either the density differences related to salinity contrast between the fluid reservoirs are the primary driving forces for fluid flow when sediments surrounding salt contain a dilute fluid, or ii) thermal effects are necessary to get the convection in brine dominated aquifers. The mixing of hot recharge dilute fluids and colder brines indicates that dilute fluids are able to convect from remoted areas, and can be chanellized along faults. Meteoric waters are heated at depth and their density allows them to ascend along drainage faults such as extensional faults (horst and graben systems). Brines are flowing downward to great depth due to their specific density.

In all studied cases, the hydraulic conductivity of the stratigraphic units influences the brine regime on a regional scale, as shown by the specific role of the conglomerate and sandstone above the regolith or weathered basement, which constitute in all studied cases a major aquifer above the fractured basement, below cap rocks such as clay rich formations (Toarcian marls in Poitou, clay-rich formations in the Rhine graben, FB clay formation at Oklo). Such controls are already shown in similar contexts in the North German basin (Magri *et al.* 2009).

Lessons from rather recent systems for the understanding of very old brine migrations

Analogies in fluid chemistry: fluids found in giant U deposits have the same features than brines evolved by basement interactions and found in most carbonate hosted deposits or unconformity related F-Ba-Pb-Zn deposits from western Europe and in basement rocks.

Depth of brine penetration within the archean below the unconformity: there are no limits to the brine penetration within the fractured basement, as shown by young systems such as those related to the continental rifting of the Rhine graben. The analogy between the multiple microfissuring of archean rocks and healing by sedimentary brines and the process observed at Soultz is remarkable. The infiltration of brines below the unconformity in Athabasca may therefore have reached 5 km.

Role of thermal convection: The example of Soultz and Massif Central provide some keys for the understanding of the old systems where little is known on the dynamics of fluids and on the geometry of fluid pathways. In NW-Australia as well as in the NW Massif Central, the dilution of brines in fault systems near the unconformity

is observed. In both cases, the origin of hot recharge waters may be found in analog models such as the Soultz geothermal area where recharge fluids are driven from rather remote lateral sources in outcropping areas (meteoric fluid recharge).

Similar fluid migration affects the Oklo area (Fig. 2): the main deposit is located at the vicinity of a major fault of the Mounana basement horst, which was considered as related to a double continental rift (Fanceville-Lastourville basin and Okondia rift) on both sides of the Ondii-Dambi horst (Gauthier-Lafaye 1986). Main stages of fluid migration are considered to be related to the main extensional phase around 2.05 Ma (Gancarz 1978). The formation of hydraulic breccia attests of contrasted fluid pressure (Gauthier-Lafaye 1986). The recharge fluids, as at Soultz, likely infiltrated in the basement horst relief (Chaillu granite), and mixed with brines and oil fluids from the sedimentary aquifers (FA conglomerates) along horst faults.

It is highly probable that the formation of giant U deposits in Saskatchewan was not possible if not linked to a specific geodynamic event which could have caused : I) the microfissuring and reactivation of preexisting micropermeability and faults, ii) the localized heat flows which were necessary for brine convection, as no fluid density contrast characterize the two main brines found in these deposits.

Pulsatory fluid regime: the wide variety of salinity during fluid trapping between the brines which penetrate downward in the basement and the ascending fluids was found at Oklo and in Northern Territories (Australia) but not in Saskatchewan. The analogy with recharge fluids commonly found in relation with convective systems driven by localized heat flows and recharge from emerged zone is only possible in the two latter cases. The lack of homogeneity of the brine composition is in favour of successive inputs of brine within the main fault system, and repeated pulses following models well known in aquifer systems in relation with micro- or macro-seismicity.

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Figure captions

Fig. 1: Model of fluid migration around uranium deposit in Mid-Proterozoic series with brine penetration in the basement due to both gravity driven process and thermal convection (example of the Athabasca basin).

Fig. 2: Fluid migration around the Oklo deposit showing the penetration of recharge fluids from relief zones west of the Franceville rift zone and the mixing of brines and oil with recharge fluids along the fault zones at the edge of the basin, and near the contact between the FA/FB sedimentary formations (modified from Gauthier-Lafaye, 1986).

Fig. 3: Schematic model of the fluid circulation in the north-western part of the French Massif Central at the unconformity of the basement and sedimentary cover interface, showing the upward brine migration below the Toarcian rock and mixing in fault zones (based on data from Boiron *et al.* 2002).

Fig. 4: Schematic model of the fluid circulation in the Maestrat Pb – Zn deposit (Spain) (modified from Grandia *et al.* 2003a).

Fig. 5: Fluid migration in Silesian Pb – Zn deposits (Poland) (modified from Heijlen *et al.* 2003).

Fig. 6: Model of fluid circulation occurring in the Irish carbonate hosted Pb-Zn deposits (modified from Wilkinson *et al.* 2005).

Fig 7: Model of fluid circulation in the basement of the Rhine graben showing deep penetration of sedimentary brines down to 5 km depth and fluid mixing with recharge meteoric water.

Fig. 8: Tm ice versus Th diagram applied to aqueous fluid inclusions from two unconformity related uranium deposits (Kombolgie basin, Australia and Oklo, Gabon) and two examples of fluid circulation related to extension tectonics (Northwestern French Massif Central and Rhine Graben).

Fig. 9: Overview of the Tm ice - Th relationships for several examples of mixing trends between two or three fluid end-members. i) full circle: Ca- (Mg-K) brines, ii) half circle: Na-(Ca-Mg) brines, empty circle: dilute hot recharge fluids.

Fig. 10: Na/K versus Na/Ca molar ratio diagram applied to fluid inclusion chemical data. 1 - Na-rich brines and 2 - Ca-rich brines, LA-ICPMS data, Mc Arthur River, Athabasca basin (Richard 2009) 3 - Aligator River, crush leach data, (Derome *et al.* 2005),4 - Oklo, (Mathieu *et al.* 2000), 5 - Poitou High, crush leach data, (Boiron *et al.* 2002), 6 - Oil field brines (Carpenter *et al.* 1974, Karakha *et al.*1987), 7 – Deep basin brines (Fisher & Kreitler, 1987), 8 – Silvermines Pb-Zn deposits, crush leach data, (Wilkinson *et al.* 2005), 9 - Silesia Pb-Zn deposits, crush leach data, (Heijlen *et al.* 2003), 10 – Fluorite deposits in Asturias, LA-ICPMS data, (Sanchez *et al.* 2009), 11 - Fluorite deposits NE Spain, LA-ICPMS data, (Piqué *et al.* 2008). Full circle: KTB fluids, (Möller *et al.* 2005), full triangle, Rhine graben fluids (Pauwels *et al.* 1993) full diamond: seawater, empty diamond: seawater having passed halite saturation, data from Fontes & Matray (1993). H: halite, B: bischofite.
Arrows indicate the main trends related to water-rock interactions. Pl: plagioclase, Kf: K-feldspar.

Fig. 11: Cl/Br (molar ratio) versus Cl content of fluid compositions determined by crush leach analysis. Full line: seawater evaporation trend from Fontes and Matray (1993). SW: seawater, MW: meteoric water, G: gypsum, H: halite, E: Epsomite, B: Bischofite. The two dashed lines show the composition of a mixed fluid between either seawater or meteoric water with seawater having reached epsomite saturation.
In the diagram for U deposits from Kombolgie basin,
In the upper left diagram, the grey box shows the location of the data obtained for the Mc Arthur and Rabbit Lake uranium deposit (Athabasca basin, Richard 2009*).*
In the lower left diagram (Soultz), the open circles refer to the data obtained on formation waters from Triassic to Oligocene series by Pauwells *et al.* (1993).

Fig. 12: Cl/Br ratios obtained by crush leach analysis for the different reported occurrences.

1 - Mc Arthur River, Athabasca basin (Richard 2009) 2- Aligator River, (Derome *et al.* 2005), 3- Oklo, (Mathieu *et al.* 2000), 4- Silver Mines Pb-Zn deposits, (Wilkinson *et al.* 2005), 5 - Silesia Pb-Zn deposits, (Heijlen *et al.* 2003), 6- Maestrat basin Pb-Zn deposit, Spain, (Grandia *et al.* 2003a), 7 – Cantabrian Pb-Zn deposits, Spain (Grandia *et al.* 2003b), the dash line shows high Cl/Br ratio related to the presence of salt dome, 8 – Poitou High Pb-Zn-F deposits, (Boiron *et al.* 2002), 9 – Fluorite deposits in Asturias, (Sanchez *et al.* 2009), 10 - Fluorite deposits, NE Spain, (Piqué *et al.* 2008), 11- Soultz, unpublished data.
Seawater evaporation trend from Fontes & Matray (1993), SW: seawater, H_b: halite beginning, H_{end} : halite end, E: epsomite.

Fig. 13: General conceptual model for the genesis of basement and carbonated hosted deposits near the basin / basement unconformity.

Table captions

Table 1: Geological setting, geodynamic context and ages of the host formations and mineralisations in the considered areas.
1 - Alexandrov *et al.* (2001), 2- Schuler & Steiger (1978), 3 – Todt (1976), 4- Bertrand *et al.* (2001), 5 – Enrique *et al.* (1999), 6- Grandia *et al.* (2003a), 7- Pique *et al.* (2008), 8 - Sanchez *et al.* (2010), 9 - Heijlen *et al.* (2003), 10 - Ludwig *et al.* (1987), 11- Maas (1989), 12 – Cummings & Krstic (1992), 13 – Alexandre *et al.* (2009), 14- Stille *et al.* (1993), 15 - Bonhomme *et al.* (1982), 16- Gancarz (1978), 17 - Holliger (1988)

Table 2: Summary of paleofluids data available on the different areas. Tm ice: melting temperature of ice, Th: homogenisation temperature

Table 3: Main characteristics of fluid circulation in the different areas.
X indicates the presence of the considered process, XX indicates that the process is relatively important and (X) that the process is suspected.

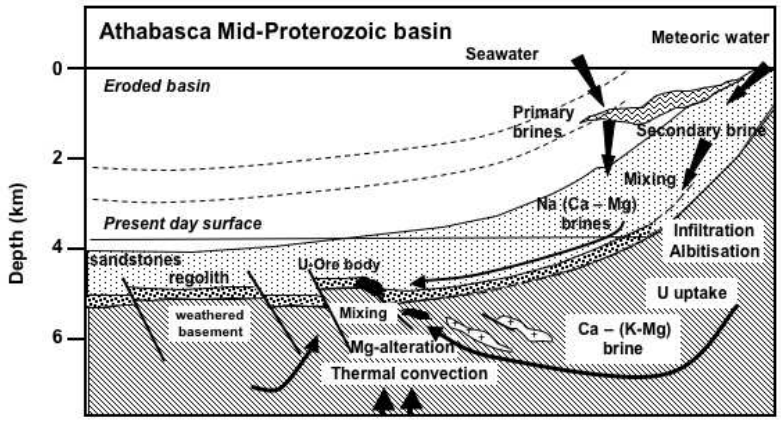

Fig 1 Boiron et al.

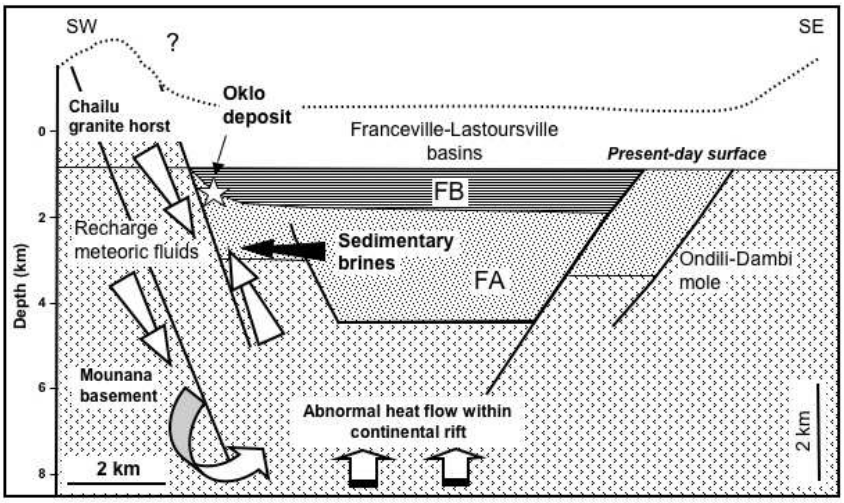

Fig 2 Boiron et al.

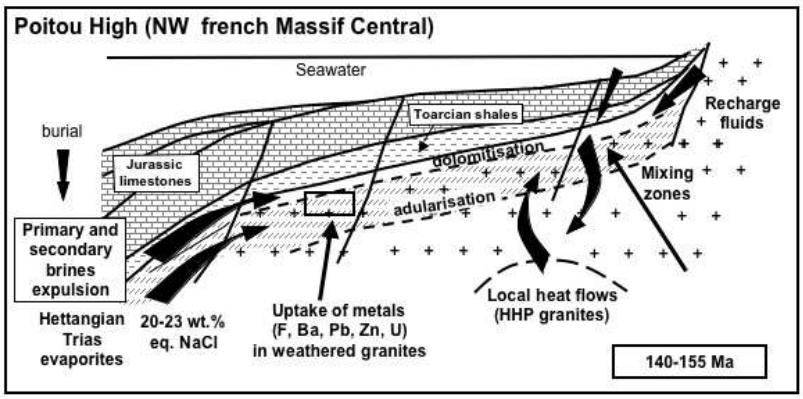

Fig 3 Boiron et al.

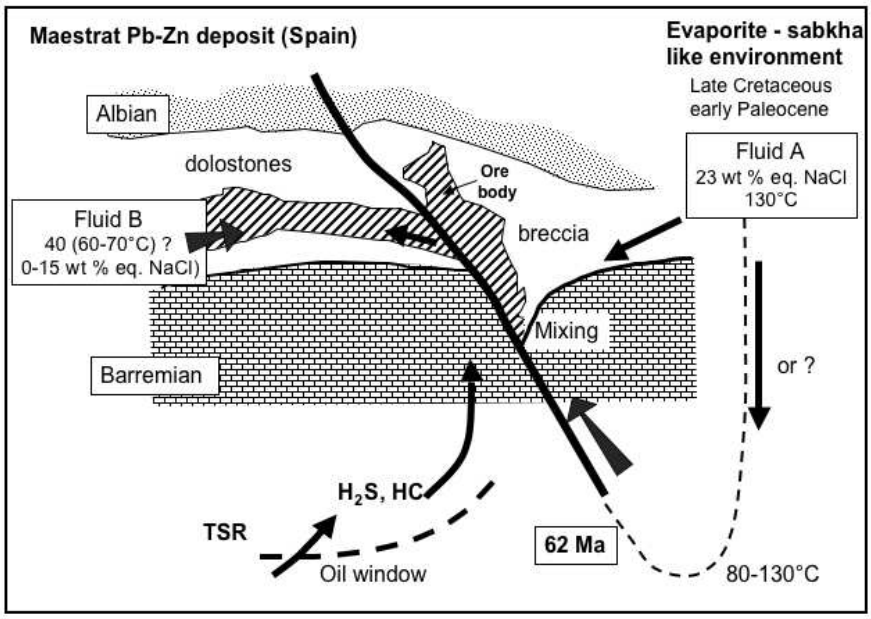

Fig 4 Boiron et al.

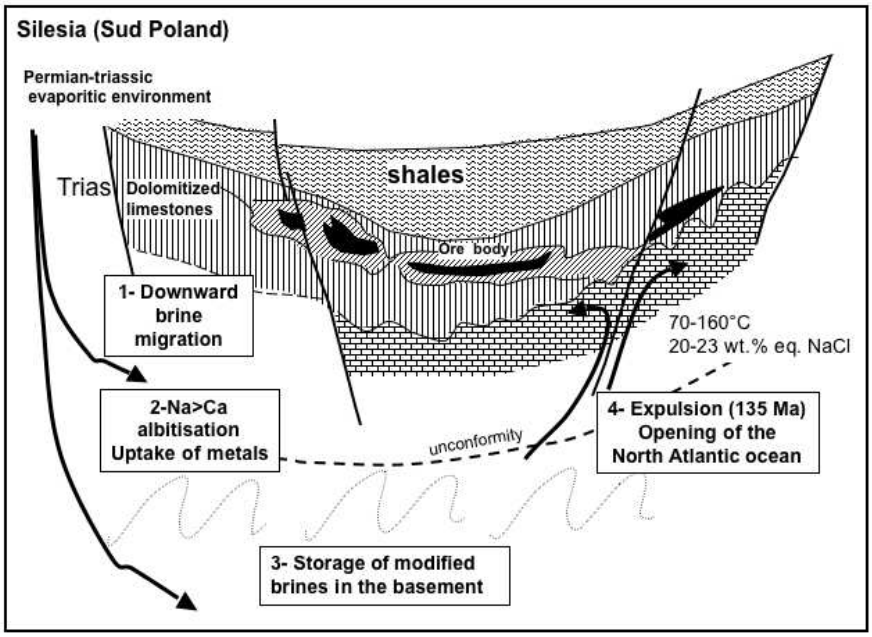

Fig 5 Boiron et al.

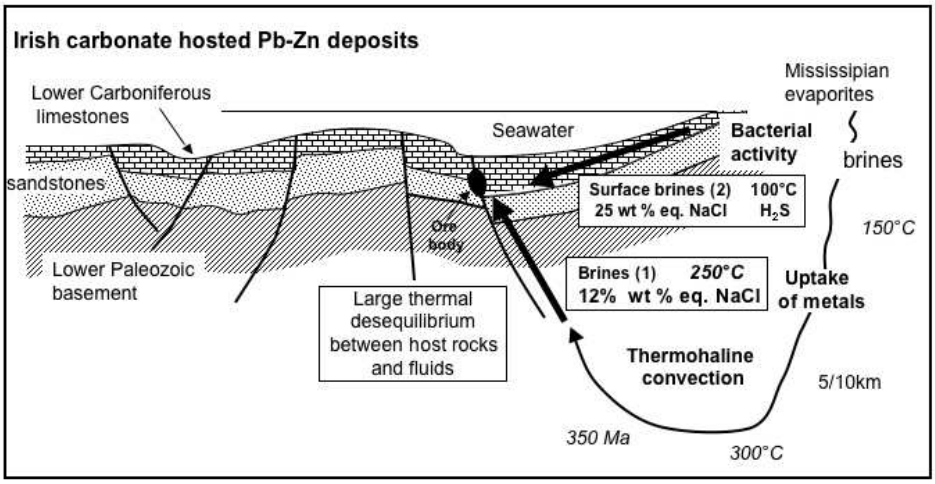

Fig 6 Boiron et al.

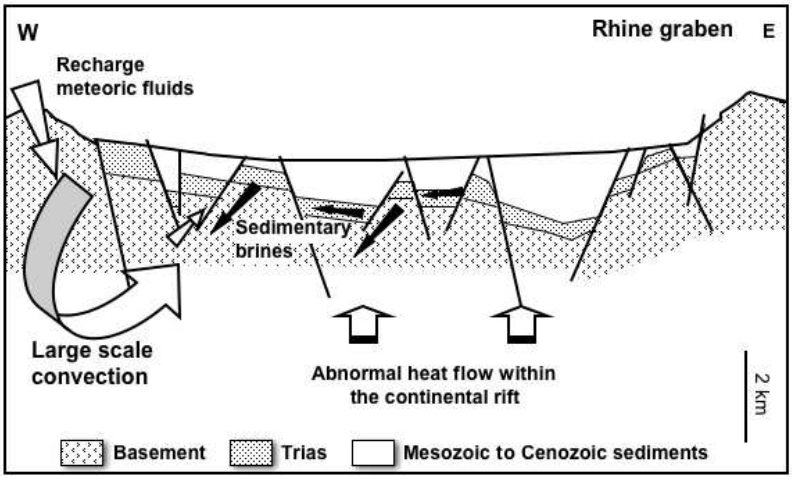

Fig 7 Boiron et al.

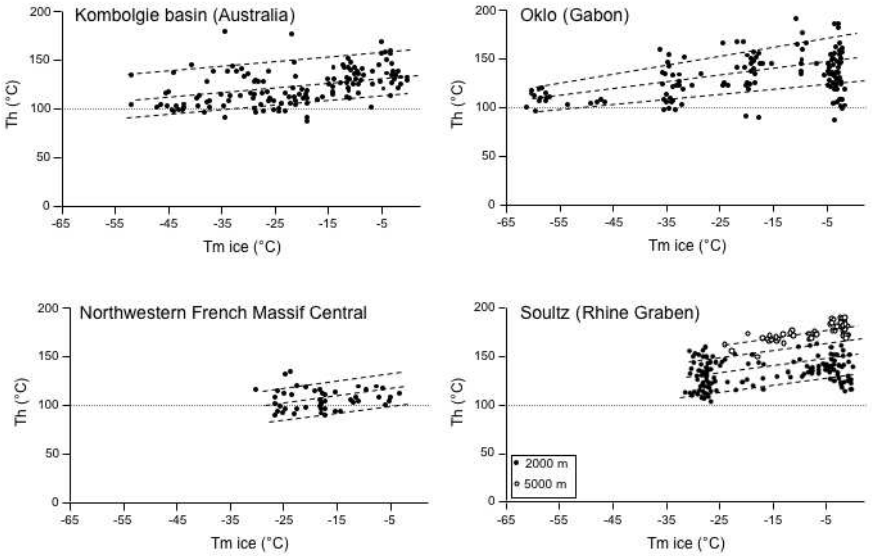

Fig. 8 Boiron et al

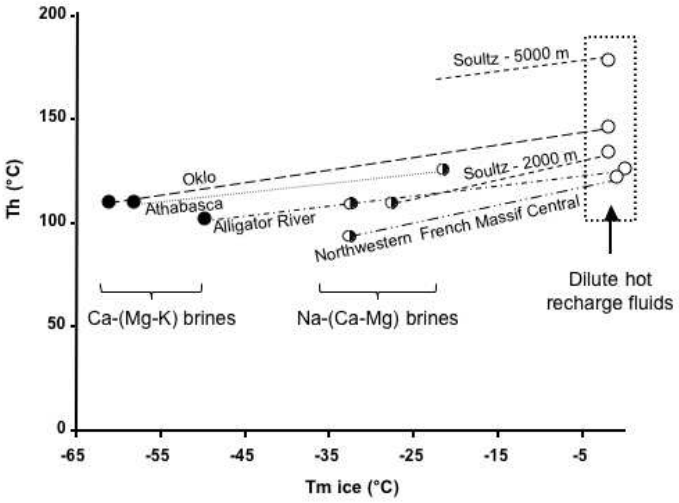

Fig. 9 Boiron et al

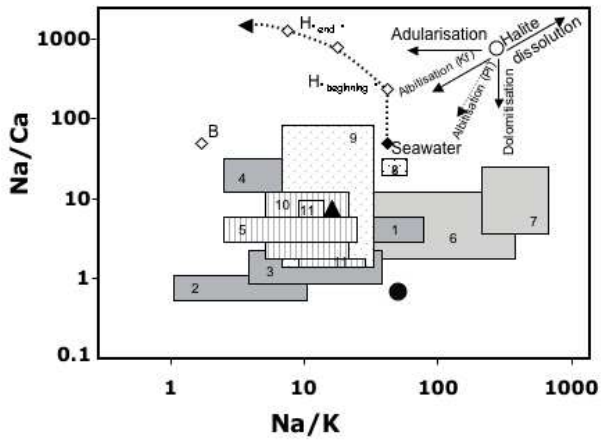

Fig. 10 Boiron et al

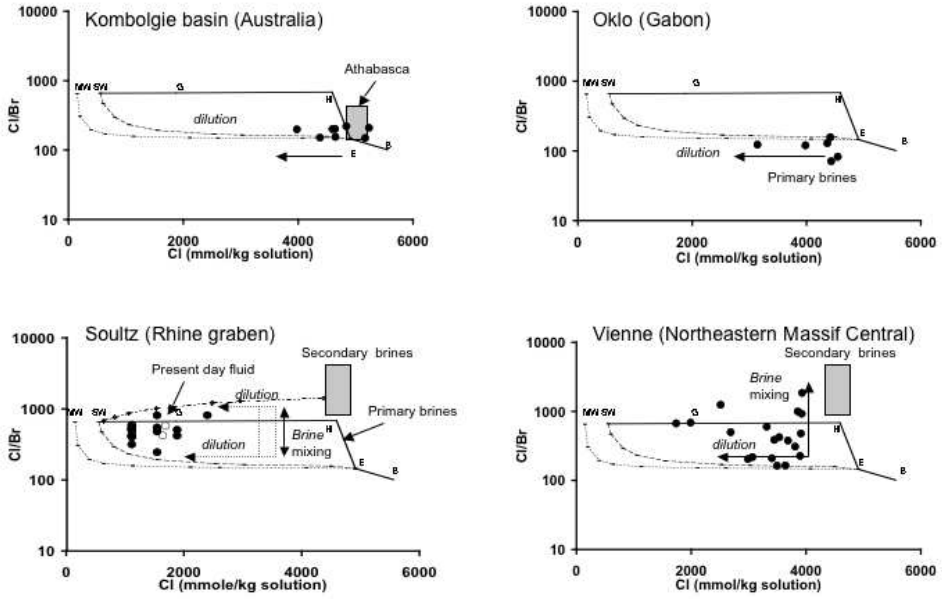

Fig. 11 Boiron et al

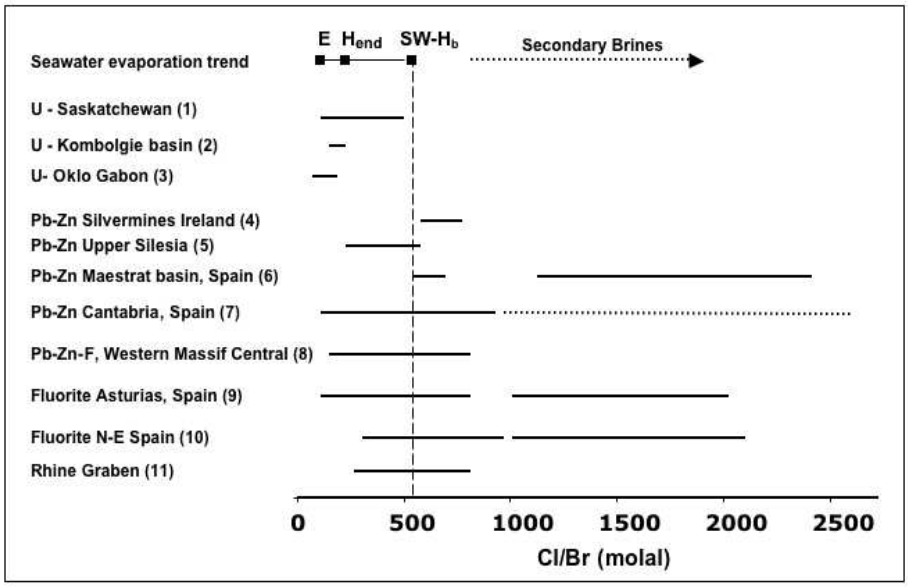

Fig. 12 Boiron et al

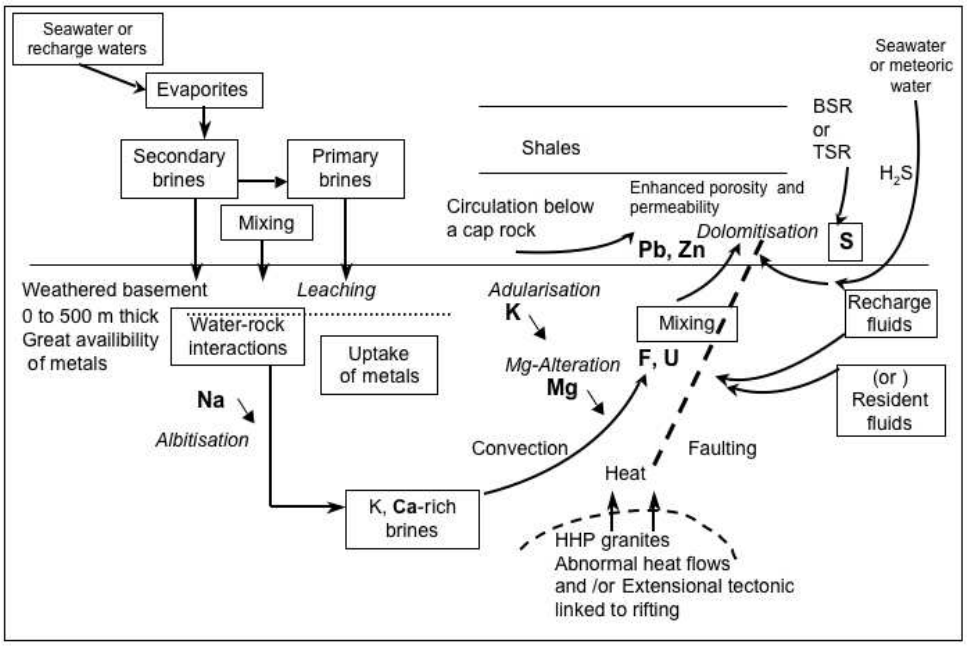

Fig 13 Boiron et al

	Location	Sedimentary cover	Basement	Age of evaporite	Ages of mineralisation (Ma)	Time gap between sedimentation and fluid movement	Geodynamic context
F-Ba	Rhine Graben Soultz sous Forêts	Eocene to Oligocene marls and clays Triassic sediments	Hercynian monzogranites (331±9 Ma) (1)	Keuper Trias	20 to present day	180 to 200 Ma	Oceanic extension - Jurassic Continental extension - Tertiary
Pb-Zn-F-Ba	Schwarzwald district Germany	Triassic sandstones Marine carbonate rich sediments	Albtal and Malsburg granites 326±2 Ma and 328±6 Ma (2,3)	Keuper Trias	Jurassic (110-150) Tertiary	70 to >130 Ma	Oceanic extension - Jurassic Continental extension - Tertiary
Pb-Zn-F-Ba	North Western French Massif Central	Marine infra-Lias to Dogger series	Hercynian tonalites to granodioirte 350 to 360 Ma (4) Peraluminous intrusions (320 Ma)	Trias at 200km Hetttangian	140-155	40 to 50 Ma	Atlantic Ocean extentional tectonic
F - Ba	Albigeois	Eroded	Paleozoic basement	Trias Hettangian Continental basin	150	40 to 50 Ma	Atlantic Ocean extentional tectonic
Pb-Zn	Malines	Triassic calcareous shales silt, evaporite + Jurassic series	Lower and middle Cambrian dolomitic limestones	Trias	at less post Hettangian probably Kimeridgian	55 Ma (Trias) 340 (Cambrian)	Extensional tectonic
Pb-Zn	Maestrat basin Eastern Spain	Late Jurassic to early Creataceous sediments	Paleozoic basement	Late Cretaceous Early Paleocene	62± 0.7 (6)	0	Sligtly post-rift Gascogne gulf
F - Ba	North Eastern Spain	Triassic carbonates and evaporites Jurassic- Creatceous limestones	Granodiorite 287 ± 2.8 Ma (5)	Trias	137 ±25 (Sm-Nd)(7)	50- 60 Ma	Extension opening atlantic ocean
F - Ba	Asturias (Spain)	Permo - Triassic series	Cambrian to Devonian basement	Permo-Trias	185 ±28 Ma (Sm-Nd) (8)	>20 Ma	Extension Atlantic Ocean opening
Pb-Zn	Upper Silesia	Trias dolomitized limestones	Carboniferous basement	Trias	135 ± 4 (9)	80 Ma	Pemian grabben
Pb-Zn	Silvermines District Ireland	Lower carboniferous limestones	Low grade paleozoic metasediments	Mississipian	350 Ma	0	Local extensional rift zone or extending tectonics passive margin
U	Alligator River Australia	Kombolgie sandstones and conglomerates marine origin	Archean to early Proterozoic granito gneiss	1.7 Ga	1737 ± 20 (10) 1600 -1650 (11)	100 to 200 Ma	see discussion
U	Athasbaca basin Canada	Proterozoic sandstones	Paleoproterozic gneiss and pegmatoids	1.7 Ga	1400- 1500 (12, 13)	200 to 300 Ma	see discussion
U	Franceville basin Oklo (Gabon)	Francevillian series, Conglomerate to fine sandstones (2100 Ma) (14)	Archean K-rich plutonites 2880 to 2400 Ma (15)	in the sediment series	1960 to 2050 (16, 17)	50 to 200 Ma	continental extension

	Location	Tm ice (°C)	Th (°C)	Cl/Br (molar)	δ ^{18}O fluid (‰)	δ D fluid (‰)	References
F-Ba	Rhine Graben Soultz sous Forêts	2000 m : -0.2 to -31.6 5000 m : -0.1 to -24.6	2000m : 100 to 165 5000m : 150 to 184	250 to 800 *	-3 to 2	-37 to -42	Dubois et al. (1996) Smith et al. (1998) Cathelineau & Boiron (2009) Pauwels et al. (1993)
Pb-Zn-F-Ba	Schwarzwald district Germany	-0.1 to -36	80 to 200	not available	- 11.6 to -3	-10 to -60	Baatartsogt et al. (2007)
Pb-Zn-F Ba	North Western French Massif Central	-3.8 to -30.2	80 to 130	160 to 1800	5 to 9	-19 to -50	Boiron et al. (2002)
F - Ba	Albigeois	-16.7 to -20.6	125 to 170	not available	0.1 to 3.2	-15 to -63	Munoz et al.(1999)
Pb-Zn	Malines	-10 to -16	150	not available	5.5 to 7.8	-13 to -31	Charef & Sheppard (1988)
Pb-Zn	Maestrat basin Eastern Spain	-1 to -26	70 to 130	550 to 700 1100 to 2400	0 to 3	not available	Grandia et al. (2003)
F - Ba	North Eastern Spain	-4.9 to -21.6	85 to 195 (110)	300 to 970 1000 to 2100	not available	not available	Pique et al. (2008)
F - Ba	Asturias (Spain)	-0.1 to -24.3	80 to 170	100 to 800 1000 to 8000	0.3 to 7.4	not available	Sanchez et al. (2009, 2010)
Pb-Zn	Upper Silesia	0 to -23.3	70-160	248 to 560	0 (to -3)	-10 to -30	Heijlen et al. (2003)
Pb-Zn	Silvermines District Ireland	12-18 wt %	170-240	600-770	not available	not available	Wilkinson et al. (2005)
U	Alligator River Australia	-0.3 to -52	90 to 160	150 to 220	0.9 to 3.3	not available	Derome et al. (2007)
U	Athasbaca basin Canada	-20 to -55	70 to 195	100 to 500	-3 to 6	-55 to -147	Richard (2009)
U	Franceville basin Oklo (Gabon)	-1.3 to -63	90 to 175	70 to 160	-6 to 0	not available	Mathieu et al. (2000) Mathieu (1999)

	Location	Fluid origin		Fluid recharge		Mixing	Fluid in the basement	Water-rock interaction	Main cause of metal deposition
		Primary brine	Secondary brine	Hot fluid	Cold fluid				
F-Ba	Rhine Graben Soultz sous Forêts	X	Probable	hot dilute fluid 170°C at 2000m 200°C at 5000m		X	> 5km	Illitisation	Dilution
Pb-Zn-F-Ba	Schwarzwald district Germany		deep aquifer at 300 - 350°C		resident fluid	X	7 -8 km	Illitisation	Mixing dilution
Pb-Zn-F-Ba	North Western French Massif Central	X	X	dilute in some places		X	> 1km	Adularisation (basement) Dolomitisation (infra-Lias)	Dilution Cooling
F - Ba	Albigeois		X				a few km	Silicification preceeding Fluorite deposition	Cooling
Pb-Zn	Malines		Connate waters but Triassic evaporites		resident fluid	X	X	Dolomitisation	Dilution Cooling
Pb-Zn	Maestrat basin Eastern Spain	X	X		resident fluid	X		Dolomitisation	Mixing of 2 brines
F - Ba	North Eastern Spain	X	X			X (dilution)	XX		Dilution at constant temperature
F - Ba	Asturias (Spain)	X	X		resident fluid	X	XX	Dolomitisation Silicification	Mixing with less saline surficial derived fluid present in sediments
Pb-Zn	Upper Silesia	X				X (Dolomite)	deep penetration	Dolomitisation Albitisation (basement)	Mixing Cooling
Pb-Zn	Silvermines District Ireland	deep circulating brines		cooler Ca - brine			XX	Dolomitisation in limestones	Cooling, mixing of 2 brines including a S-rich brine
U	Alligator River Australia	X	(X)	ascending hot dilute fluid		X	XX	Chlorite	Dilution
U	Athasbaca basin Canada	X	(X)	Ca- brine		X	> 1 km	Sudoite - illite (quartz dissolution)	Mixing (cooling)
U	Franceville basin Oklo (Gabon)	X	(X)	hot dilute fluid		X	X recharge	chlorite	dilution