Changes in Zn speciation in the rhizosphere of graminaceous plants induced by phytostabilization of a contaminated sediment

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INTRODUCTION

Context : The maintenance of waterways generates large amounts of dredged sediments, which are deposited on adjacent land surfaces. These sediments are often rich in metal contaminants and present a risk to the local environment.

Possible Solution : **Phytostabilization** is a cost-effective technique usually employed for polluted soils to **limit the release of metals in the environment.**

General goal of the study : To understand how Zn is immobilized at the molecular scale during phytostabilization to formulate effective metal containment strategies. In this study, mineralogical transformations of Zn-containing phases induced by two graminaceous plants (*Agrostis tenuis* and *Festuca rubra)* in a contaminated sediment ([Zn] = 4700 mg kg-1 , [P2O5] = 7000 mg kg-1, pH = 7.8), untreated or amended with hydroxylapatite (AP) or Thomas basic slag (AS), were investigated after two years of pot experiment.

MATERIALS

SEDIMENT

The sediment was collected in the Scarpe river (north of France), sieved (< 2 cm), homogenised and kept under cover during 3 months to allow its maturation.

Element	Zn	Pb	Cd	Cu	Mn	Fe	Mg	Ca	Al
Concentration (mg.kg^{-1})	4700	700	123	150	180	16000	1870	36600	8800
SD	±150	±110	±10	±10	±10	±1200	±15	±1240	±1900

Others features	pH	Eh (mV)	TOC (%)	IC (%)	Humidity (%)
	7.8	143	7.2	0.7	28

The speciation of Zn in a sediment collected in the same river was previously determined (Isaure et al, 2002) :

➔ 60-70% sphalerite (ZnS), 0-10% willemite ($ZnSiO_4$)

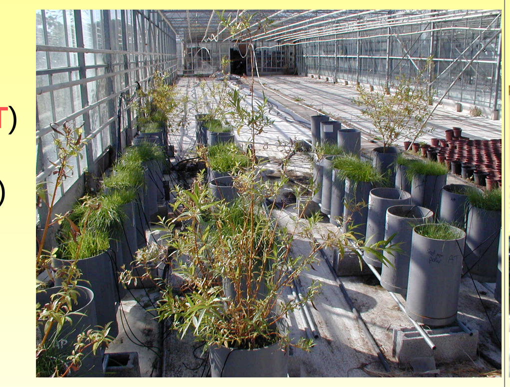
➔ 20-30% Zn- Fe-oxyhydryoxides, 0-10% Zn-phyllosilicates

VEGETAL SPECIES AND SUBSTRATES

2 plant species :

• *Agrostis Tenuis* (AT)

• *Festuca Rubra* (FR)



3 substrates :

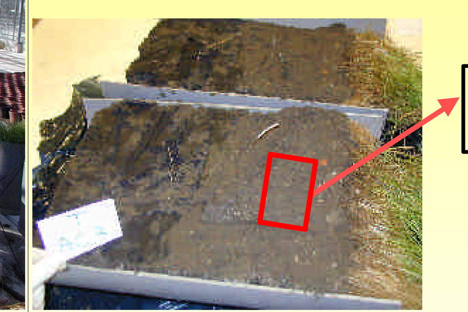
• Sediment

• Sediment + Hydroxylapatite (AP), $Ca_{10}(PO_4)_6(OH)_2$ (3 % weight added)

• Sediment + Thomas Basic Slag (AS) (5 % weight added)
AS is a by-product of the steel industry which contains **phosphates**, lime and iron oxides among other.

SAMPLES

Phytostabilization was conducted in a greenhouse. The 3 substrates were placed in pots. In some of them plants were grown, and others were kept without plant in the same conditions



After one year and a half :

Sampling of undisturbed bulk samples (6 rhizospheres and 3 substrates without plants)

Embedding in resin ➔ Thin sections | Drying and grinding ➔ Powders

The names of the samples are as follows :

species \ Substrate	Sed. + AS	Sed. + AP	Sed.
FR	ASFR	APFR	TFR
AT	ASAT	APAT	TAT
T (without plant)	TAS	TAP	TT

ANALYSIS OF THIN SECTIONS

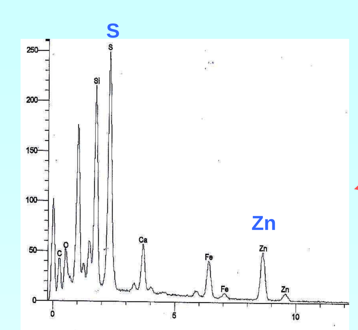
METHODS

➡ Zn-rich regions and chemical associations were first localized and determined by SEM-EDX and µSXRF (µ-Synchrotron X-Ray Fluorescence).

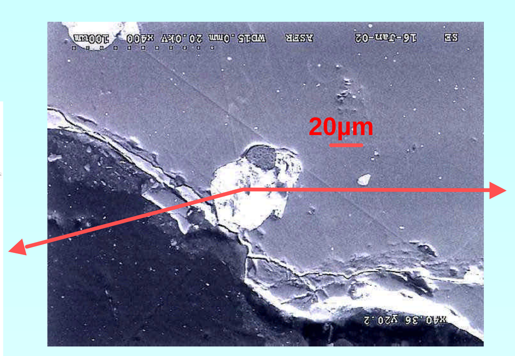
➡ Zn speciation at the molecular-level was then determined by µEXAFS **(µ-Extended X-Absorption Fine Structure)**, with a beam size of about 5 µm x 5 µm.
µEXAFS and µSXRF experiments were performed at the Advanced Light Source (Berkeley, CA, USA), on beamline 10.3.2 .

➡ µEXAFS spectra were treated by the statistical approach named Principal Component Analysis (PCA) in order to determine the number of Zn species and to identify them (Manceau *et al*., 2003). The proportion of the Zn species was then determined for each spot analyzed by Linear Combination Fitting (LCF).

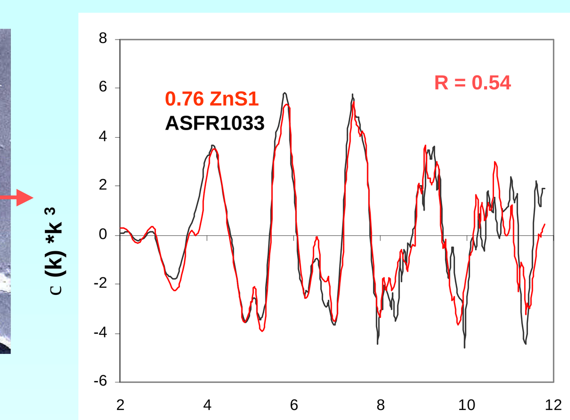
Figure 1 : spot containing pure sphalerite



EDX spectrum

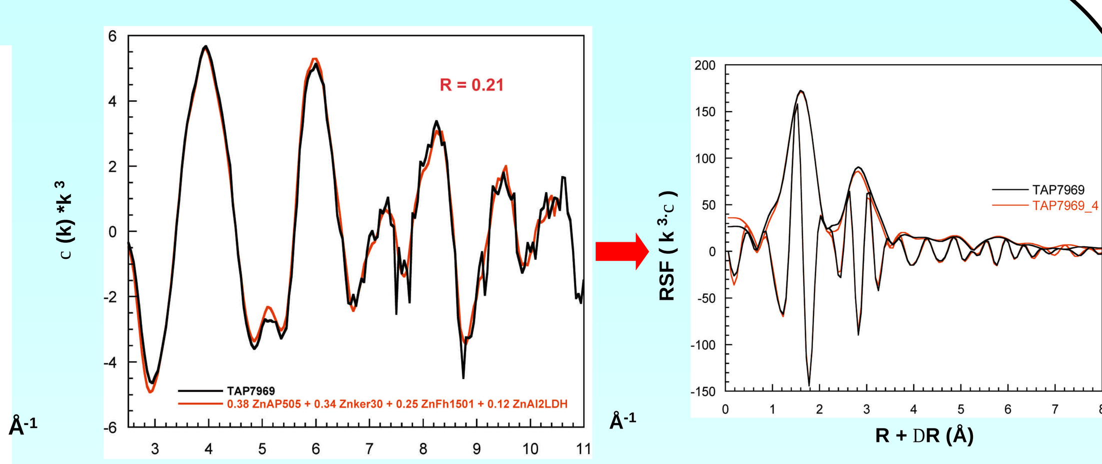


SEM picture (x 400)



experimental µEXAFS Spectrum
Sphalerite (ZnS)

Figure 3 : spot containing a mixture of several species



Even at the scale of a few µm³, Zn is present as a mixture of several Zn species. In this example, Zn-phosphate, Zn-kerolite, Zn-Ferrihydrite and Zn-hydrotalcite.

RESULTS

34 µEXAFS spectra (see below) were recorded on the different thin sections. In some cases, pure Zn mineral species were identified (e.g. Fig. 1 and 2) but most of the spots analysed contained a mixture of several Zn species (e.g. Fig. 3)

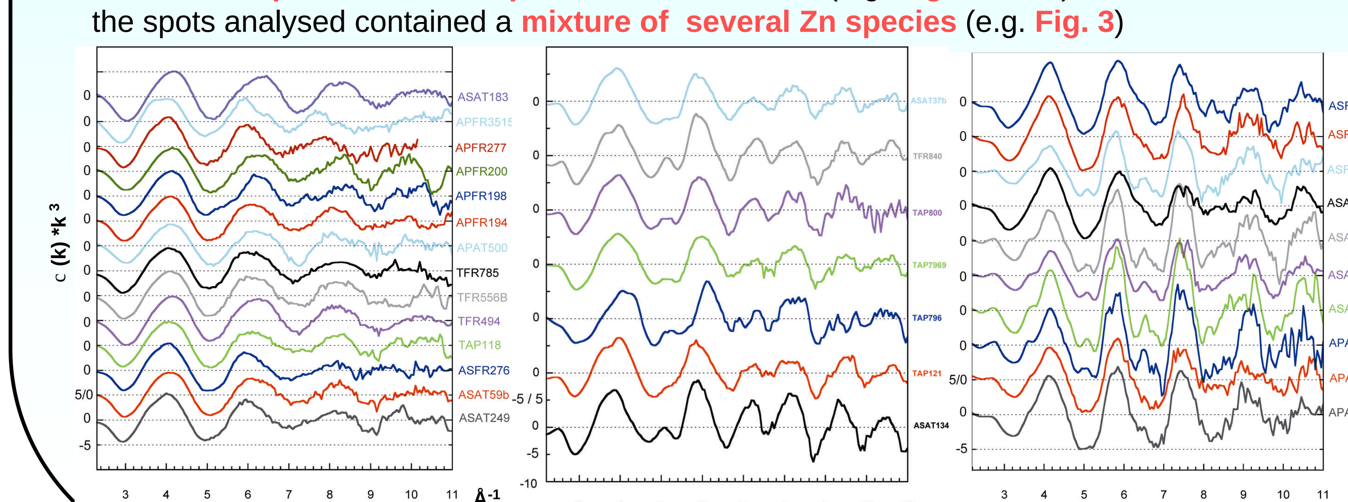
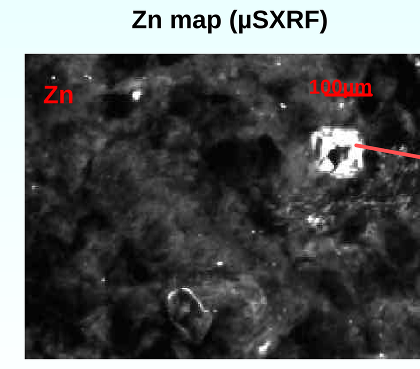
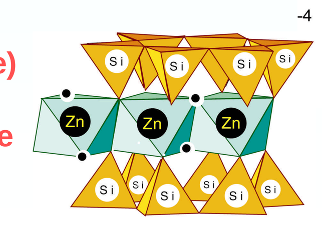


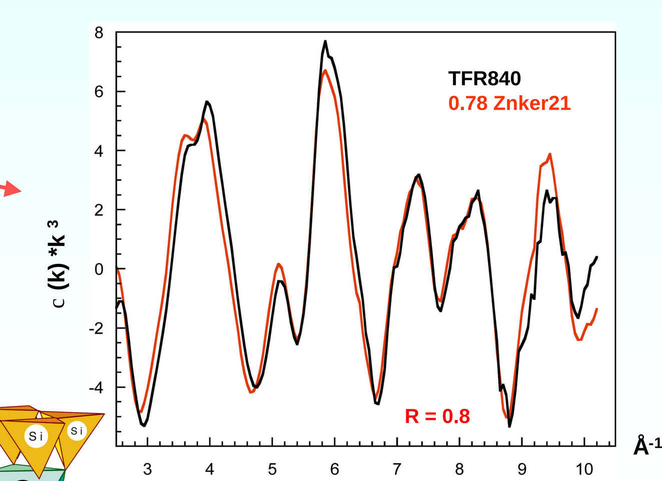
Figure 2 : spot containing pure Zn-kerolite

Zn map (µSXRF)



Zn-kerolite (Zn-phyllosilicate) was directly observed in a polluted environment for the first time.





experimental µEXAFS Spectrum
Zn-kerolite

CONCLUSION

The study of the thin sections at the microscopic scale allowed the identification of 7 Zn mineral phases.

Primary minerals :
(from anthropogenic source)

➔ Sphalerite (ZnS) :
- Ore mineral.
- Possible mobilization of Zn under oxic conditions.

➔ Gahnite ($ZnAl_2O_4$) and franklinite ($ZnFe_2O_4$) :
- Low solubility.

Secondary minerals :

➔ Zn-kerolite (Zn-Ker) : Zn-phyllosilicate.

➔ Zn-hydrotalcite (Zn-Hydtal) : Zn-Al Layered Double hydroxide.

➔ Zn-phosphates (Zn-P), poorly crystallised.

➔ Zn-Fe oxyhydroxide (Zn-Fh).

ANALYSIS OF POWDERS

METHODS

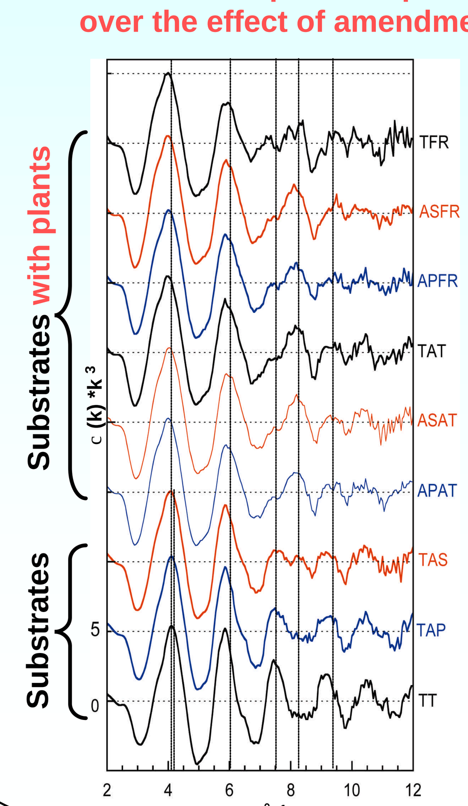
➡ In order to quantify at the macroscopic scale the proportion of the 7 Zn mineral species previously identified, EXAFS spectra of bulk samples of substrates and rhizospheres were recorded and simulated by LCF (Fig. 1, 2 and 3).

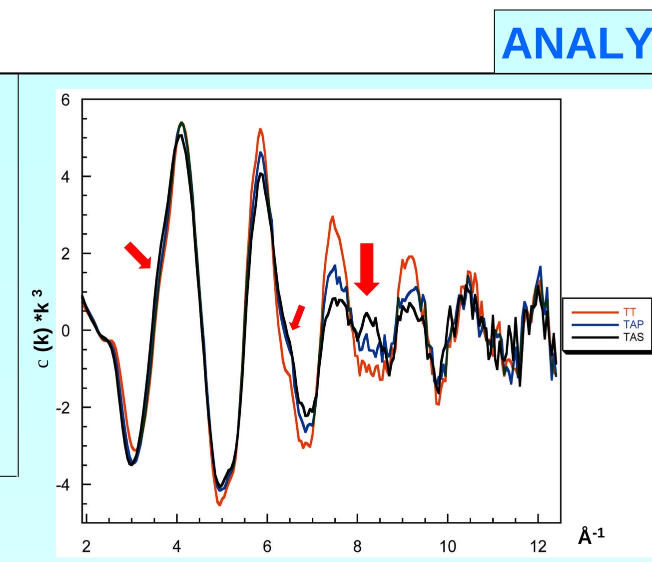
Conventional EXAFS experiments were performed at the European Synchrotron Radiation Facility (France) on beamline FAME.

RESULTS

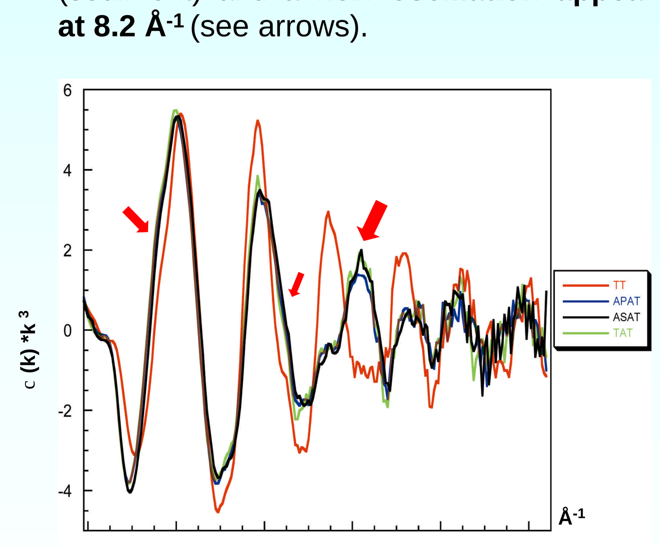
9 EXAFS spectra of bulk substrates and rhizospheres were recorded (see below).
Whatever the substrates, in the presence of plants (AT or FR) EXAFS spectra are almost identical.

➡ The effect of plants is prevailing over the effect of amendments.





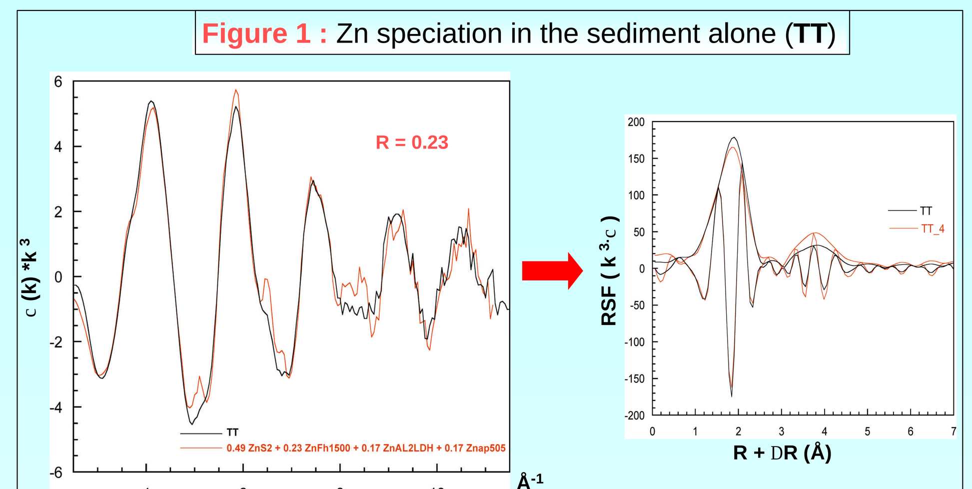
• For the 3 substrates, the oscillations are in phase. However **in the presence of AP** or **AS** the **first** and **second oscillation are enlarged in comparison to TT spectrum** (sediment) and **a new oscillation appears at 8.2 Å^{-1}** (see arrows).



• **The modifications** of the EXAFS spectra induced by the amendments **are enhanced in the presence of plants** (see arrows), but **no new feature appears in these EXAFS spectra :**

➡ Plants speed up the process of Zn phases transformation.

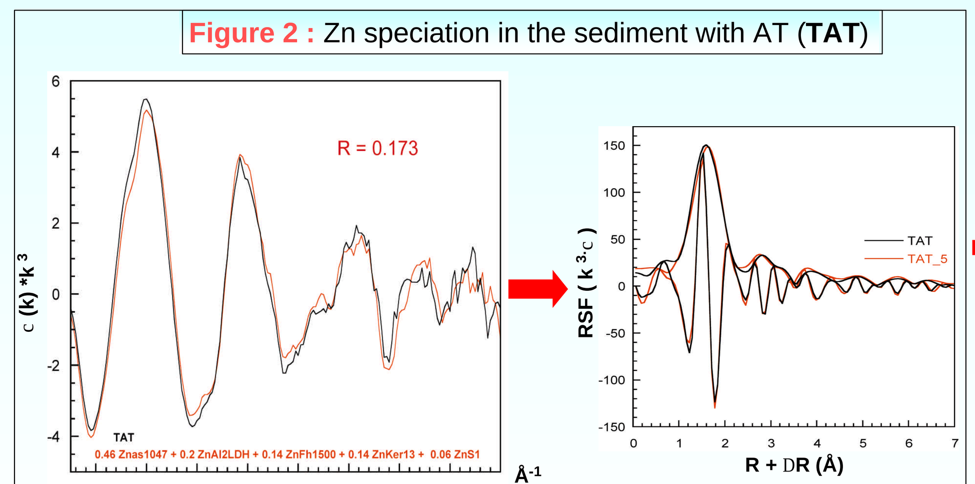
Figure 1 : Zn speciation in the sediment alone (**TT**)



Best reconstruction with (%) :

49 ZnS 17 ZnHydtal
23 ZnFh 17 Zn-P

Figure 2 : Zn speciation in the sediment with AT (**TAT**)



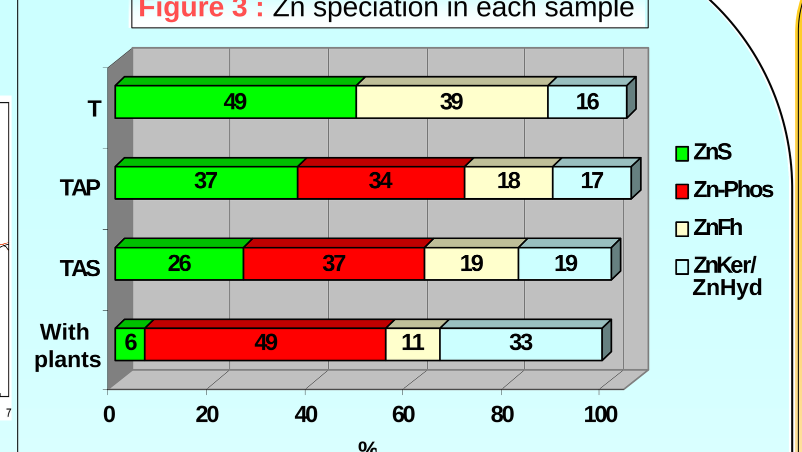
Best reconstruction with (%) :

46 Zn-P 14 ZnFh
31 Znker / ZnHydtal ‡ 6* ZnS

* *accuracy of EXAFS spectra reconstruction is usually about 10 % for a mineral specie, but in the case of a well ordered crystal structure such as sphalerite, the accuracy is lower.*

‡ EXAFS spectra of Zn-Ker and Zn-Hydtal are very close to each other, consequently these minerals were grouped in one single fraction.

Figure 3 : Zn speciation in each sample



CONCLUSION

➡ **In the sediment amended with AP or AS**

• ZnS fraction decreases and Zn-P fraction increases. The weathering of the substrate probably favours the oxidation of ZnS. Phosphates provided by amendments react with Zn to form Zn-phosphates.

• Zn-P fraction increases as follows :
TT < TAP < TAS.

➡ **In the rhizospheres**

• whatever the plant species and the substrate, the global speciation of Zn is almost the same. The effect of the plants is prevailing over the effect of amendments.

• ZnS fraction decreases dramatically. The kinetics of the oxidation of ZnS is increased by plants.

• Zn-P and ZnKer / ZnHydtal become the main pools of Zn.
Plants favour the formation of Zn-Ker / Zn-Hydtal.

GENERAL CONCLUSIONS

The approach presented here, combining electronic microscopy and synchrotron-based radiation techniques, all applied at the micrometer-scale of resolution, demonstrates the potential of this new approach to speciate metals in heterogeneous environmental matrices. Such an approach showed quantitatively the effects of amendments and plants on the global Zn speciation in a contaminated sediment :
• **Hydroxylapatite** and **Thomas basic slag** favour the formation of poorly crystallised Zn-phosphates.
• In cultivated substrates, whatever the plants species used, the global speciation of Zn is the same. **Geochemistry of sediment is deeply affected by plants (aeration of the medium by roots, plant nutrition, micro-organisms activity …).** The main effect of plants is the dramatic oxidation of ZnS. Other elements are mobilised (P, Al and Si which are nutriments) and form Zn-secondary mineral phases, such as Zn-phosphates and Zn-hydrotalcite / Zn-Kerolite, which are more stable than ZnS in oxic conditions.

REFERENCES

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