Trace metal pore water geochemistry of Ghar El Melh lagoon sediments (Northern Tunisia)

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Abstract

Five cores of 70 cm length were manually collected from Ghar El Melh lagoon sediments in January, April, June, August and November in order to study the dynamic of metals and their seasonal variation. The pore waters were extracted from the sediment under an inert atmosphere, and analyzed for dissolved iron, manganese, lead, zinc, cobalt, nickel, cadmium and copper. In general, iron, manganese, cobalt, lead, zinc and nickel increased with depth below the sediment-water interface and their concentrations are higher in the spring and the summer than in winter and autumn. Contrary to these metals, copper and cadmium are more released from the sediment in winter. Their profiles showed a decrease with depth. The formation of metallic sulfides and/or coprecipitation with iron sulfides apparently controls the distribution of these metals in the pore fluids in the layer 5-15 cm of the sediment. However, metal carbonate precipitation is absent in the sediment and the low values of saturation index can be due to analytical and calculation error.

Key words: Sediment, Pore water, Sulfides, Metals, Ghar El Melh lagoon

I. INTRODUCTION

Metal distribution between solid phase and liquid phase directly influences their mobility. This distribution is related to both physical and chemical conditions of the sediment, the composition of the dissolved and solid phase, modified by the activity of biota during early diagenesis, and the intrinsic properties of metals: oxidation, solubility, affinity for other components and different carrier phases. In the oxic sediment layer, most of metals are associated solid phase by adsorption and coprecipitation with Fe and Mn oxyhydroxides. In suboxic horizons, deeper, reduction of oxides released into the pore water Mn, Fe and initially associated metals. Under anoxic and reducing conditions, the production of metal sulphides will however make metals poorly soluble (Fernex et al., 1986; Tessier et al., 2011; Tessier, 2012) because most have strong affinities for these phases (Huerta Diaz and Morse, 1990; Piou et al., 2009; Rigaud, 2011), by surface adsorption, coprecipitation or inclusion as sulfurized metal salt (Morse and Luther, 1999). In contrast to the stable and refractory pyrite (Billon et al., 2002), some newly formed sulfides are poorly crystallized, unstable and easily reoxydable; they are grouped under the term "acid volatile sulphides" (AVS) (Tack, 1988; Cooper and Morse, 1998) and can induce rapid acidification when oxidized. Throughout the sediment column, metals initially immobilized by complexation to the particular organic matter are also released into the pore water when it is mineralized.

This work is part of the biogeochemical cycles of metals and consists of the results and discussion of the dissolved phase of the sediment (pore water). The determination of metals in the interstitial water and the solid phase will take us to undertake thermodynamic equilibrium calculations to identify the key processes of precipitation and dissolution of certain phases and insertion reactions of minor elements in other minerals.

II. MATERIAL AND METHODS

II.1. Cores collection and Eh measurement

Five cores of 70 cm length were manually collected from Ghar El Melh lagoon sediments in January, April, June, August and November. The pore waters were extracted from the sediment under an inert atmosphere. Determination of redox potential (Eh) was made using combination electrodes (SenTix pH, ORP, WTW, Weilheim, Germany).
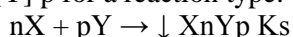
II.2. Trace metal analysis

Iron co-precipitation technique (Welch et al., 1990) was used to concentrate dissolved metals in pore water samples. To each water sample (5 ml), was added 100µl of 1M $FeNO_3$ solution at pH = 7 and the precipitate which forms is then recovered by filters (0.45µm), and dissolved in a solution of HNO_3 (10%). Iron was determined directly on raw sample by Thermo SOLAAR AA Spectrometer and the Relative Standard Deviation (RSD) is low than 10 %. Whereas, Concentrations of Mn, Ni, Pb, Zn, Cu, Cd and Co were determined by thermo SOLAAR graphite furnace FS95. Their RSD are lower than 5%.

II.3. Presentation of the thermodynamic equilibrium calculations (MINEQL$^+$) software

For clarity, we decided to present the operation of MINEQL$^+$ through a concrete example. However, we present here only the functionalities of the software that we used in our calculations: (i) an imposed pH (measured in our sediment) and (ii) no precipitate since we started manually the calculation of saturation and coefficient of distribution.
To quantify the saturation state of an element X present in a water with respect to the mineral XpYn formed or not in the sediment, we used ionic activity product (IPA) defined by: IPA = [X.] n [Y] p for a reaction type:
$$nX + pY \rightarrow \downarrow XnYp \; Ks$$
If PAI <Ks, the element X is said under-saturated with respect to the precipitate XnYp.

If PAI> Ks, the element X is said over-saturated with respect to precipitate XnYp.

If PAI = Ks, the element X is said in equilibrium with the precipitate XnYp.

For our calculations, we considered the cations Cd^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and the anions CO_3^{2-}, S^{2-} and SO_4^{2-}. Moreover, in the marine environment, so in waters where the salinity is high, we have taken into account in the calculations, the ionic force which was calculated using the relationship established by Gomez Parra and Forja (1994):

$$S: \text{salinity} \quad \mu = \frac{19.919 \times S}{1000 - 1.00198 \times S}$$

Activity coefficients (γ) of dissolved charged species, for their part, were determined using the equations of Davies (1962) and Whitfield and Turner (1980):

$$Z_A i \quad \text{Log } \gamma_A = \frac{0.5108 \times Z_A^2 \times (0.3 \times \mu - \sqrt{\mu})}{1 + \sqrt{\mu}}$$

In the case of uncharged species, Mantoura et al. (1978) propose the use the following equation: log (γ) = -B x μ with B value is 0.1 for a couple of 1:1, 0.3 for a couple 1:2, and 0.5 for other couples.

III. RESULTS AND DISCUSSION

III.1. Vertical profiles of metals in the pore water

III.1.1. Iron and manganese

The oxic layer thickness is one centimeter in winter and the concentrations of dissolved iron and manganese are relatively low. In summer, the thickness of the oxic layer is less than one centimeter with dissolved Mn and Fe concentrations higher than in winter. Below this layer, the suboxic area is marked by dissolved Fe and Mn peaks but with different thicknesses depending on the season (Fig. 2).
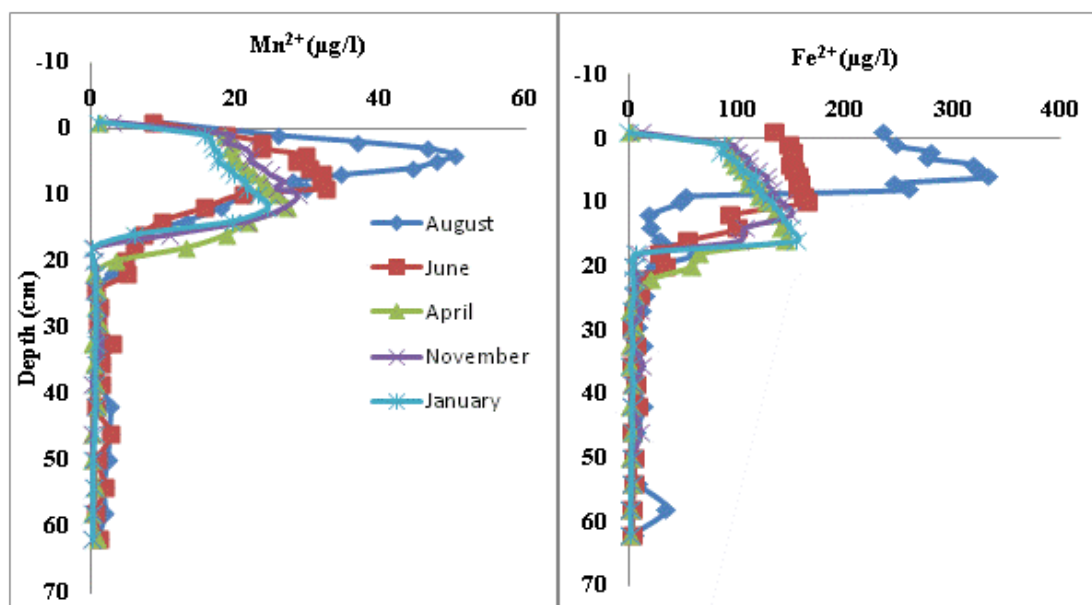
Fig. 2. Vertical variations of Fe and Mn in pore water in the lagoon of Ghar El Melh lagoon (core SS).

III.1.2. Cobalt, Nickel, Lead, Zinc, Cadmium and Copper

That a small amount of trace metals is present as dissolved species in pore water (<0.1% of the total metal content; Van Den Berg et al., 2001), metal concentrations in these pore waters are the most sensitive to environmental change settings, and are useful as indicators of mineral phases control in sediments.

Table 1 shows the minimum and maximum concentrations of metals in pore water. Only nickel and cobalt concentrations which are comparable to those found in the world. The concentrations of the other metals are very high and this can be explained either by contamination of sediments of the Ghar El Melh lagoon by these metals and especially Pb, Zn, Cd or by the mobilization of these metals by various biogeochemical processes that release these metals to the pore water.

Table1. Levels of metals in pore water in the Ghar El Melh lagoon and other aquatic environments in the world (nmol/l).

Study site	C	C	P	Z	C	N
Ghar El Melh lagoon (this study)	4 -1600	2-1000	2 -3500	3 -9000	2 -200	2-60
Ontario lake (Huerta Diaz et al.,	5 -6	2. -2	2. -2	1-500		
Venise lagoon (Bertolin et al., 1997)	1-300	1. -6	-2	1 -1500		
Ontario lake (Tessier et al., 1985)	5 -60	2. -8	1 -2	110-43		
Delaware bay, , (Boulègue et al., 1982)	7 -53					
Ria Formosa (Caetano et Madureira, 2007)	2-150	2. -2				
Galveston bay (Warnken et al., 2001)				1. -1		1. -3
Galician Ria (Santos Echeandia et al.,2009)	2-120		2. -2	5-150	2. -2	1-16

We tried to group profiles of all metals in all different sampling dates (august, june, april, november and january) in a graph (Fig. 3) to better interpret the dynamics of the elements in question depending on the depth. We clearly see:

-Like Fe and Mn, Co, Ni, Pb and Zn are more released in the pore water in summer and winter.
-Concentrations are higher in the surface layer.
-All metals are correlated as shown in Table 2.
-Cu and Cd are more released in winter (January and April). Concentrations are very low in summer and autumn.

Based on these comments, we will try to draw conclusions about the behavior of all metals studied (we have already started with the iron and manganese).

The peaks centered on an average depth of 10 cm indicating a release of metals involved in the dissolved phase mainly below the interface. However, in some cases, these peaks occur before or after deep. These enriched zones are followed by a sharp decrease in dissolved concentrations, indicating incorporation of metals in particulate phase.

In August, the peak concentrations for all metals are centered on 4-5 cm depth like Mn. However, subtraction of the dissolved metal phase differs from one metal to the other. Unlike other metals whose concentrations in pore water appear until about 20 cm deep like

Mn, Pb shows a different behavior and it appears that following iron here. This metal is rapidly subtracted from the dissolved phase. It turns out that it is immediately incorporated into the particulate phase.

In June, the peaks of dissolved Mn and Fe appear at 10 cm depth with concentrations less than those recorded in August. The peak of Co appears after this depth while those of Ni, Zn and Pb appear at 6 cm depth.

The subtraction of cobalt from dissolved phase remains slow in November, January and April. In November, the peak of Co^{2+} appears at 16 cm depth while the peaks of all metals appear almost at the same depth that is 12 cm with concentrations similar to those in June.

Table 2. Correlation matrix between concentrations of metals in pore water of the Ghar El Melh lagoon. n = 146.

	Cd	Ni	Zn	Cu	Pb	Co	Fe	Mn	Eh
Cd	1								
Ni	0.022	1							
Zn	0.031	0.891	1						
Cu	0.983	0.045	0.047	1					
Pb	0.307	0.807	0.832	0.343	1				
Co	-0.037	0.853	0.818	-0.016	0.727	1			
Fe	0.346	0.721	0.737	0.381	0.754	0.656	1		
Mn	0.188	0.876	0.845	0.216	0.887	0.845	0.812	1	
Eh	-0.134	-0.566	-0.536	-0.180	-0.605	-0.643	-0.499	-0.685	1

In January, the enrichment area of trace metals extends over a layer of 20 cm for Co, Ni and Zn and a lesser thickness for Mn, Pb, and Fe (10, 14 and 16 cm respectively). The behavior of metals in April is like that in January.

Contrary to other metals, copper and cadmium present different behavior in the dissolved and particulate phase in the sediment. These two very toxic trace metals have a negative concentration gradient at the sediment-water interface (Oueslati et Added, 2011) suggesting the release to the water column in the majority of the sampling dates. They are also better released in summer and winter.

IV. Chemical equilibrium between the liquid and solid phases

Analyzes, conducted on interstitial waters, have allowed us access to total content of each element. However, for equilibrium calculation, it is necessary to evaluate the concentration and mainly the activity of the free form of the element. This approach leads us to use the software for thermodynamic calculation MINEQL[+] (Schecher and McAvoy, 1998) which, from the overall contents of the constituents of water, to achieve their speciation and to reach concentrations of different soluble complexes existing in the studied pore water.
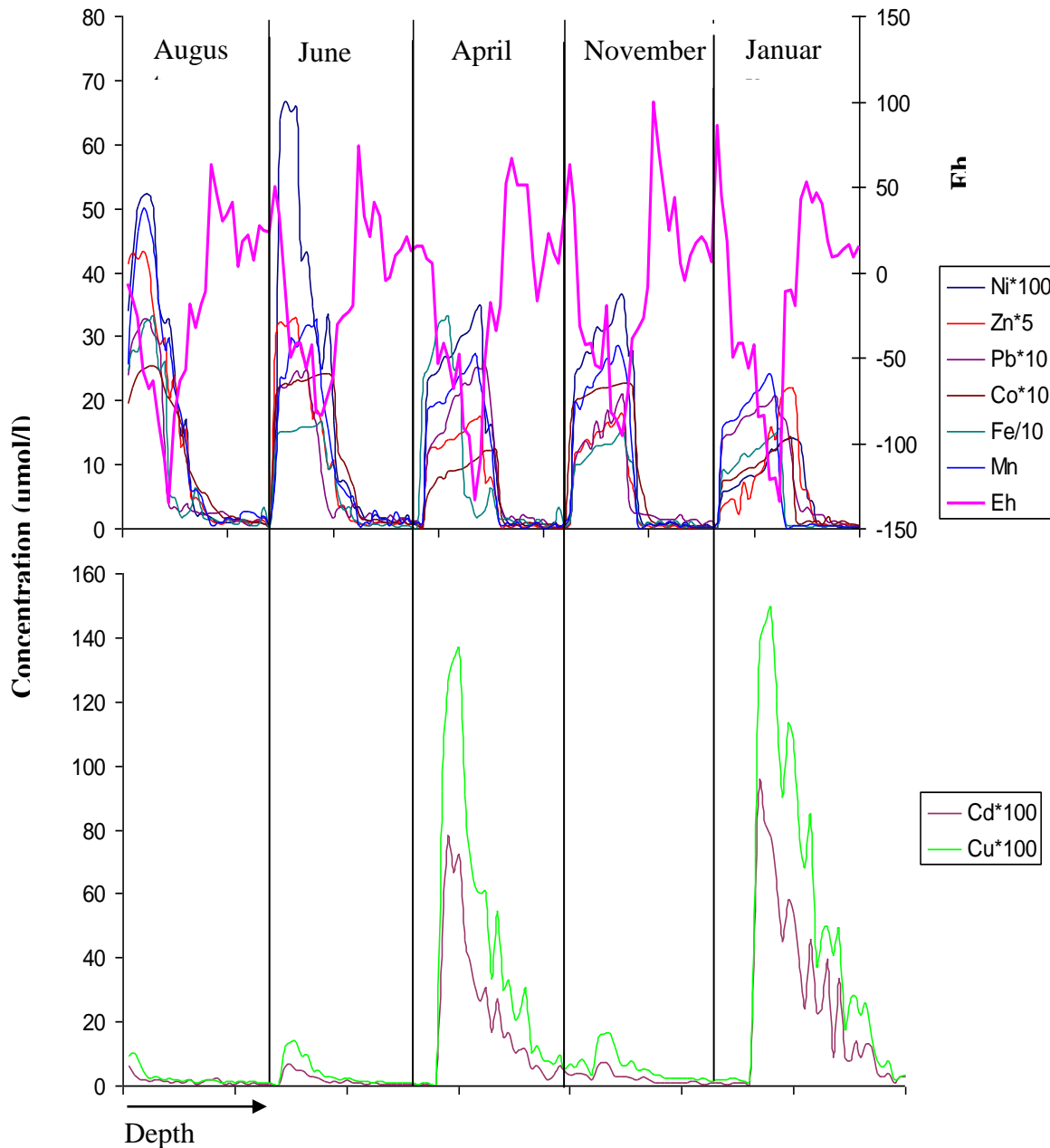
Fig.3. Vertical Variations of metals in pore water in the Ghar El Melh lagoon.

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IV.1. Iron

Results obtained in the form of vertical profiles of the saturation index (Fig. 4) suggest that iron sulfides precipitate from 1 cm depth (the presence of AVS is indeed important

in the first centimeters). In addition, throughout the core, the activity product $(Fe^{2+})(S^{2-})$ which was determined from the data analysis and data processing MINEQL$^+$, corresponds the best to mackinawite [pK mackinawite = 17.5 (Davison, 1991)]. However, we can't exclude the presence of greigite [pK greigite = 18.3 (Davison, 1991)] in the surface layer of our sediment. The

presence of amorphous iron sulfide was excluded because of the large difference (> 2.74 pK unit) between log (PAI) and the negative logarithm of the solubility product of FeS$_{am}$. About siderite [pK siderite = 10.7 (Morel and Hering, 1993)], an over-saturation can be seen from 4 cm deep (Fig. 4).
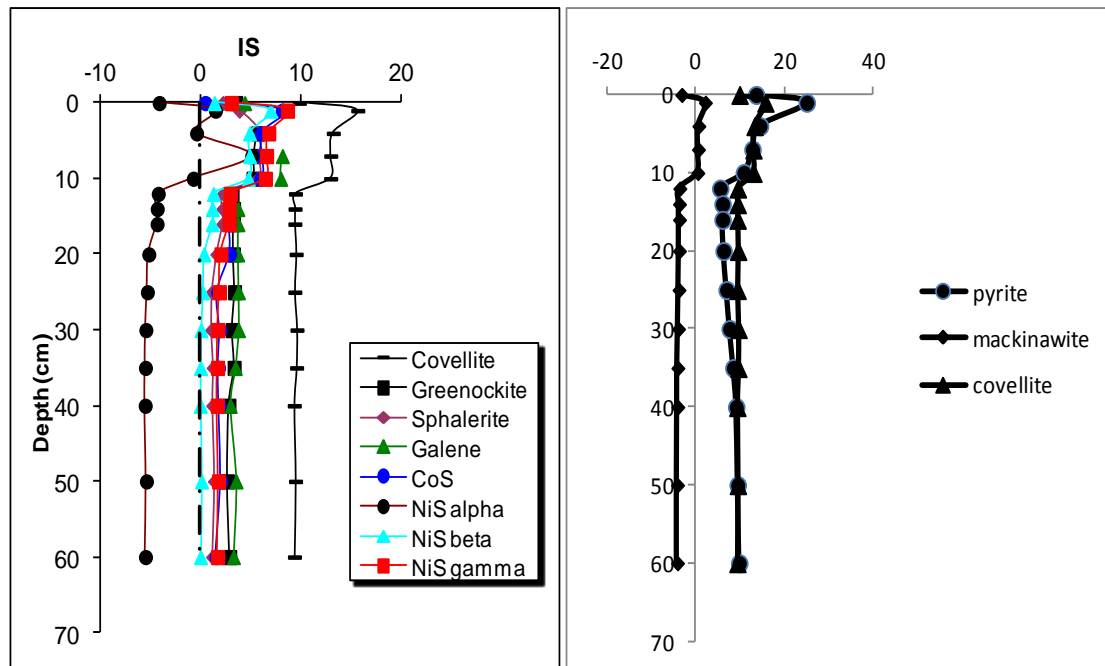

Fig.4. Saturation Index of metal sulphides.

IV.2. Manganese

The comparison between the values of PAI (Mn^{2+})(S^{2-}) and solubility products of manganese sulfides indicates that pore water is largely undersaturated in mineral MnS [Ks ^{MnS}(green) = 13.5 and Ks ^{MnS}(pink) = 10.5 (Smith and Martell, 1976)]. However, the values of PAI (Mn^{2+}) (CO$_3^{2-}$) (Figure 5) are greater than the solubility product of rhodochrosite (MnCO$_3$) but lower than 5. Thus, Mn (II) does not precipitate with carbonates in the 4-20 cm layer of the sediment (Added, 2001) in spite of results of chemical extraction confirmed that manganese is essentially linked to the carbonate phase in the Ghar El Melh lagoon (Oueslati et al., 2010b).

IV.3. Cadmium, copper, lead, cobalt, nickel and zinc

As opposed to the carbonate phase, Cd, Cu, Pb, Co, Ni and Zn have a high affinity for sulphides so that their ionic activity product

Sequential extraction (Oueslati et al., 2010b) showed that only Cd and Zn are present in the carbonate fraction (in order of decreasing percentage was: Cd > Zn). These observations are consistent with the studies of Reeder (1983) and Mucci (1999) which indicated that a number of metallic elements (Ba^{2+}, Cd^{2+}, Sr^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) are firstly adsorbed on the surface of carbonate calcium before being inserted or form new pure separated phases. It is therefore legitimate to consider the saturation states with regard to metallic carbonates. Obtained values show that pore water is undersaturated with respect to CuCO$_3$, CdCO$_3$, PbCO$_3$ and NiCO$_3$ except ZnCO$_3$ and CoCO$_3$ in surface sediments (Fig.5).

These calculations suggest that these metals are rather inserted in calcite under solid solution form Ca$_{1-x}$Me$_x$CO$_3$.

PAI = $(Me^{2+})(S^{2-})$ is greater than their solubility product: Ks (MeS) (Fig. 4). These metals thus form discrete phases CdS, CuS, PbS and ZnS (without of course exclude the presence of Cd, Cu, Pb and Zn co-precipitated with iron sulfides), which is consistent with the work on anoxic sediments from lakes in Canada: "Canadian Shield lakes" (Huerta Diaz et al, 1998).
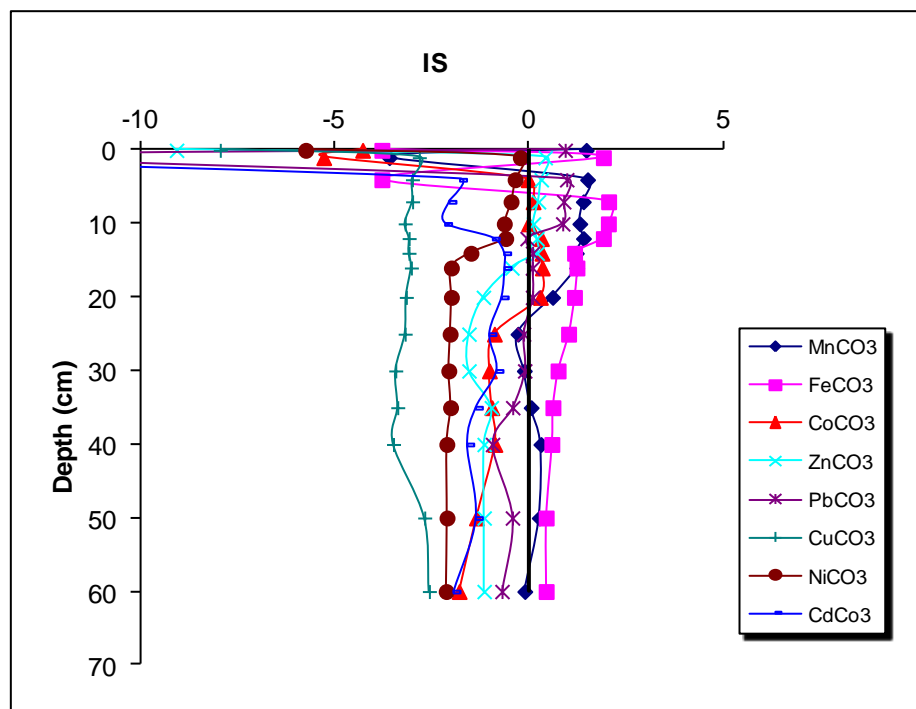

Fig.5. Saturation Index of metal carbonates.

In reality , significant supersaturation of cadmium , copper, lead and zinc from the fact that the calculations of presumed thermodynamic equilibrium existing in our sedimentary environment does not fully reflect the reality because organic complexes (such as humic and fulvic acids) are not considered and the complex metal-sulfur do not take into account polysulfides [in the case of cadmium, for example, only the following complexes were introduced into the database MINEQL$^+$ software $Cd(HS)_4^{2-}$, $CdHS^+$, $Cd(HS)_3^-$ and $Cd(HS)_2$]. Jacobs and Emerson, (1985) and more recently Huerta Diaz et al., (1998) have published studies related to these problems. It follows that for the sulphide-rich pore water ($\geq$ 10^{-7} mol.dm^{-3}), cadmium, lead and zinc are extensively complexed by sulfur compounds (and in particular by disulfides) at the outlay of humic substances, cysteine or glycine (note however that thiols can also effectively complex Pb). Copper also form very stable complexes with sulphides and polysulphides, which explains the high supersaturation of the metal with regard to covellite (CuS). Saturation indices of all metals are higher in surface than in depth (Fig. 4) indicating that metal sulphides are formed preferentially in the first ten centimeters of the sediment. These indices increase in the first centimeter below the sediment-water interface and then decrease to 12 cm depth before leveling beyond this depth. This rate is in contradiction with the monosulphides profile. Indeed the peak at 1 cm seems to be weird reflecting the problem of organic complexing agents discussed above. However, this appears resembling profiles of the majority of metals in the solid phase of the sediment on the one hand and the reactive phase in the other (Oueslati et al., 2010a and 2010b).

Figure 6 shows that the saturation index of metal sulphides is very well correlated with that of mackinawite checking the correlation between metals and iron in the reactive fraction and the similarity between the profiles of metals in the pore water in the Ghar El Melh lagoon.
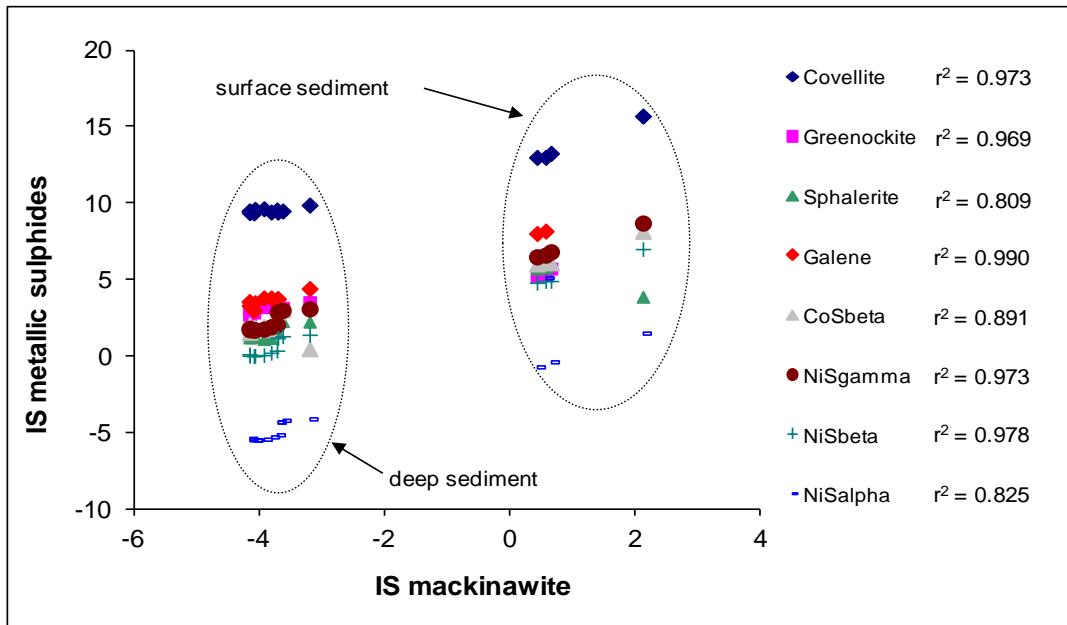
Fig.6. Correlations between the saturation index of mackinawite and saturation indices of other metal sulphides.

Figure 7 shows that the saturation index of the pyrite is negatively correlated with saturations indices of metal sulphides in deep sediments. By cons, these indices are positively correlated in surface sediment. Thus, in depth, metals are associated with pyrite and don't form their own sulphides. This is explained by the increase of the degree of trace metal pyritization (DTMP-Me) with depth and the correlation between DTMP-Me and the degree of pyritization (DOP) (Oueslati, 2011). IS-Me decreases with the depth while DTMP-Me increases.
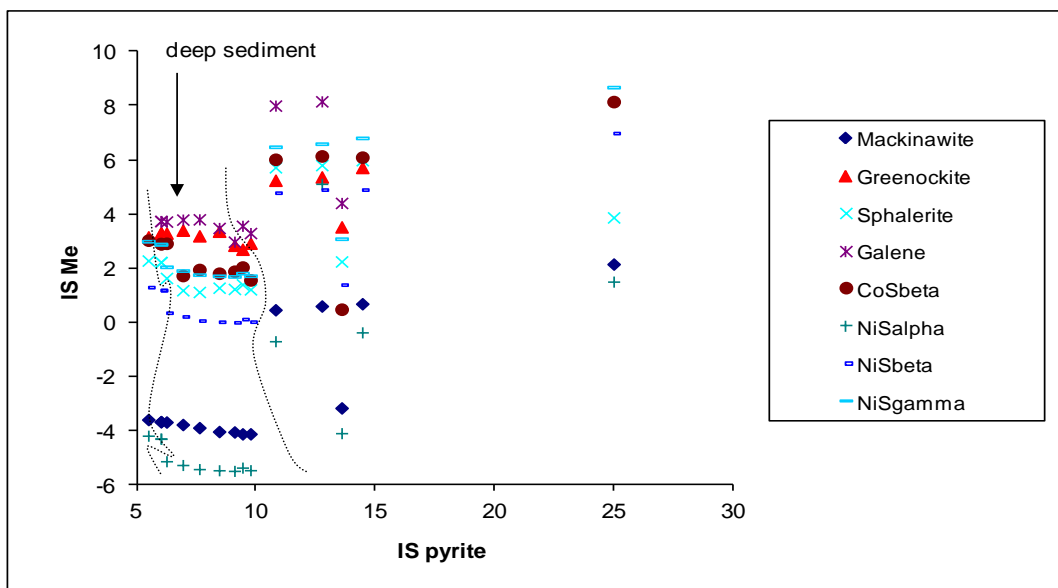

Fig.7. Correlations between the saturation index of pyrite and saturation indices of metal sulfides. In the deep sediment, the correlations are negative.

V. CONCLUSION

The study of the vertical distribution of metals in pore waters showed that metals can be classified into two groups. The first group (Mn, Fe, Pb, Zn, Ni, Co) is characterized by a distribution showing an increase of concentrations below the interface, followed a sharp decrease below 25 cm depth. The second cluster (Cd and Cu) shows a decreasing profile with depth. We have shown that the accumulation of metals is due to diagenesis and their reduction is controlled by precipitation (pyrite). The mineral precipitation is confirmed by thermodynamic calculations indicating that precipitation of rhodochrosite $MnCO_3$, cerusite ($PbCO_3$) is difficult. Nevertheless, metal sulphides excepted MnS is possible between 10-12 cm.

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