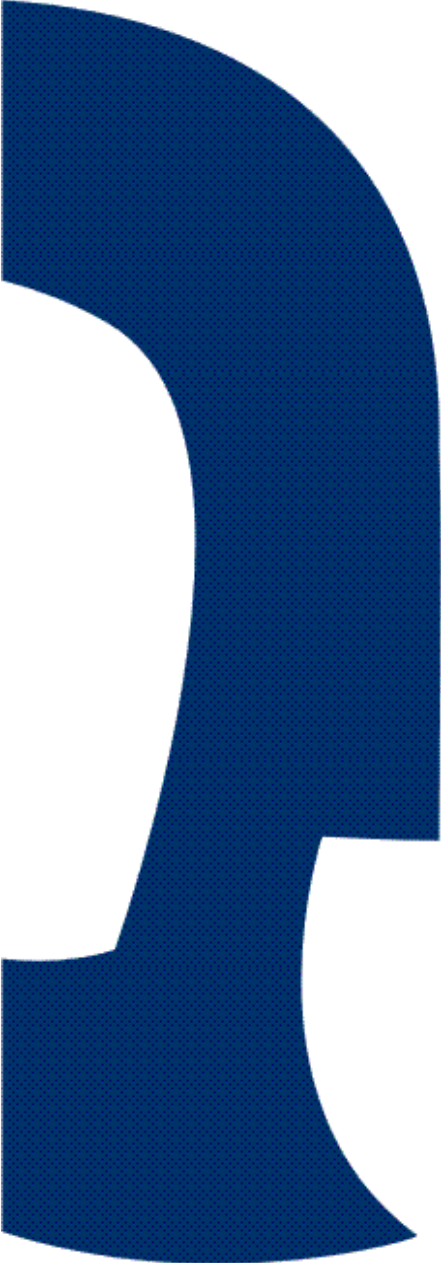


**MASTER UNIVERSITARIO EN OCEANOGRAFÍA**

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**The role of humic acids on the  
iron speciation and the  
competitive effect with copper in  
seawater**

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## Abstract

The role of humic acids (HA) on the iron speciation and the competitive effect with copper were studied in artificial seawater as a function of the ionic strength ( $0.1 - 0.7 \text{ mol L}^{-1}$ ), pH ( $6.0 - 8.5$ ) and temperature ( $5 - 30^\circ\text{C}$ ) by using the geochemical numerical code Visual Minteq. The simulations were in a good agreement with the data collected from the literature in terms of Fe speciation, where the presence of humic acids produced the formation of Fe organic species (Fe-L) that showed a higher contribution to the total iron species when HA were higher than  $1000 \text{ nmol L}^{-1}$  in artificial seawater as a function of ionic strength, pH and temperature. The presence of copper produced a competitive effect with the Fe speciation due to the formation of Cu-organic complexes (Cu-L) that were more abundant than the Fe-L species at pH higher than 7.5. These ligands are considered weak ligands in the ocean and their Fe and Cu complexing capacities are defined by the conditional stability constants and their hydrolysis constants with the major Fe and Cu species in seawater.

The current numerical code also allows to study the Fe mineral formation under the physico-chemical conditions previously considered as well as their solubility index. In this sense, the oversaturated Fe minerals in artificial seawater were  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$ , ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnesioferrite. After the copper addition, the Fe-Cu mineral cupric ferrite was formed with a saturation index above 14. These minerals could be found in deep seafloor and marine sediments.

The numerical codes are useful geochemical toolboxes in order to predict the trace metal speciation in seawater and to better understand the competitive mechanisms between metals and organic ligands, as well as the mineral formation. In this sense, most of the numerical codes have been developed at low ionic strength and future experiments should improve the existing databases.

## 1. Introduction

Iron (Fe) and copper (Cu) are essential trace metals in the ocean because of their participation in a number of metabolic processes (Morel and Price, 2003) and in various enzymatic pathways as carbon and nitrogen cycles (Jacquot et al., 2014). Nevertheless, Cu can be toxic to microorganisms at certain levels (Buck and Bruland, 2005). The iron and copper speciation in seawater are controlled by the presence of organic ligands where these organic complexes are playing a key role in the mobility, solubility, residence time and bioavailability (Buck and Bruland, 2005; Gledhill and van den Berg, 1994; Kogut and Voelker, 2001; van den Berg and Kramer, 1979).

The structure and nature of these organic ligands are still unknown. However, one of the most studied metal-organic binding ligand groups are the humic substances (HS) (Abualhaija et al., 2015; Hering and Morel, 1988; Kogut and Voelker, 2001; Laglera et al., 2011; Mantoura et al., 1978; Whitby and van den Berg, 2015; Yang and van den Berg, 2009) which are components of the pool of natural organic matter in aqueous systems (Duursma, 1965). HS are important in the chemistry of trace metals in seawater due to their abundances (Frimmel et al., 2008; Obernosterer and Herndl, 2000) that are at  $\mu\text{g HS L}^{-1}$  levels (Obernosterer and Herndl, 2000) and constitute 10 – 30% of the dissolved organic carbon in seawater (Thurman, 2012). Humic substances are divided into humic acids (HA) and fulvic acids (FA) based on their solubility. Humic acids have a mixture of functional groups that can bind cations in natural waters such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or transitional metals such as Fe and Cu (Benedetti et al., 1995). Among the different functional groups, carboxyl and phosphoryl-like groups are the most important in terms of metal binding (Rashid, 2012). The cationic metal-binding process with HA is strongly influenced by their chemical heterogeneity (Benedetti et al., 1995).

Humic substances, together with the rest of organic ligands mainly produced by microalgae, control the iron and copper speciation in seawater (Laglera and van den Berg., 2009; Laglera et al., 2011; Whitby and van den Berg, 2015). Recent studies showed a competitive effect between Fe and Cu for the binding sites in humic substances (Abualhaija et al., 2015; Whitby and van den Berg, 2015) that have an effect on their speciation in natural waters. Then, the potential competitive role between trace metals and major cations present in seawater is a future challenge to fully understand the global biogeochemical cycles of metals and organic matter. Seawater is a complex electrolyte

solution that contains different ions capable to compete for the binding sites in HA in a greater or lesser extent (Benedetti et al., 1995). Among them, cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  compete for the same binding sites than Fe (Buffle, 1988) and other model binding ligands as catechol, sinapic acid and catechin (Santana-Casiano et al., 2010; 2014).

In the present study, the Fe speciation was theoretically studied under the presence and absence of HA at different ionic strength ( $0.1 - 0.7 \text{ mol L}^{-1}$ ), pH ( $6.0 - 8.5$ ) and temperature ( $5 - 35 \text{ }^\circ\text{C}$ ) in artificial seawater (ASW), by using the chemical speciation software Visual Minteq (Gustafsson, 2008). The use of numerical codes allows a rapid estimation of metal speciation giving a very useful and quickly knowledge about the behaviour of metal in different environments (Shahid, 2010). Visual Minteq is the second-most used chemical equilibrium software cited by more than 400 research manuscripts and is considered as the best simulation software to study the role of organic ligands (Shahid et al., 2012). The main goal of this current investigation is to demonstrate the applicability of this numerical code in seawater as an additional toolbox for the geochemistry of trace metals in order to better understand the role of humic acids on the Fe speciation as well as the competitive role of Cu by the binding sites in the humic acids.

## **2. Materials and methods**

### **2.1. Software description**

The simulation software Visual Minteq v.3.1 (Gustafsson, 2008) was used to compute the iron speciation and the saturation index (SI) of the formed Fe minerals in artificial seawater. The software simulation provides the concentration of each inorganic and organic dissolved species, solid phases and mass equilibrium under the different conditions studied that can be formed under the composition of the desired solution. The HA considered in this study are characterized by a discrete distribution of binding sites as are normally found in the marine environments (Gustafsson, 2008). The discrete ligand approach refers to a small set of ligands that are designed to represent divalent metal binding sites (Herndon, 1998), cation to ligand stoichiometry is treated as 1:1 (Cabaniss and Shuman, 1988). The equilibrium constants for Fe and Cu-humic acid ( $\log K'$ ) referred to free iron and copper with humic acids used in this study were 11.68 and 16.41, respectively. They are in good agreement with Fe and Cu-binding ligands in natural

waters (Abualhaija et al., 2015; Guy and Chakrabarti, 1976; Jardim and Allen, 1984; Kogut and Voelker, 2001; Laglera and van den Berg., 2009, 2011; (Abualhaija et al., 2015;; Mantoura et al., 1978; Shuman and Cromer, 1979; Whitby and van den Berg, 2015; Yang and van den Berg, 2009).

The saturation index respect to the mineral phase obtained from the software simulation, is defined as function of ionic activity product (IAP) and solubility product ( $K_{sp}$ ),  $SI = \log(IAP/K_{sp})$ . In this case, the Fe minor species, in terms of concentration, will be considered together as Fe-Ing species, where their contribution will never reach more than  $3.91 \times 10^{-7} \%$  of total Fe species concentration under the experimental conditions considered in the present study. This group of species were formed by:  $Fe(SO_4)_2^-$ ,  $Fe_2(OH)_2^{4+}$ ,  $Fe_3(OH)_4^{5+}$ ,  $FeBr^{2+}$ ,  $FeCl^{2+}$ ,  $FeF^{2+}$ ,  $FeF_3$ ,  $FeH_2BO_3^{2+}$ ,  $FeSO_4^+$ . In addition, Fe-L and Cu-L will correspond with the Fe and Cu-organic species formed under the presence of HA in ASW.

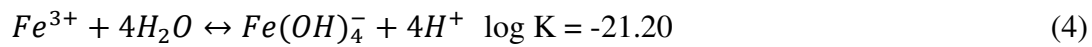
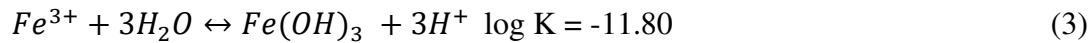
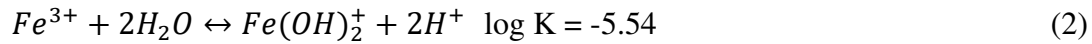
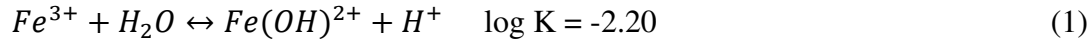
## 2.2. Experimental conditions

The Fe speciation was studied as a function of HA concentration (0 and 1000 nmol  $L^{-1}$ ) in ASW ( $S = 37$ ) as electrolyte solution described by Millero (2007). The concentration of Fe was always 100 nmol  $L^{-1}$ . The role of HA on the Fe speciation was also studied as a function of ionic strength (0.1 – 0.7 mol  $L^{-1}$ ), pH (6.0 – 8.5) and temperature (5 – 35 °C). The range of parameters are covering most of the environmental conditions in natural waters (Benedetti et al., 1995; Buffle et al., 1980; Byrne et al., 1988). When the role of one of these parameters was studied, the other ones were kept constant at pH = 8.0,  $I = 0.7$  mol  $L^{-1}$  and  $T = 25$  °C. All the studies were performed considering that the ASW was in equilibrium with the atmosphere in terms of  $CO_2$  and oxygen concentration.

In addition, the competitive role of Cu and Fe by the humic acids was also studied by considering a 1:1 concentration ratio between Fe and Cu. The software used to plot the results was SigmaPlot v.10 (Systat Software, 2008).

### 3. Results and discussion

The hydrolysis of Fe in aqueous solutions can be defined by the next equations (Millero et al., 1995):



where K is the stability constant for each Fe hydroxide species.

Under the presence of organic ligands, dissolved Fe is organically complexed and their equilibrium is defined by the conditional stability constant (K'). The speciation of Fe in seawater is directly related with the ionic strength, pH and temperature that is also controlling the solubility of Fe in natural waters (Liu and Millero, 2002; Millero et al., 1995). Fe is present in seawater as Fe(II) and Fe(III), where Fe(III) is the thermodynamically stable form in seawater. In this sense, the Fe species in seawater are  $FeHCO_3^+$ ,  $FeCO_3$ ,  $Fe(CO_3)_2^{2-}$ ,  $FeOH^+$ ,  $Fe(OH)_2$ ,  $FeCl_2^+$ ,  $FeCl_2^+$ ,  $FeFe^2$ ,  $FeF_2^+$ ,  $FeF_3$ ,  $FeSO_4^+$ ,  $FeOH^{2+}$ ,  $Fe(OH)_2^+$ ,  $Fe(OH)_3$ ,  $Fe(OH)_4^-$  (Millero et al., 1995). In the case of seawater solutions, the Fe speciation is mostly as Fe(III), referred as Fe along the manuscript. Then, the most abundant Fe species at standard seawater conditions (pH = 8, T = 25 °C and I = 0.7 mol L<sup>-1</sup>) are  $Fe(OH)_3$ ,  $Fe(OH)_2^+$  and  $Fe(OH)_4^-$  (Millero et al., 1995).

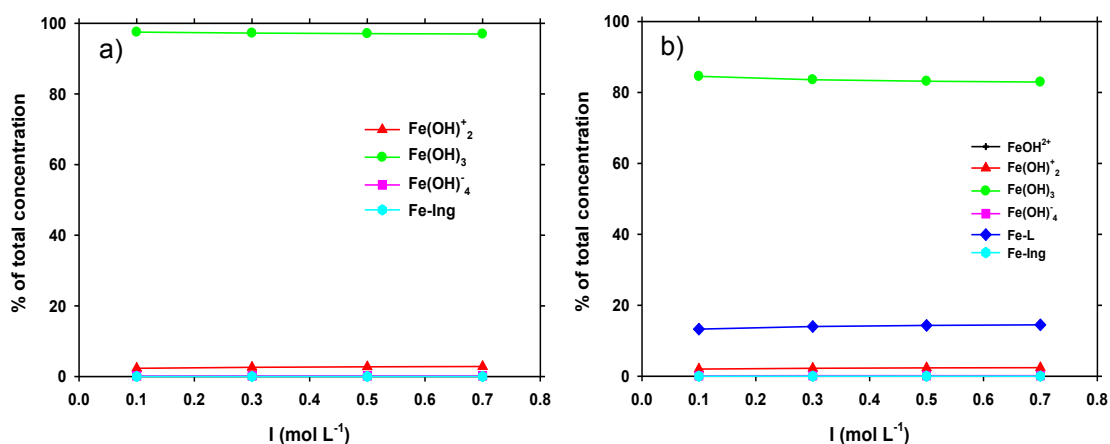
The next subsections will show the numerical results of Fe speciation as a function of the ionic strength, pH and temperature, in order to cover most of the physico-chemical conditions of natural waters.



### 3.1. Ionic strength effect

The Fe speciation was studied as a function of ionic strength from 0.1 to 0.7 mol L<sup>-1</sup> under different HA levels (0 and 1000 nmol L<sup>-1</sup>) (Fig. 1). The Fe speciation in the absence of HA (inorganic solution) was shown in Fig. 1a, where the most abundant Fe species were Fe(OH)<sub>3</sub> from 97.5% to 96.9% at I = 0.1 mol L<sup>-1</sup> and 0.7 mol L<sup>-1</sup>, respectively. These results were also comparable with the Fe speciation in seawater (Millero et al., 1995) and NaCl solutions (Liu and Millero, 1999).

The presence of HA invoked the formation of the Fe-L species (Fig. 1b). When the HA concentration was 1000 nmol L<sup>-1</sup> (Fig. 1b), the main Fe species, Fe(OH)<sub>3</sub>, decreased from 84.56% at I = 0.1 mol L<sup>-1</sup> to 82.93% at I = 0.7 mol L<sup>-1</sup>. Fe-L species varied from 13.28% to 14.49% at I = 0.1 mol L<sup>-1</sup> and I = 0.7 mol L<sup>-1</sup>, respectively. That speciation suggested that HA play a key role in the Fe speciation as it has been previously reported in natural waters (Abualhaija et al., 2015; Laglera and van den Berg, 2009). These results performed in ASW showed a good correlation with experimental data of Millero (2001), Millero et al. (1995) and Liu and Millero (1999) that examined the effect of ionic strength on the Fe speciation and its solubility in NaCl and seawater at different physico-chemical conditions.



**Fig. 1:** Fe speciation in ASW as a function of ionic strength, a) without humic acids, b) with 1000 nmol L<sup>-1</sup> of humic acids. The pH and temperature were kept constant at 8.0 and 25 °C.

The rest of the available binding sites in the HA were complexed with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ . At  $I = 0.7 \text{ mol L}^{-1}$ , the Fe-L species were only the 2.3% of the total organic binding sites of HA.

The concentration of Fe-L species is directly related with the conditional stability constant of the HA and the concentration of them in solution. In this sense, if we considered the  $\log K' = 13.7$ , instead 11.68, the Fe-L at  $I = 0.7 \text{ mol L}^{-1}$  ( $\text{pH} = 8.0$  and  $T = 25^\circ$ ) will be 54.32%. Then, in terms of Fe-L species, the presence of HA can explain from the 14.5% to 54.32% of the Fe speciation in ASW. In addition, when the  $\log K' = 20$ , respect to the free Fe in solution, the % of Fe-organically complexed will be > 99% that has been previously measured in the ocean (Gledhill and van den Berg, 1994).

### 3.2. pH effect

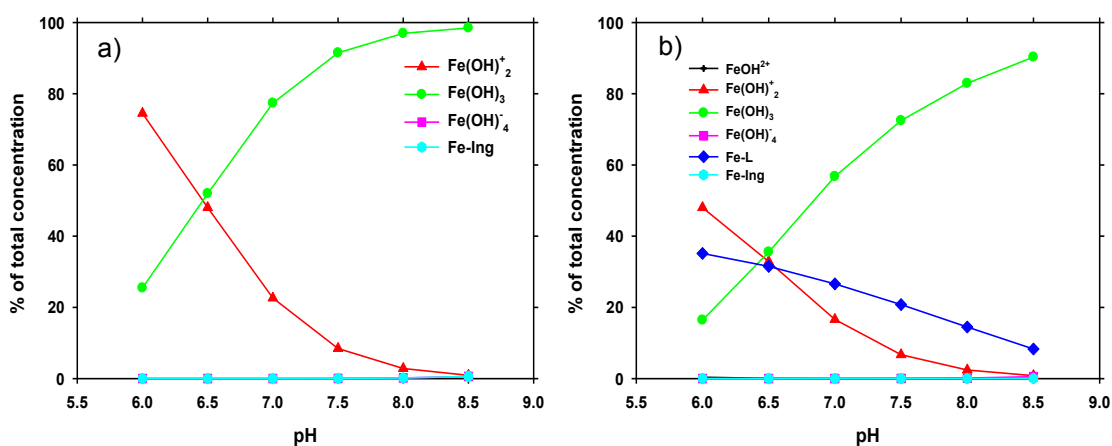
The pH effect on the Fe speciation has been studied by a number of scientist in natural waters (Byrne and Kester, 1976; Kuma et al., 1996; Millero, 2001; Millero et al., 1995; 2009). The results collected from the simulations were shown in Fig. 2.

In the absence of HA (Fig. 2a), at  $\text{pH} < 7$ ,  $\text{Fe}(\text{OH})_2^+$  was the dominant species ( $\approx 74.5\%$ ), at  $\text{pH} > 7$  this only contributed to the total iron concentration by 0.91% at pH 8.5.  $\text{Fe}(\text{OH})_3$  increased in over the entire pH range studied, where they became the most abundant at seawater pH (close to 8.0). These results are in a good agreement with the Fe speciation studied by Millero et al. (1995) in seawater, where  $\text{Fe}(\text{OH})_3$  species were 91.8% of the total iron species at pH 8.

When the HA were considered (Fig. 2b), the  $\text{Fe}(\text{OH})_2^+$  and  $\text{Fe}(\text{OH})_3$  species decreased their % of the total Fe concentration due to the formation of Fe-L species that increased as a consequence of the binding capacities of the organic moieties. Fe-L species were ranked from 35.15% to 8.30% at pH 6.0 and 8.5, respectively. At the higher pH (8.5) studied, the Fe-L species were only bound with 1.3% of the total binding sites of HA while  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  occupied 18.9% and 4.1%, respectively. The free HA in ASW was 33.8% at  $\text{pH} = 8.5$ . At pH 6.0, the role of Fe-L species within the HA pool was only 5.5%. Then, the rest of binding sites at  $\text{pH} = 6.0$  were occupied by the major cations in seawater or still free in solution. The complexing capacity of HA, by considering higher conditional constants ( $\log K' = 13.7$ ) will mostly explain the Fe-organic speciation in seawater. For

example at pH = 8.5, the Fe-L species will be 40% of total Fe species in ASW. In addition, the conditional stability constants for humic substances have been carried out at pH 8 by a number of authors (Abualhaija et al., 2015; Laglera et al., 2011; Laglera and van den Berg, 2009; Yang and van den Berg, 2009), who reported conditional stability constants for Fe-binding ligands from 11.0 to 11.2. However, the stability constants for Fe and humic acid equilibrium have not ever been determined at acidic (pH < 7) or very basic solution (pH > 8.5) in seawater. Then, to better understand the pH dependence of Fe-HA interaction, further experiments are needed.

These results demonstrated the importance of the conditional stability constant in order to explain the Fe-organic speciation in natural waters. In this sense, it is important to highlight that there a lack of information about the nature of the natural binding ligands, making the experimental chemistry of Fe-ligand interactions one of the main challenge for the next future, improving the existing databases and the global biogeochemical models, in order to better understand the global carbon cycle (Tagliabue et al., 2016).



**Fig. 2:** Fe speciation in ASW as a function of pH, a) without humic acids, b) with 1000 nmol L<sup>-1</sup> of humic acids. The ionic strength and the temperature were kept constant at 0.7 mol L<sup>-1</sup> and 25 °C.

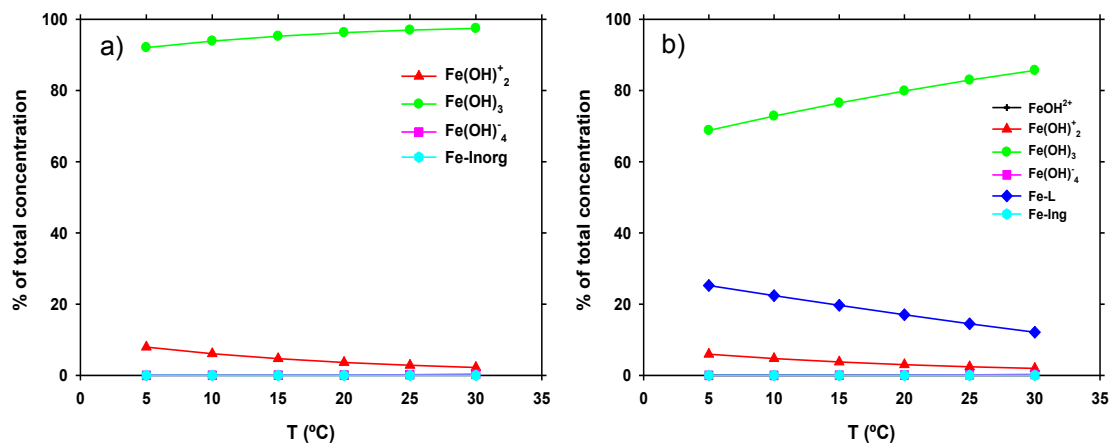
### 3.3. Temperature effect

The Fe speciation without humic acids as a function of temperature (Fig. 3a) showed that Fe(OH)<sub>3</sub> was the most abundant Fe species at the studied temperature range

(5 – 30 °C), increasing from 92.05% to 97.46% at 5 °C and 30°C, respectively. Similar results were found by Byrne et al. (1988) in seawater at 8.2 where increasing the temperature from 5°C to 25°C, the dissolved metal concentration also increased due to the strong hydrolysis of Fe in seawater (Eq. 1-4). The Fe speciation as a function of temperature was highly impacted by the presence of HA (Fig. 3b), where the Fe-L species became the second more abundant Fe species within the studied temperature interval (5 – 30°C). However, the % of total Fe species corresponding to the Fe-L species decreased with temperature (at pH = 8.0 and I = 0.7 mol L<sup>-1</sup>). At T > 20°C, the concentration of Fe-L decreased from 17.03% to 12.13%, and at T < 20°C, Fe-L achieved the major concentration (19.68 – 25.25%). That Fe speciation was directly related with the solubility of Fe where the Fe-L stability decreased at higher temperatures (Rashid, 2012). This statement should be also linked with the conditional stability constant of the natural binding ligand as well as with the nature of the ligands. As temperature increased, the non-reductive dissolution of Fe-L species became important, this mechanism consists in a desorption reaction that removes only the more reactive sites, and is characterized by a high activation energy (Panias et al., 1996).

In addition, by considering stronger Fe-ligands (log K' = 13.7) and at 5°C (pH = 8.0 and I = 0.1 mol L<sup>-1</sup>), the Fe-L species will dominate the Fe speciation with 82.5%, while it will be 43.9% at 35°C. Generally, these responds are mainly focused on the Fe-binding mechanisms because the humic substances could be unaltered until 250°C (Kolokassidou et al., 2007).

These results demonstrated that the temperature is one of the key parameters to be studied in the next future in terms of Fe-binding ligands. The experiments about Fe and organic ligands interaction as a function of temperature allow to compute key thermodynamic parameters such as the energy of activation, enthalpy of activation and entropy of activation. It has extensively considered in terms of Fe(II) oxidation in seawater under the presence of natural organic ligands (Gonzalez et al., 2012; 2014b; Santana-Casiano et al., 2000) but there is a lack of information about the role of temperature on the Fe complexation in seawater.



**Fig. 3:** Fe speciation in ASW as a function of temperature, a) without humic acids, b) 1000 nmol L<sup>-1</sup> of humic acids. The ionic strength and the pH were kept constant at 0.7 mol L<sup>-1</sup> and 8.0.

### 3.4. Mineral composition

The current numerical code is highly appreciated by the scientific community due to the possibility to obtain all the possible mineral forms and their SI in a certain solution. Then, the SI was reported under the same conditions of ionic strength, pH, and temperature, together with different concentrations of humic acids (Table 1). Accordingly, the mineral over saturation level (SI > 0) were Fe(OH)<sub>2.7</sub>Cl<sub>3</sub>, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnesioferrite. The higher SI were found for hematite, magnesioferrite, Fe(OH)<sub>2.7</sub>Cl<sub>3</sub> and goethite (Table 1). The Fe minerals under saturation levels (SI < 0) on the simulations were ferric sulfate, Na-Jarosite, K-Jarosite and H-Jarosite (Table 1). The SI as a function of ionic strength, pH and temperature were shown in Fig. SI-1 and Fig. SI-2 (Supporting Information File).

These Fe minerals formed in ASW under these physico-chemical conditions are generally found in deep seafloor and marine sediments. Ferrihydrite has been found in marine sediments in the Pacific Ocean (Canfield, 1989), East Pacific Rise (Dill et al., 1994; Stoffers et al., 1993), Red Sea (Chukhov et al., 1974), and in hydrothermal deposits in the Mid-Atlantic Ridge (Fouquet et al., 2010). Goethite is a very stable iron oxyhydroxide and it is formed from ferrihydrite (Stoffers et al., 1993) and found in seawater, deep sea environments in Angola Basin (Glasby and Schulz, 1999), South Pacific (Stoffers et al., 1993), Red Sea (Degens and Ross, 2013) and hydrothermal

deposits (Fouquet et al., 2010). On the other hand, hematite is usually found within the Fe-Cu rich chimneys along the Mid-Atlantic Ridge (Fouquet et al., 2010), and Red Sea brines (Degens and Ross, 2013). As a secondary products, from goethite, lepidocrocite, maghemite and magnesioferrite can be found in marine sediments and brines as in the Red Sea thermal brines (Degens and Ross, 2013).

The presence of organic ligands can affect the polymerization of Fe minerals (González et al., 2014a), where the authors demonstrated that the presence of carboxyl and phosphoryl functional groups were able to reduce the polymerization of Fe oxyhydroxides at low ionic strength. In addition, the presence of organic acids such as citric and tartaric acids, also retarded the precipitation and crystallization of ferrihydrite and goethite, while they accelerated the formation of hematite at 70°C and pH = 10 (Cornell and Schwertmann, 1979). These effects could be explained by the incorporation of organic molecules on the chemical structure of the minerals. However, in the current simulation, the presence of 1000 nmol L<sup>-1</sup> of HA were not significantly affecting the SI of Fe minerals in ASW at different ionic strength, pH and temperature (Table 1). It is explained because of the lack of information about the interaction of organic moieties on the precipitation-dissolution iron minerals in seawater. Most of these studies have been performed at low ionic strength and pure solutions. This is a new example of the need of new experimental investigations in terms of iron geochemistry in natural waters.

**Table 1.** Fe minerals formed and their saturation index in artificial seawater as a function of ionic strength from 0.1 to 0.7 mol L<sup>-1</sup>, pH from 6.0 to 8.0 and temperature from 5 to 30°C. When one parameter was studied the rest were kept constant at I = 0.7 mol L<sup>-1</sup>, pH = 8.0 and T = 25°C.

	Mineral name	Formula	Saturation Index (SI)			
			Without HA		1000 nmol L <sup>-1</sup> HA	
			Min	Max	Min	Max
Ionic Strength	Fe(OH) <sub>2.7</sub> Cl <sub>3</sub>	-	5.31	5.37	5.25	5.30
	Ferric sulfate	$(Fe_2(SO_4)_3)$	-41.89	-41.73	-42.01	-41.87
	Ferrihydrite	$(Fe^{3+})_2O_3 \cdot 0.5H_2O$	1.60	1.66	1.54	1.59
	Goethite	$\alpha - FeO(OH)$	4.31	4.38	4.25	4.31
	Hematite	$Fe_2O_3, \alpha - Fe_2O_3$	11.02	11.16	10.90	11.03
	H-Jarosite	$(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6$	-17.03	-16.85	-17.21	-17.05
	K-Jarosite	$KFe_3^{3+}(OH)_6(SO_4)_2$	-5.58	-5.40	-5.77	-5.61
	Lepidocrocite	$\gamma - FeO(OH)$	3.43	3.50	3.37	3.43

	Maghemite	$\gamma - Fe_2O_3$	3.22	3.36	3.09	3.22	
	Magnesioferrite	$Mg(Fe^{3+})_2O_4$	6.74	6.84	6.62	6.71	
	<i>Na-Jarosite</i>	$NaFe_3^{3+}(SO_4)_2(OH)_6$	-9.60	-9.42	-9.78	-9.62	
<b>pH</b>	<b>Mineral name</b>	<b>Formula</b>	<b>Saturation Index (SI)</b>				
			<b>Without HA</b>		<b>1000 nmol L<sup>-1</sup> HA</b>		
			<b>Min</b>	<b>Max</b>	<b>Min</b>	<b>Max</b>	
		Fe(OH) <sub>2.7</sub> Cl <sub>3</sub>	-	5.39	5.22	5.20	5.19
		Ferric sulfate	$(Fe_2(SO_4)_3)$	-30.90	-44.72	-31.28	-44.79
		Ferrihydrite	$(Fe^{3+})_2O_3 \cdot 0.5H_2O$	1.08	1.66	0.89	1.63
		Goethite	$\alpha - FeO(OH)$	3.80	4.38	3.61	4.35
		Hematite	$Fe_2O_3, \alpha - Fe_2O_3$	10.00	11.18	9.62	11.10
		H-Jarosite	$(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6$	-10.59	-18.83	-11.16	-18.94
		K-Jarosite	$KFe_3^{3+}(OH)_6(SO_4)_2$	-1.14	-6.88	-1.72	-6.99
		Lepidocrocite	$\gamma - FeO(OH)$	2.92	3.50	2.73	3.47
		Maghemite	$\gamma - Fe_2O_3$	2.20	3.37	1.82	3.30
		Magnesioferrite	$Mg(Fe^{3+})_2O_4$	1.68	7.85	1.30	7.78
		<i>Na-Jarosite</i>	$NaFe_3^{3+}(SO_4)_2(OH)_6$	-5.16	-10.90	-5.73	-11.01
	<b>Temperature</b>	<b>Mineral name</b>	<b>Formula</b>	<b>Saturation Index (SI)</b>			
<b>Without HA</b>				<b>1000 nmol L<sup>-1</sup> HA</b>			
<b>Min</b>				<b>Max</b>	<b>Min</b>	<b>Max</b>	
		Fe(OH) <sub>2.7</sub> Cl <sub>3</sub>	-	6.29	5.15	7.18	6.66
		Ferric sulfate	$(Fe_2(SO_4)_3)$	-42.85	-41.48	-41.07	-38.46
		Ferrihydrite	$(Fe^{3+})_2O_3 \cdot 0.5H_2O$	1.32	1.73	2.21	3.24
		Goethite	$\alpha - FeO(OH)$	4.54	4.34	5.43	5.85
		Hematite	$Fe_2O_3, \alpha - Fe_2O_3$	11.39	11.11	13.18	14.13
		H-Jarosite	$(H_3O)Fe_3^{3+}(SO_4)_2(OH)_6$	-16.83	-16.86	-14.15	-12.33
		K-Jarosite	$KFe_3^{3+}(OH)_6(SO_4)_2$	-3.85	-5.77	-1.17	-1.24
		Lepidocrocite	$\gamma - FeO(OH)$	4.42	3.28	5.32	4.79
		Maghemite	$\gamma - Fe_2O_3$	5.21	2.93	7.00	5.95
		Magnesioferrite	$Mg(Fe^{3+})_2O_4$	5.21	7.21	7.00	10.23
		<i>Na-Jarosite</i>	$NaFe_3^{3+}(SO_4)_2(OH)_6$	-8.31	-9.68	-5.63	-5.15

### 3.5. The competitive role of Cu by the humic acids

The effect of Cu on the Fe chemistry has been studied in natural waters (Buxton et al., 1995; Cher and Davidson, 1955; Huffman and Davidson, 1956; Matocha et al.,

2005; Parker and Espenson, 1969; Sayin, 1982; Sedlak and Hoigné, 1993; Stumm and Lee, 1961). In addition, a recent investigation demonstrated the role of Cu on the Fe(II) oxidation in seawater (González et al., 2016), that was previously considered by other authors (Santana-Casiano et al., 2005, 2006; Zafiriou et al., 1998). On the other hand, Whitby and van den Berg (2015) demonstrated the competitive effect of copper and iron for humic acids at pH 8.2 in estuarine waters.

The use of the numerical code will allow to study the competition between Fe and Cu by the binding sites of the HA in ASW, as well as define the new experimental lines that should be developed in order to better understand the Fe biogeochemical cycle in the ocean.

### **3.5.1. Ionic strength effect**

Inorganically, the presence of Cu did not have any effect on the Fe speciation in ASW (Fig.SI-3a), that was in concordance with the inorganic speciation of Cu and Fe in seawater, where Cu is mainly as carbonate and hydroxide forms (González-Dávila et al., 2009; Millero et al., 1991; Pérez-Almeida et al., 2013). The presence of Cu had an effect on the Fe-L formation due to the formation of Cu-L species and their competition by the available binding sites of the HA (Fig. 4a). The Fe-L concentration decreased from 14.49% to 3.14% at  $I = 0.7 \text{ mol L}^{-1}$  without HA and with HA, respectively. The Cu-L species, respect to the total Cu concentration, achieved 31.60% at  $I = 0.7 \text{ mol L}^{-1}$ . In this sense, Fe-L and Cu-L were complexed by 0.44% and 4.8% of the total binding sites of HA at  $I = 0.1 \text{ mol L}^{-1}$  (pH = 8.0 and T = 25°C), respectively. At  $I = 0.7 \text{ mol L}^{-1}$ , Fe-L and Cu-L represented 0.5% and 4.9% of the total binding sites of HA.

The different degree of interaction between Fe and Cu with the HA in ASW are determined by the equilibrium constants. In this case, the log K' for the Cu-binding ligand was stronger than that for Fe-L. Simulating a comparable log K' value for Fe and Cu-binding ligands, the Fe-L will increase at  $I = 0.7 \text{ mol L}^{-1}$  to 48.86%, while Cu-L achieve 19.30%. These simulations highlighted the relevance of the experimental determination of the stability conditional constants for Fe and Cu model ligands in the ocean, where their chemistry are dominated by the presence of organic ligands. The Fe and Cu



biogeochemical cycle could only be fully understood through the developing of new experimental experiences and including these results within the chemical databases.

### **3.5.2. pH effect**

The Fe-inorganic speciation after the addition of Cu to the simulation and as a function of pH showed the same distribution exposed in the earlier section (Fig. SI-3b). Attending to the addition of HA (Fig. 4b), the Fe-L species were significantly affected due to the reduction of the binding sites that were also complexing Cu in ASW. The maximum concentration of Fe-L was 35.15% at pH 6.0, while it was 8.30% at pH 8.5 without the copper addition. When Cu was present in ASW, the Fe-L species decreased their concentration until 34.76% at pH 6 and 0.5% at pH 8.5. The Cu-L species were from 0.8% at pH 6.0 to 42.24% at pH 8.5.

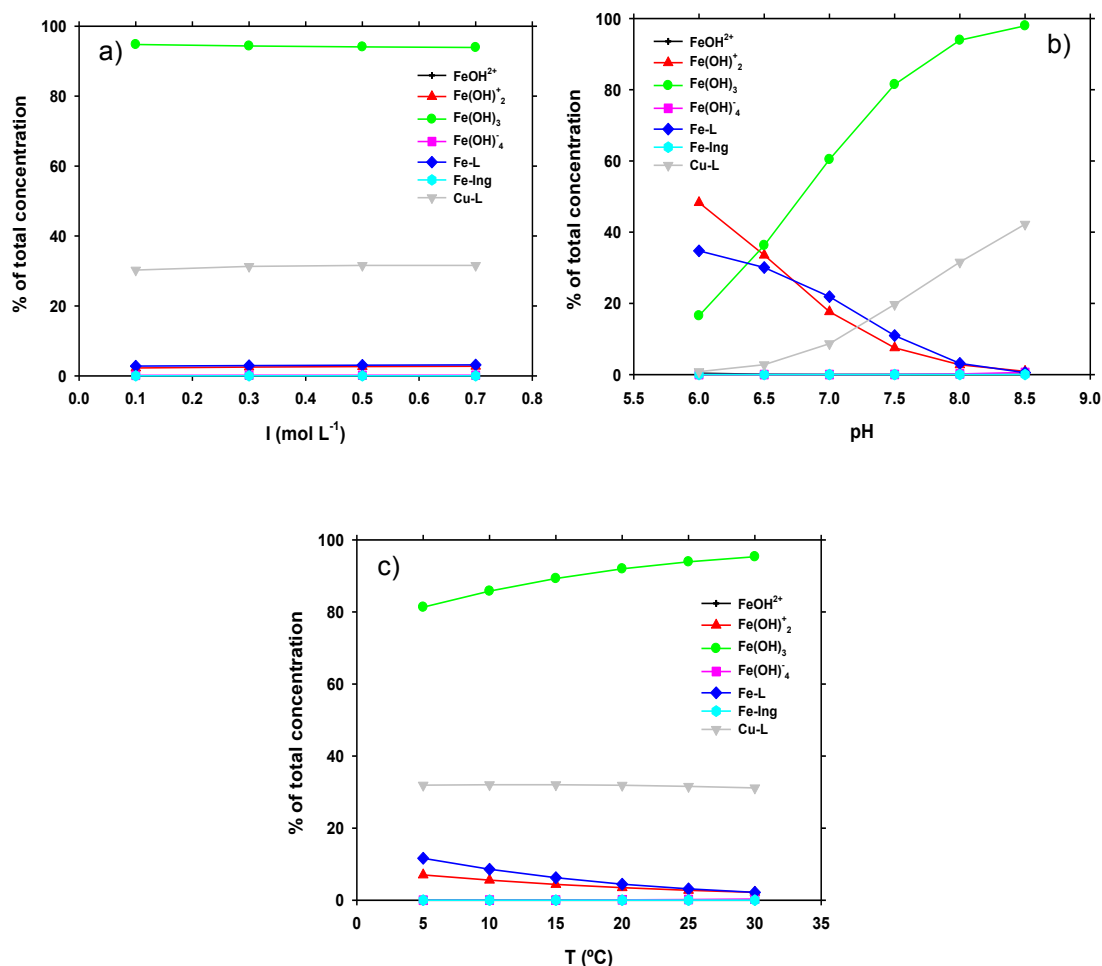
The different behaviour observed for Fe-L and Cu-L formation as a function of pH can be explained by the hydrolysis constant used for formation the Fe-HA and Cu-HA. These values were  $\log K = -4.6$  and  $-13.6$ , respectively (Gustafsson, 2008). Similar results were found by Whitby and van den Berg (2015) where they observed a decrease in the Cu-HA formation with an addition of  $10 \text{ nmol L}^{-1}$  of Fe. Yang and van den Berg (2009) and Abualhaija et al. (2015) also found that the Fe-HS decreased as the competitive binding effect of copper addition.

The Fe-L speciation under the presence of Cu highlighted the relevance of Fe and Cu competitive mechanisms in natural waters. Then, together with the recent studies about the role of Cu on the Fe(II) oxidation rates, new experiments should be developed in order to better understand the Fe and Cu marine biogeochemical cycles.

### **3.5.3. Temperature effect**

The Fe-inorganic speciation as a function of temperature showed the same distribution previously described despite the Cu addition (Fig.SI-3c). Again, the presence of Cu altered the Fe-L formation in ASW (Fig. 4c). In this case, the Fe-L species decreased respect to that in the absence of Cu from 25.25% to 11.65% at  $T = 5^\circ\text{C}$  and

25.12% to 2.19% at  $T = 30^\circ\text{C}$ . The Cu-L species slightly decreased from 31.92% to 31.18% in the same temperature range.



**Fig. 4:** Fe speciation in ASW with  $1000 \text{ nmol L}^{-1}$  of humic acids and  $100 \text{ nmol L}^{-1}$  of Cu a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at  $I = 0.7 \text{ mol L}^{-1}$ ,  $\text{pH} = 8.0$  and  $T = 25^\circ\text{C}$ .

The temperature is one of the key parameters to be studied in terms of Fe and Cu-binding ligands because allow to compute the energy of activation, entropy of activation and enthalpy of activation for the Fe and Cu-binding reactions. This kind of experiments will support a high value thermodynamic improvements for individual Fe and Cu model ligands in natural waters. Future experiments should be developed to better understand the competitive role between Fe and Cu by the binding ligands, especially to be able to

construct global models where many oceanographic regions are included, covering from the high latitudes to the equatorial regions.

### 3.5.4. Mineral composition

Attending to the SI of the Fe mineral phases in ASW under the presence of Cu, they did not present any differences respect to the copper addition (Table 2, Fig.SI-4 and 5), except the formation of Fe-Cu mineral, cupric ferrite ( $\text{CuFe}_2\text{O}_4$ ), with a  $\text{SI} > 0$  in all the experimental conditions taken into account in these simulations. Cupric ferrite is considered one the most important phase of  $\text{Cu}^{2+}$  in marine sediments and it is stable at deep sea conditions of  $2^\circ\text{C}$  and pH of 6 - 14 (Glasby and Schulz, 1999).

**Table 2. Fe minerals formed and their saturation index in artificial seawater as a function of pH from 6.0 to 8.5 at ionic strength  $0.7 \text{ mol L}^{-1}$  and T  $25^\circ\text{C}$  and  $100 \text{ nmol L}^{-1}$  of Cu.**

Mineral name	Formula	Saturation Index (SI)			
		Without HA		1000 nmol L <sup>-1</sup> HA	
		Min	Max	Min	Max
$\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$	-	5.39	5.22	5.13	5.22
Ferric sulfate	$(\text{Fe}_2(\text{SO}_4)_3$	-30.90	-44.72	-31.40	-44.73
Ferrihydrite	$(\text{Fe}^{3+})_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$	1.08	1.66	0.82	1.66
Goethite	$\alpha - \text{FeO}(\text{OH})$	3.80	4.38	3.54	4.38
Hematite	$\text{Fe}_2\text{O}_3, \alpha - \text{Fe}_2\text{O}_3$	10.00	11.18	9.50	11.17
H-Jarosite	$(\text{H}_3\text{O})\text{Fe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$	-10.59	-18.83	-11.35	-18.84
K-Jarosite	$\text{KFe}_3^{3+}(\text{OH})_6(\text{SO}_4)_2$	-1.14	-6.88	-1.90	-6.89
Lepidocrocite	$\gamma - \text{FeO}(\text{OH})$	2.92	3.50	2.66	3.50
Maghemite	$\gamma - \text{Fe}_2\text{O}_3$	2.20	3.37	1.69	3.37
Magnesioferrite	$\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$	1.68	7.85	1.17	7.85
Na-Jarosite	$\text{NaFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$	-5.16	-10.90	-5.92	-10.91
Cupric ferrite	$\text{CuFe}_2\text{O}_4$	6.87	11.70	6.36	11.38

The presence of HA as a model organic ligand did not produce any significant effect on the Fe mineral saturation index. As it was mentioned above, the presence of Fe and Cu-binding ligands affect the polymerization of Fe minerals, generally by the

introduction of these organic functional groups on the mineral structure. This lack of information can be successfully corrected by the development of new measurements in X-Ray Absorption Spectroscopy (XAS) via Synchrotron Analysis (González et al., 2014a).

#### **4. Software application and future improvements**

The numerical code Visual Minteq is widely applied in different fields such as geochemistry, metal speciation in soils, fresh or marine waters and wastewaters, both for the academic science as well as for the industrial applications. One of the most important use of Visual Minteq is to simulate the metal speciation in different aqueous media. Then, Visual Minteq has also been used in riverine environments (Charriau et al., 2011), drainage waters from mines (Jung et al., 2012), in freshwater systems (Nystrand et al., 2012), and Fe and Cu mineral formation in seawater (González et al., 2016). On the other hand, the easily modification of the database makes Visual Minteq one of the most useful geochemical software. In addition, the international community is continuously including new equilibrium and hydrolysis constants for most of the elements.

However, most of the geochemical experiments are normally carried out in low ionic strength medium, then this is a future challenge for the marine scientists. The new inclusions of marine data to the global database for Fe and Cu will highly improve our interpretation of the mineral chemistry, because of the grade of polymerization is playing a key role on the Fe and Cu bioavailability for the microorganisms. Together with the experimental determination of the conditional stability constants for Fe and Cu-binding ligands in seawater under different physico-chemical conditions (I, pH and T) will help to better understand the Fe and Cu marine biogeochemical cycles and as the last step, the global carbon cycle.

#### **Conclusions**

Visual Minteq is a powerful toolbox to predict the Fe speciation in artificial seawater as a function of the ionic strength, pH and temperature, with and without considering the presence of humic acids. The most abundant Fe species at standard

seawater conditions ( $\text{pH} = 8$ ,  $T = 25\text{ }^\circ\text{C}$  and  $I = 0.7\text{ mol L}^{-1}$ ) were  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2^+$  and  $\text{Fe}(\text{OH})_4^-$ . The Fe speciation was affected by the presence of HA by the formation of Fe-organic species (Fe-L). In this sense, the formation of Fe-L species was directly affected by the hydrolysis of Fe oxyhydroxide species as well as the conditional stability constant for Fe-L species in artificial seawater. The simulations also revealed that most of the available binding sites of HA were occupied by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

In terms of Fe mineral phases, the Visual Minteq is able to generate all the Fe minerals theoretically formed in ASW, with the range of saturation index. Accordingly, in ASW, the oversaturated Fe mineral species were  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_3$ , ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnesioferrite, generally found in deep seafloor and marine sediments. Here, the presence of HA did not reflect any significant modification of the saturation index for the formed Fe minerals. This could be explained by the lack of information about the precipitation and dissolution experiments in seawater. Most of the data collected used by this numerical code have been obtained in low ionic strength solutions.

Visual Minteq also predicted the competitive role of Cu with Fe by the binding sites of the humic acids in ASW as a function of ionic strength, pH and temperature. In this sense, the presence of Cu invoked in a decreased of the Fe-L species respect to that in the absence of Cu. When Fe and Cu were present in ASW, a new Fe-mineral phase was formed, cupric ferrite, that was oversaturated under the standard seawater conditions ( $\text{pH} = 8.0$ ,  $I = 0.7\text{ mol L}^{-1}$  and  $T = 25^\circ\text{C}$ ).

These simulations highlighted the relevance of the experimental determination of the stability conditional constants of model ligands in the ocean, where the Fe and Cu chemistry are dominated by the presence of organic ligands. The Fe and Cu biogeochemical cycle could only be fully understood through the developing of new experimental experiences and including these results within the chemical databases.

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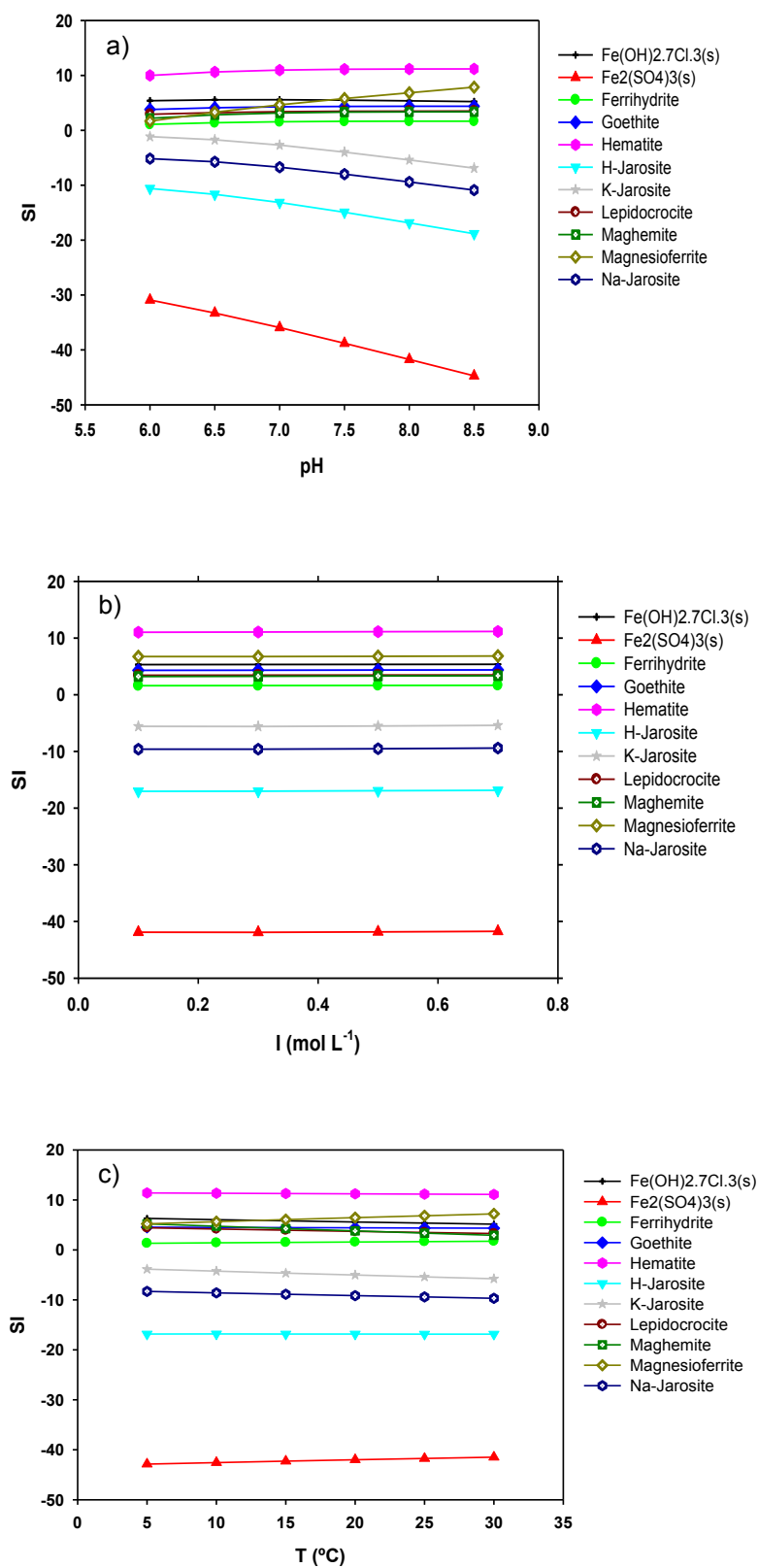
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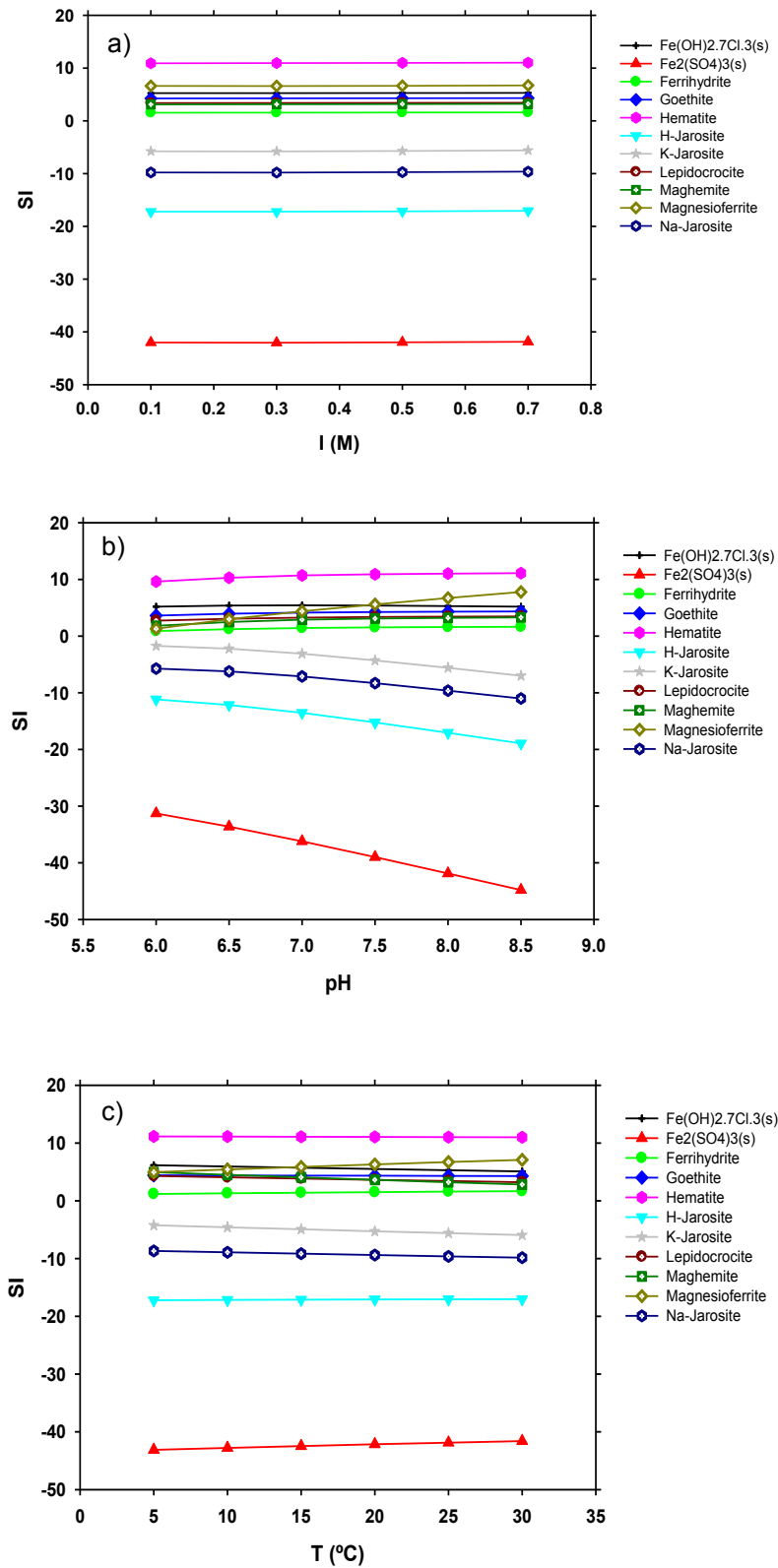
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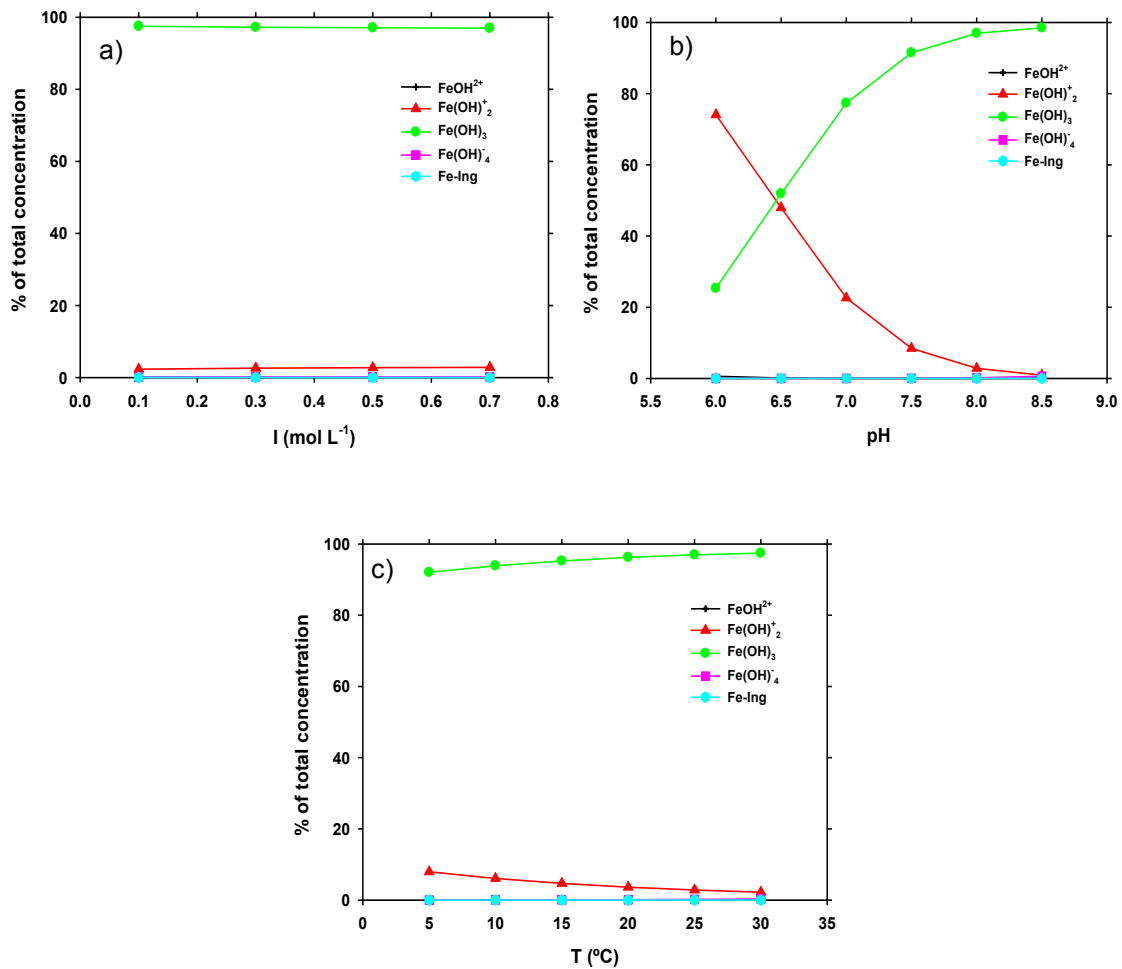
## Supporting Information File



**Fig. SI-1: Saturation index of Fe mineral formation without humic acids a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at  $I = 0.7 \text{ mol L}^{-1}$ ,  $\text{pH} = 8.0$  and  $T = 25^\circ\text{C}$ .**



**Fig. SI-2: Saturation index of Fe mineral formation under the presence of 1000 nmol L<sup>-1</sup> of humic acids a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at I = 0.7 mol L<sup>-1</sup>, pH = 8.0 and T = 25°C.**



**Fig.SI-3: Fe speciation in ASW without humic acids and with the addition of 100 nmol L<sup>-1</sup> of Cu a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at I = 0.7 mol L<sup>-1</sup>, pH = 8.0 and T = 25°C.**

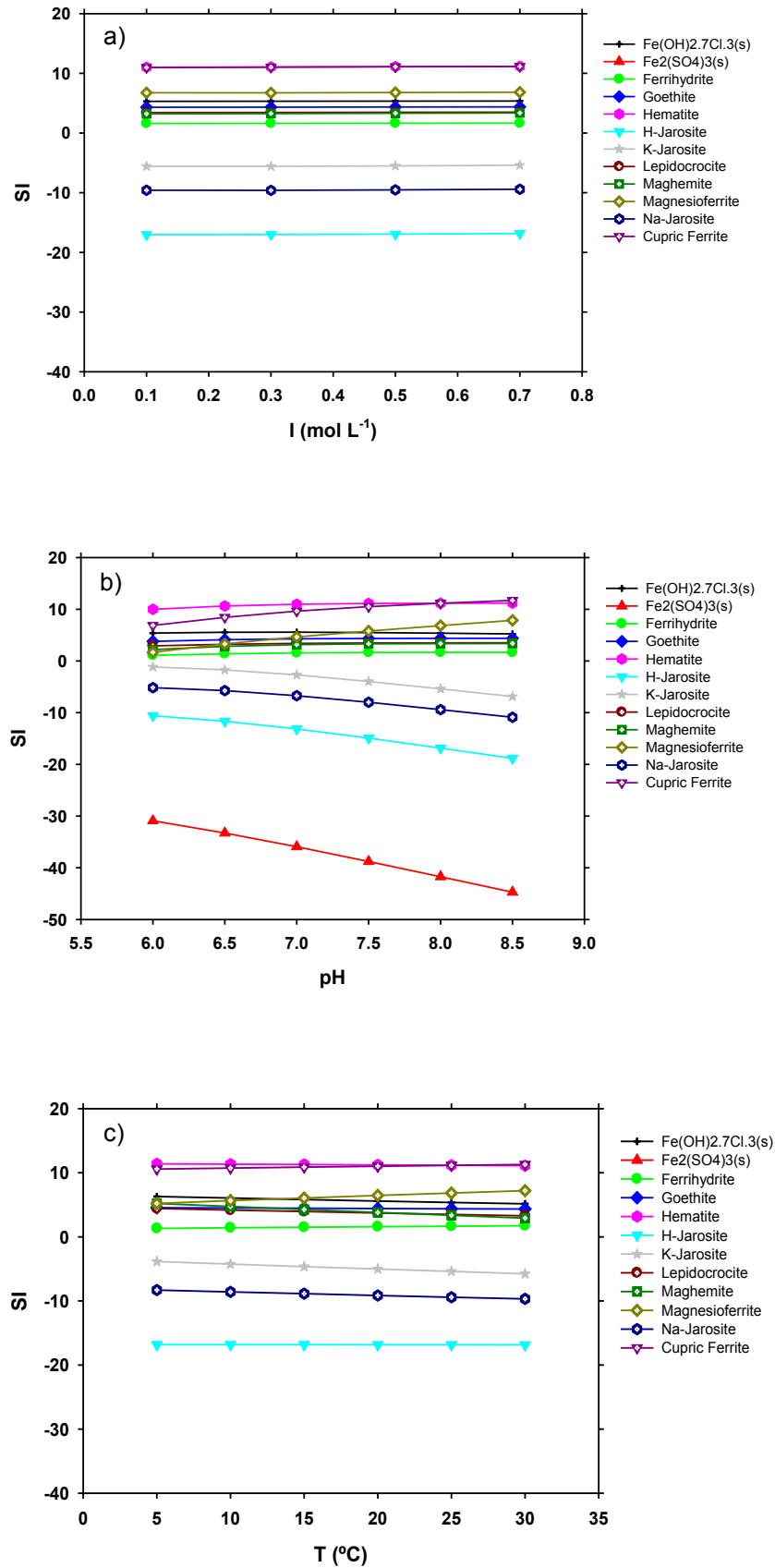


Fig. SI-4: Saturation index of Fe mineral formation without humic acids and with the addition of 100 nmol L<sup>-1</sup> of copper a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at I = 0.7 mol L<sup>-1</sup>, pH = 8.0 and T = 25°C.

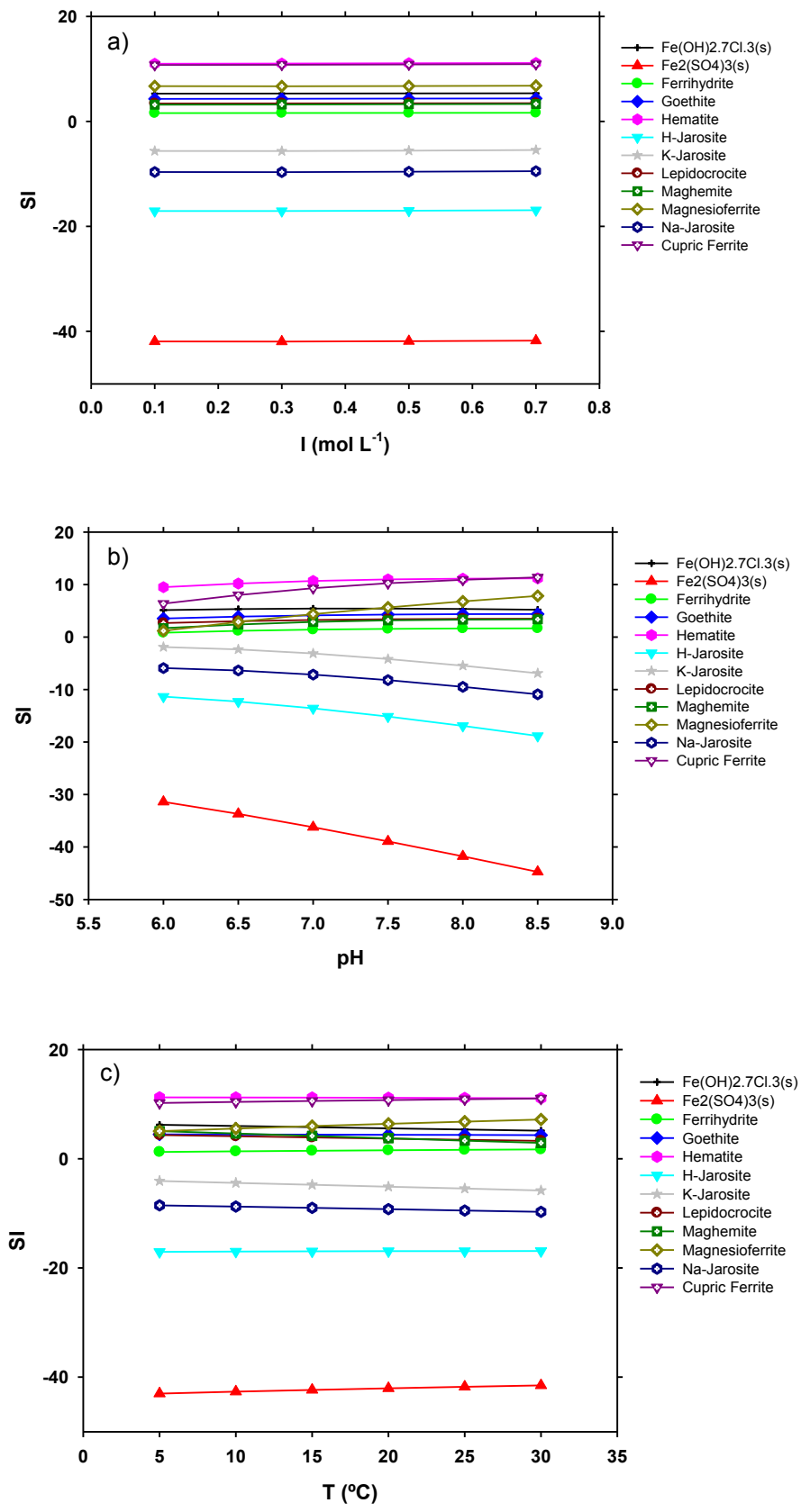


Fig. SI -5: Saturation index of Fe mineral formation with 1000 nmol L<sup>-1</sup> humic acids and 100 nmol L<sup>-1</sup> of copper a) as a function of ionic strength, b) pH and c) temperature. When one parameter was studied the rest were kept constant at I = 0.7 mol L<sup>-1</sup>, pH = 8.0 and T = 25°C.

## **Appendix**

### **Descripción detallada de las actividades desarrolladas durante la realización del TFT.**

Como se trata de un trabajo teórico, se realizaron varias simulaciones con el programa Visual Minteq (Gustafsson, 2008) y una búsqueda de bibliografía adecuada para el cumplimiento de los objetivos propuestos para la realización del trabajo de fin de máster (TFM).

Aprendí el tratamiento de datos posterior a la realización de las simulaciones en el programa citado anteriormente, con el fin de obtener resultados que después se puedan comparar con datos obtenidos de la búsqueda de bibliografía. La parte de la búsqueda bibliográfica se llevó a cabo durante todo el proceso de la realización del TFM dado que se trataba de un tema que no conocía a fondo y resultaba de vital importancia para una correcta escritura del trabajo. Se obtuvieron datos experimentales que se usaron en la comparativa de resultados con el fin de evaluar la calidad de los resultados obtenidos de las simulaciones.

El proceso de realización del TFM, así como la parte de tratamiento de datos y simulaciones con el programa han sido siempre supervisados por los tutores. Durante este proceso ha aumentado mi conocimiento sobre la geoquímica de metales traza en el océano, la importancia de los ligandos orgánicos en la química de Fe y Cu en agua de mar, la utilidad de programas informáticos y de cómo es su uso en el ámbito científico.

### **Formación recibida.**

- Funcionamiento y manejo del programa Visual Minteq.
- Aprendizaje sobre tratamiento de datos obtenidos del programa usado.
- Aplicación de los resultados obtenidos de las simulaciones.



### **Nivel de integración e implicación dentro del departamento y relaciones con el personal.**

Me he integrado plenamente en el grupo QUIMA del IOCAG y del Departamento de Química de la Universidad de Las Palmas de Gran Canaria. La relación con mis tutores, tanto interno como externo, ha sido muy profesional y cordial. Sus aportaciones y sus consejos me han ayudado a desarrollar este TFM, como también a aumentar mi conocimiento sobre la química de metales en el océano y la importancia de la materia orgánica en la especiación de metales.

### **Aspectos positivos y negativos más significativos relacionados con el desarrollo de las prácticas.**

Obtener experiencia en el manejo de una nueva herramienta que es de gran utilidad en el ámbito científico ha sido un aspecto muy positivo de cara al campo al que me quiero dedicar profesionalmente.

### **Valoración personal del aprendizaje conseguido a lo largo de la práctica.**

A lo largo de todo el trabajo teórico y de la búsqueda bibliográfica he tenido la oportunidad de aprender la utilidad del uso de programas informáticos en el desarrollo de trabajos experimentales como un primer acercamiento en el caso del uso nuevas técnicas o como comparativa de la fiabilidad de los datos obtenidos de simulaciones con datos experimentales.

Tener a los tutores con plena disponibilidad para resolver cualquier duda o inconveniente que se me presentase ha sido fundamental a la hora de un buen desarrollo del TFM.