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# Continental-scale environmental and geochemical distal effects of the Rochechouart impact at the lower Hettangian

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**Abstract.** We give arguments showing that the Pb Ag Ba F Tl anomalies on the 200 Ma paleo-(sub)surface in western Europe likely have an impact-driven epithermal origin. We propose that they derive from the dust cloud induced by a bolide fall at Rochechouart (NW French Massif Central, France), then removal by rain and percolation along reactivated crustal lineaments. Coeval alterite formation resulted from a greenhouse effect related, and favoured Ba and Pb release from feldspars.

**Keywords.** Impact, firestorm, fumarole type metals, epithermal mineralizations, boiling, continental alteration, greenhouse effect

## 1 Introduction

Impact events are now well recognized as important markers of terrestrial geological history, as well as objects of prime economic potential. World class ore deposits are directly or indirectly related to giant (>130 km-wide) meteorite craters, e.g., the Sudbury Cu-Ni-PGM ores or the Witwatersrand Au-U mineralizations in Paleoproterozoic cratons (Pirajno 2009). At the scale of North America, the current worth of impact-related valuable substances has been estimated to \$5 billion per year (Grieve and Masaitis 1994). In hypervelocity impact craters, a huge amount of kinetic energy is converted to heat. Target rocks are partly molten and vaporized, they are brecciated and comminuted as a compression wave propagates through them. Hot and permeable fall back and fall out ejecta as well as impact-induced fractures below and around the crater are thus favourable settings for post-impact hydrothermal circulations. Based on mineralogy, geochemistry and fluid modelling, the concentrations of Au, U, Pb-Zn sulfides to be found in crater rocks are shown to result from long duration fluid flows ( $10^3$  s to  $10^6$  years), which extend at the crater-scale and deeper than 1 km below it (e.g., Komor et al. 1988; Naumov 2005).

It may seem paradoxical that, whereas terrestrial meteorite impacts may cause global environmental catastrophes (Pierazzo and Artemieva 2012), the economic potential of an impact has seldom been documented to extend at a continental scale so far. In France, the economic importance of the Hettangian paleosurface has long been recognized (e.g., Samama 1980; Lhégu and Touray 1980), but no single unified metallogenic model was ever proposed to account for the complex interplay of hydrothermal and continental weathering processes on this paleosurface. Recently,

Schmieder et al. (2010) suggested that some Hettangian Pb-Zn-U-F-Ba mineralizations could be related to the Rochechouart crater (RC), based on their new dating of the impact at  $201 \pm 2$  Ma. Figure 1a shows the crater,  $\approx 20$  km in diameter, located on the NW margin of the French Massif Central (FMC) part of the Variscan belt and on the NE edge of the Aquitaine basin. It affected a mixed crystalline target primarily composed of granitic, metamorphic and intrusive igneous rocks of the Variscan orogeny (Lambert 1977, 2010; Chèvrement et al. 1996). In this context, we review and discuss some metallogenic and high-energy environmental effects recorded in the lower Hettangian (LH) of western Europe (WE), in the scope of the Rochechouart impact.

## 2. Biological, mineralogical, and geochemical features of the Hettangian paleosurface

The scientific problem addressed here is reverse to that of the Chixculub crater in the 80's. At the Cretaceous/Tertiary (K/T) limit, various biological and geochemical features were suggestive of a coeval impact, but no crater was identified. Some of the environmental changes that had been recognized as indicative of a meteorite fall at this K/T period include (e.g. Van den Bergh 1989): (i) mass extinctions, (ii) many evidences of fire (soot) in stratigraphically-relevant sediments, with associated fusinite; (iii) the development of continental alterites, due to an abrupt increase in atmospheric CO<sub>2</sub> (greenhouse gas effect), in turn inducing acid rain. Similar environmental signals characterize the LH sedimentary record in WE. (i) Benton (1985) documented rates of high extinction and of negative diversification for all Tetrapod groups in the early Jurassic. On the St Bride's Island on the shoreline of the early Jurassic Sea (Bristol-Mendip district (BM), Fig. 1c), extensional fissures are filled with abundant Synapsids (mammal-like reptiles) and fusain (Evans and Kermack 1997). The hypothesis of a bolide impact as a cause of this incineration/killing is re-inforced by the fact that an early Jurassic seismite unit overlain by a tsunamite extends over 250 000 km<sup>2</sup> NE of the BM area (Simms, 2003; Fig. 1c). (ii) All over WE, basal Hettangian sediments typically show high energy features, beside tsunamis and seisms: intense brecciation, high-energy currents and/or ferruginous oolitic sedimentation (e.g. Coiteux 1982). (iii) At Chaillac (Fig.1a), barytinized and oxidized wood debris have been entrained into conglomeratic channels, post-Rhaetian in age, by turbulent waters

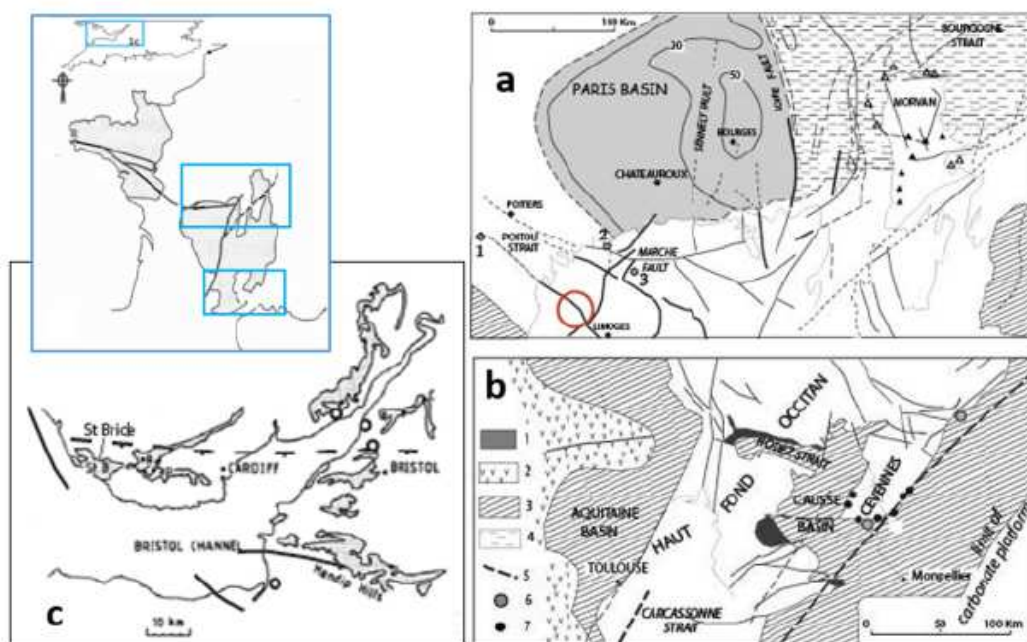


Fig. 1. Distribution of stratabound and vein F Ba Pb Fe Mn ores on the LH paleosurface close to north and south FMC basement rocks (Fig. 1a and 1b, respectively, modified after Blès et al. 1989), and Mn ores from the Bristol-Mendip area (Fig. 1c, modified after Evans and Kermak 1997). The relative position of the 3 selected areas is given in inset. Legend of figures 1a and 1b: 1= Permian; 2= evaporites; 3= carbonate platform; 4= marls. 5= flexure. Selected ores in Fig. 1a: 1=Pb Ag mine of Melle; 2=vein and stratabound Ba F Fe Mn ores from Chaillac; 3= Fanay U mine; triangles = stratabound (empty symbols) and vein fluorite (full symbols) from Morvan. Black star: iron mines from Burgundy. White star: ochres from Auxerre region. The large circle represents the Rochechouart crater. Fig. 1b: 6= Pb Zn mines (Largentière to the north and Les Malines to the south) and showings (= 7) from the Cévennes margin, after Macquar et al. (1990). Empty dots in Fig. 1c are outcropping deformed soft sediments after Simms (2003). See text for reference

flowing on the Hercynian basement (Chateaufneuf 1980). These fusinitised debris show unusually high oxidation ratios in the range 190-650 mg CO<sub>2</sub>/g TOC (Hotton et al. 2014, unpubl. Rock Eval data, ISTO), ≈10 times higher than that of hydrothermally altered carbon compounds associated with U-ores for instance (Landais 1996). (iv) LH sediments all around the FMC, either clay-rich and silicified (jasper) on the NW side, or carbonated further south and on the eastern side, contain strata-bound baryte, fluorite and/or galena (Fig.1). In Les Malines Pb-Zn mine area, the unmineralized LH sediments display Pb (Cd Cu) anomalies (Treuil et al 1970; Fig. 1b). Incompatible elements like Pb or P should be highly mobile in post-impact fluids from RC, a conclusion that also applies to the LIL element Ba. As for fluorine, it is fractionated into high T fluids coexisting with melts in Babaudus-type breccias (impact molten rocks) from RC, as shown by the presence of gaseous vesicles filled with F-rich illite (K<sub>0.87</sub>[Si<sub>3.2</sub> Al<sub>1.8</sub>][Al<sub>0.85</sub> Fe<sub>0.04</sub> Mg<sub>0.1</sub>][OH<sub>1.6</sub>F<sub>0.04</sub>]) in these melts. (v) Additionally, numerous Fe Mn oxide-rich clay pods lie on the LH paleosurface or are interstratified in LH units, often in close association with Ba F Pb ores (e.g. Chaillac; Fig.1a; Sizaret et al. 2004). They have been exploited from the BM district (Mn ores from Mendip Hills, UK dated at ≈200Ma; Haggerty et al. 1996) to the margin of north FMC (the Redoutières Fe-Mn-rich strata exploited for Ba at Chaillac, the Beaujolais-Burgundy ochres and iron ores, Fig. 1c; Guillaume 1997; Monin 1999), and from the eastern margin of the Aquitaine basin to the Causse basin (Macquar et al. 1990; Fig. 1b). Fe-Mn pods lying on the LH surface

have often been interpreted as Tertiary continental alterites ('Siderolithique'), therefore as unrelated to Hettangian surface processes (e.g. Ziserman, in Samama 1980 for the Redoutières Fe-Mn oxides). However, cryptomelane from the latter area is anomalous in Tl (Jézéquel et al. 2011), similarly to the Tl-enriched pyrite in LH sediments from La Croix de Pallière, 10 km NE of Les Malines (Duchesne 1964; Fig. 1b). The Tl-anomaly apparently present in LH sediments around the FMC should allow LH Fe-Mn mineralizations to be discriminated from Tertiary alterites. (vi) Lastly, a stage of albitisation dated at the LH is also recorded in the basement and overlying Permo-Carboniferous cover from different parts of southwest MC. This is particularly the case in basins around the Rodez strait, where feldspars, either detrital or from magmatic basement rocks, have also been reset to 200-210 Ma (Schmitt et al. 1984; Fig. 1b).

### 3. Characteristic features of Ba F Pb Fe Mn veins in the Rochechouart context

Some discordant mineralizations in veins or breccia zones are scattered along the basal Hettangian-basement contact all around the FMC (Fig.1; Ba F ores from Chaillac, fluorite mines from Morvan, iron ores from Burgundy, ochres from Beaujolais; Pb-Zn ores from the Cévenole margin), and also in the Poitou strait (Ag-Pb ores from Melle), and in Somerset (Mn ores from Mendip Hills). All these epigenetic mineralizations are associated with stratabound ores and are controlled by the LH shoreline and/or extend

in veins less than 1 km-deep into the underlying basement. Many of these mineralizations were once accessible on outcrops, this is why they have been exploited as early as Roman times (fluorite from Morvan, silver-rich galenas from Melle). Their exploitation later continued in artisanal or industrial mines. For instance, Fe-Mn oxide-clays from Chaillac area were the source of pigments for the Magdalenians (Jézéquel et al 2011), ochres have been extracted until 1966 around Auxerre. Hettangian iron ores from Burgundy have been processed in artisanal forges in the 18<sup>th</sup> century and were mined until the end of the 19<sup>th</sup> century. In this paper, we have identified 3 criteria, other than the proximity to the Hettangian Sea margin, that may be used to identify more objectively the hydrothermal ores that can be primarily related to the RC: (1) ore mineralogy and texture; (2) Pb-isotope signature; (3) structural style and control.

### 3.1 Mineralogy and texture of Ba F Pb Fe Mn ores

The major characteristic features of Hettangian mineralizations are briefly summarized hereafter. The texture of fluorite veins from north FMC is quite similar to that of the R stockwork veins: cocard or banded quartz gangue, hydraulic fractures and breccia. The Chaillac Ba-F hydrothermal deposit, which associates a basement-hosted near vertical vein, richer in sulphides and mined for fluorite, with more oxidized Ba-rich ferruginous stratabound ores on the surface, presents a well-developed paragenesis (Sizaret et al. 2004). Besides sulfides, sulfates and Fe-oxi-hydroxides, it includes phosphates, molybdates, only little carbonates, and also halogen (Cl and F)-bearing minerals. At Chaillac, the high-energy extensional context favoured the development of euhedral vuggy crystals of fluorite, baryte, cerussite, pyromorphite, goethite, wulfenite (see detailed descriptions in 'le Règne Minéral' (2004), Special Issue on the Chaillac baryte and fluorite deposit). Concerning the important energy release on the LH paleosurface, we have observed two kinds of microstructures in quartz from both the Rochechouart stockwork and the Chaillac arkoses (Fig. 2). This fact points out that contemporaneous minerals from both places have been submitted to similar thermal or mechanical post-impact stresses (Flörke et al. 1981), thus suggesting similar processes in the Rochechouart crater basement and Chaillac after the impact.

### 3.2 Lead isotopes

Studying the Pb-isotopic compositions of galena from Les Malines and using Pb-Pb diagrams, Le Guen et al. (1991) discriminated, at the scale of the Cévenole Province, a homogenous, non-radiogenic lead component interpreted to represent an initial metal stock originating from local hercynian granites, and that had been frozen at about 210 Ma. Haggerty et al. (1996) also obtained a Pb-Pb age of  $\approx 200$  Ma for galenas from central MB district.

Figure 3 shows that lead isotope data from Melle and Chaillac galena also plot within the BM and Cévenole field, suggesting that these galena formed from a well

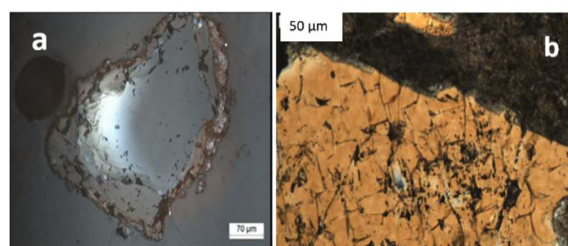


Fig. 2: a -Flaking of quartz in arkoses from Chaillac; b- quartz from Rochechouart stockwork with two fracture sets parallel to the rhomboedra

homogenized non radiogenic metal stock that had been reset at the LH.

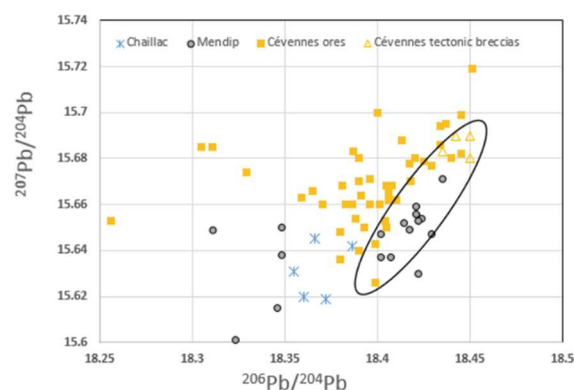


Fig. 3 :  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  isotopic ratios of various mineralizations linked to the Hettangian paleosurface in WE. Data sources: Marcoux (1987, Chaillac), Haggerty et al. (1996, Mendip Hills), Le Guen et al (1991; Cévennes). Ellipse: galena and slag field from Melle after Téreygeol et al (2004)

### 3.3 Fault control on Hettangian fluid flows

Bischoff and Oskiersky (1987) showed that the geometry of the Rochechouart stockwork was controlled by reactivated hercynian directions. Mineralizations related to the HS or dated at the Hettangian are also fault-controlled at the local scale (e.g., Nantiat fault at Chaillac: Le Carlier et al. 1999; S<sup>t</sup> Thibaut fault at Melle Pb Ag mines: Coiteux 1982). At the continental scale, they are controlled by major hercynian lineaments (Fig.1).

## 4. Interpretation and discussion

We have shown that the bolide fallen at Rochechouart 200 Ma ago probably caused, over a minimum distance of 350 km all around, mammal extinction, firestorms, tsunamis and sediment brecciation, i.e. similar environmental consequences to the ones observed at the K/T boundary around the Chixculub crater. On continental surfaces, the hydrolysis of silicates to residual clays and Fe-oxi hydroxides became active under an O<sub>2</sub>- and CO<sub>2</sub>-enriched atmosphere, Ba and Pb were released from feldspars. The post-impact submersion of the Rodez strait and of western MC can account for the observed generalised feldspar albitisation and albite neof ormation at 200Ma in the flooded Permo-Carboniferous basins and basement rocks exposed to seawater. Finally, the distribution of ores on the

Hettangian paleosurface testifies that the release of impact energy was directional, focused along Hercynian lineaments. In the Chaillac basement-hosted vein, Sizaret et al (2004) proposed that fluorite was deposited from a condensed vapour or from a residual brine following a deep boiling episode. At Fanay-Magnac U mine, 40 km SW of Chaillac (Fig. 1a), late stage fluorite and baryte, interspaced with breccia and associated with banded quartz (Leroy 1978), can be related to the LH event. Liquid-filled fluid inclusions in fluorite, with  $85^{\circ} < T_h < 130^{\circ}C$ , ( $T_h$  = homogenization temperature to liquid of the inclusion fluid) probably imply metastable or boiling solutions given the Hettangian sub-surface context, and consistently with hematite and ankerite precipitation post-dating fluorite.

A unique impact-driven epithermal model can account for the common characters of Ba F Pb ores scattered along the LH paleosurface: a strict control of Hettangian fluid flows by reactivated faults, and metastable/boiling fluids. The proposed model is similar to that of earthquake-controlled epithermal mineralizations proposed by Sibson (1987) except that, in the Hettangian case, the energy and metals do not originate from a magma but from an impact. This model also explains why an intense continental hydrolysis developed contemporaneously with the epithermal ore stage. Mobilized metals around the impact are incompatible elements leached along shear-zone pathways, Ba and Pb being released from feldspars. However, the chemical and mineralogical analogy between the paragenesis of Chaillac ores and that of fumarole deposits (including the presence of Cl Pb Ag Mo and of the highly volatile metal Tl; Africano et al 2002), plus may be the Pb isotope data, suggest that part of the latter metals have a common origin from the dust cloud generated by the impact, prior to being removed by rain and later entrained along permeable shear zones.

## Acknowledgements

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