

全国农业环境科学学术研讨会
2015.11.15-18, 福州

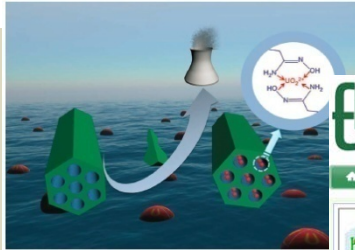
重金属离子在粘土矿物上的竞争 吸附和微观结构分析研究

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中科院等离子体物理所

Email: xkwang@ncepu.edu.cn

Zhao, AM, 2011
 Zhao, EST, 2011
 Sun, EST, 2012
 Sun, EST, 2013



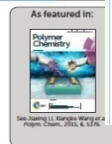
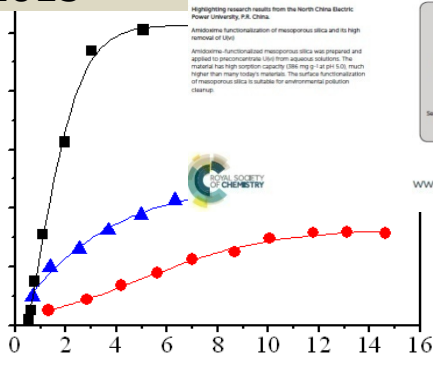
ENVIRONMENTAL
 Science & Technology

Sun, EST, 2015
 Jin, EST, 2015
 Yang, CPC, 2015

Shao, JPCB, 2009
 Shao, JPCC, 2010
 Hu, JPCB, 2010

Heavy Metal Free Environment with Plasma-Modified Carbon Nanotubes

Scientists at Institute of Plasma Physics, CAS, have developed a way to modify multiwalled carbon nanotubes to enhance their dispersion properties and adsorption capacities.



Heavy metal ions Adsorbed by graphene oxide

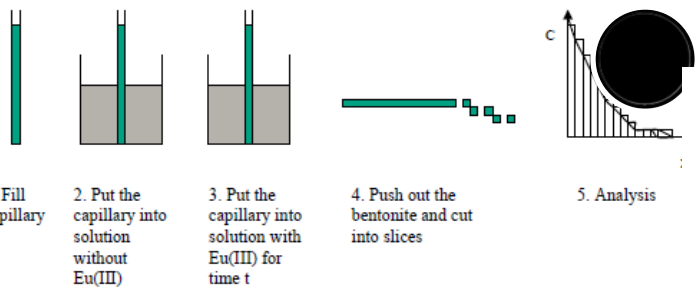
Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management

Guoqing Zhao, Haifeng Li, Yueshen Ren, Changjun Chen, and Xiangke Wang

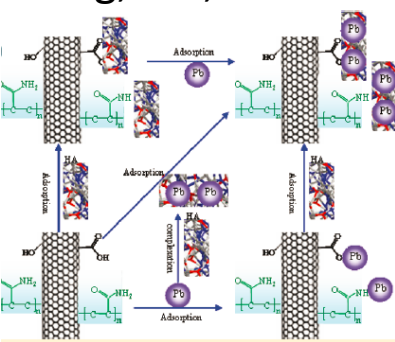
Adsorption and Desorption of U(VI) on Functionalized Graphene Oxides: A Combined Experimental and Theoretical Study

Yubing Sun, Shubin Yang, Yue Chen[†], Congcong Ding, Wencai Cheng, and Xiangke Wang^{*}

Tan, EST, 2008, 2009
 Fan, EST, 2009
 Sheng, EST, 2011
 Yang, GCA, 2011, 2013, 2015
 Sun, GCA, 2014
 Ding, GCA, 2015



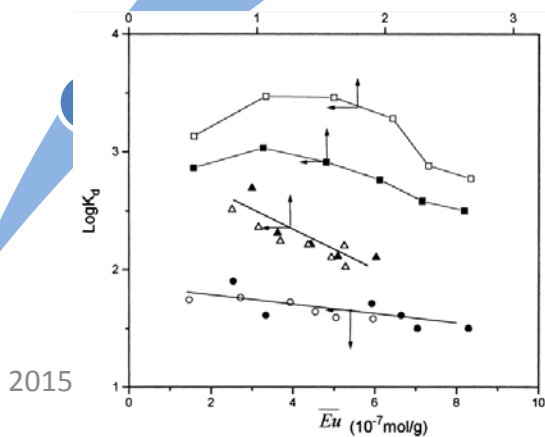
Wang, EST, 2005
 Tan, Carbon, 2008
 Chen, EST, 2009
 Yang, EST, 2011
 Wang, EST, 2015



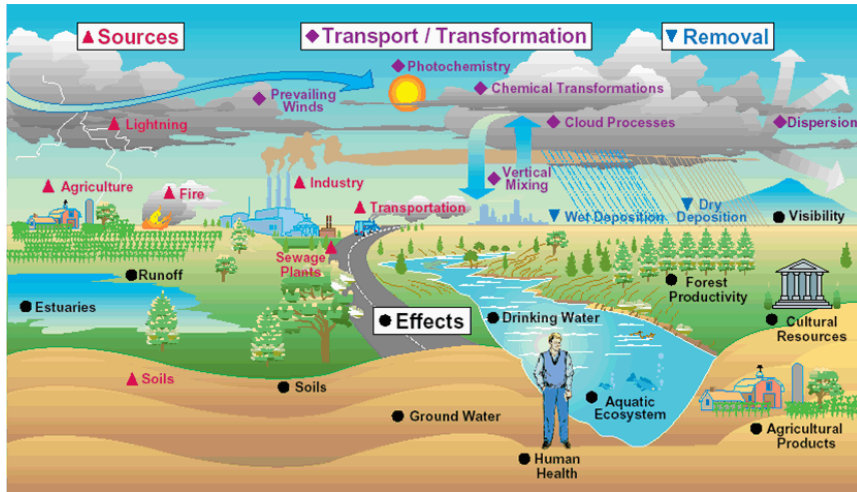
ACS Publications High quality. High impact.

ENVIRONMENTAL Science & Technology

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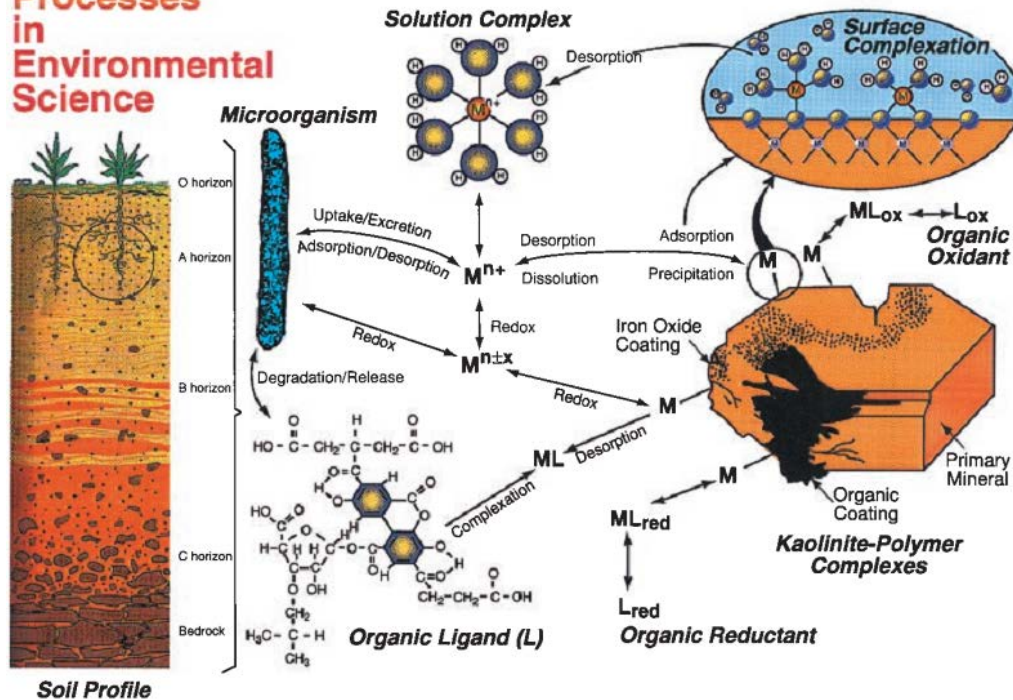
研究背景



重金属离子在环境体系中的迁移转化

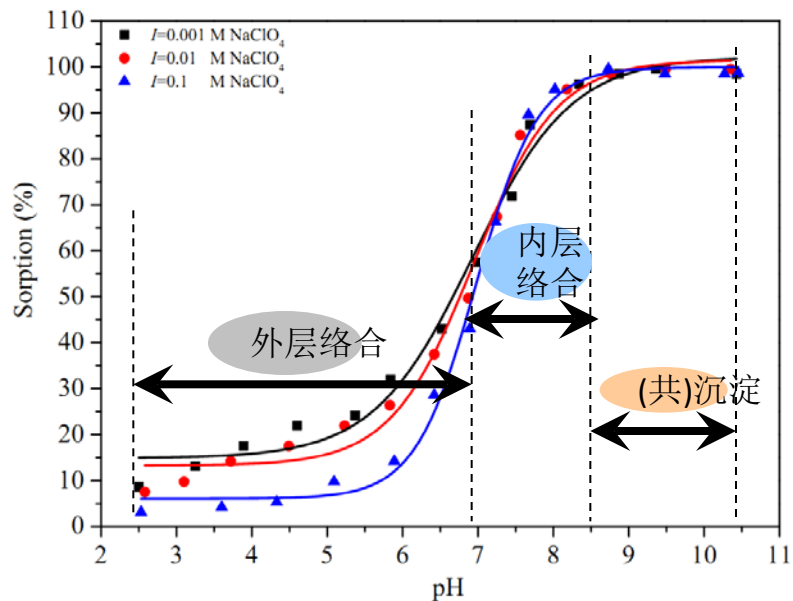
吸附解吸、离子交换、络合螯合、氧化还原、表面(共)沉淀

Molecular-Scale Processes in Environmental Science

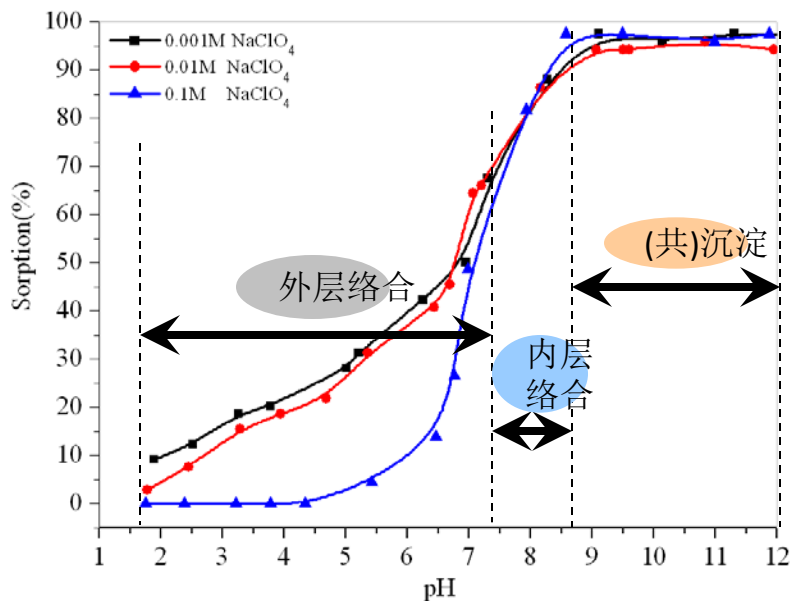


重金属离子进入天然环境体系的途径

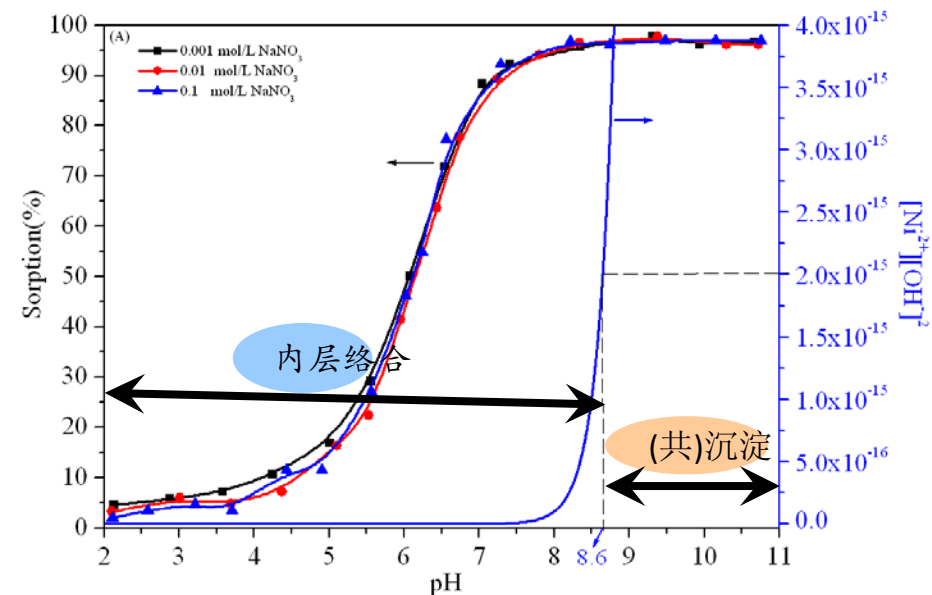
体系pH和离子强度对Ni(II)宏观吸附行为的影响



伊利石/Ni(II)体系



膨润土/Ni(II)体系

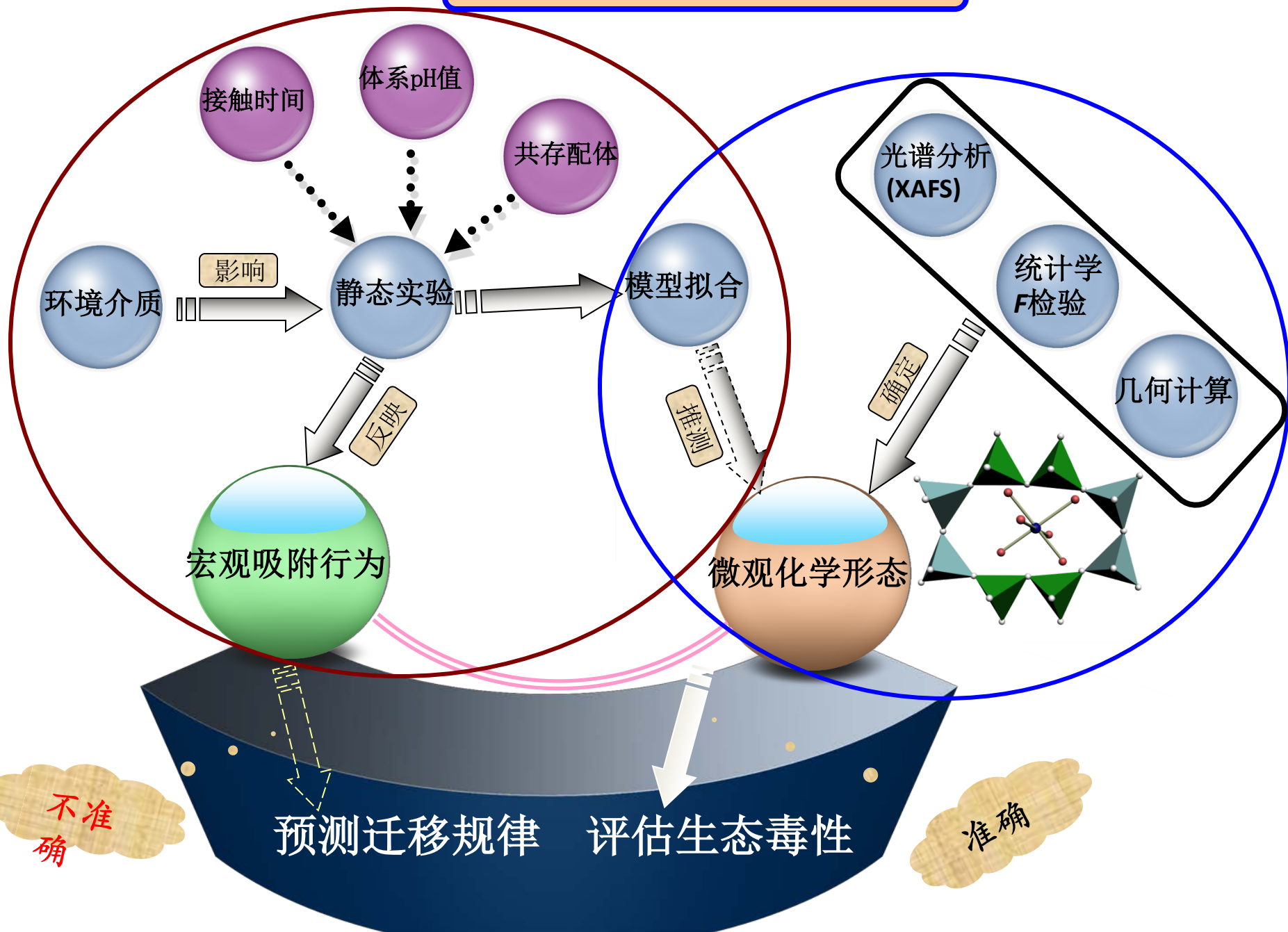


氧化铝/Ni(II)体系

思考??

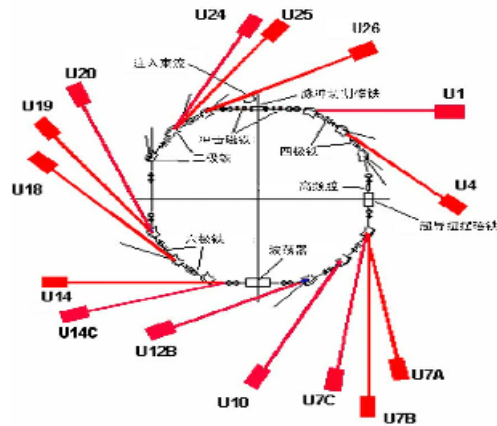
1. 不同水环境化学因素对Ni(II)吸附形态的影响规律?
2. Ni(II)吸附形态和矿物类型及晶体结构的关联机制?
3. Ni(II)微观结构的稳定性与迁移转化行为的相关性?

2. 微观水平形态结构分析



EXAFS方法研究Eu在氧化钛表面的微观结构

背景



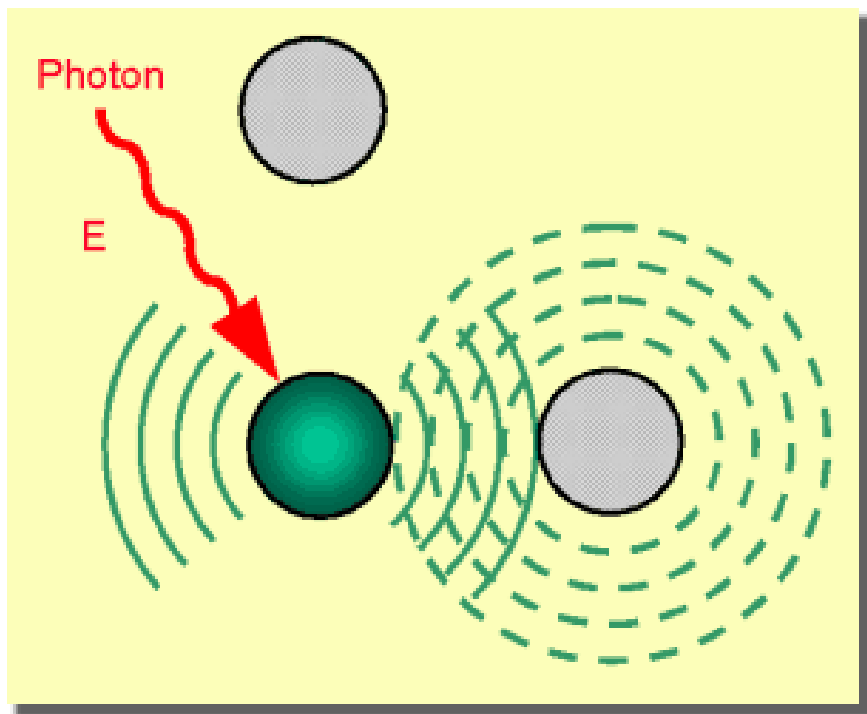
- U1 : 光刻
- U4 : 红外与远红外光谱
- U7A : 高空间分辨X射线成像
- U7B : X射线散射与衍射
- U7C : 扩展X光吸收精细结构
- U10 : 燃烧
- U12A: 软X射线显微术
- U14A: 原子与分子物理
- U14C: 真空紫外分析
- U18 : 表面物理
- U19 : 软X射线磁性圆二色

色

- U20 : 光电子能谱
- U24 : 真空紫外光谱
- U25 : 光声与真空紫外圆二色光谱
- U26 : 光谱辐射标准与计量

- ▶ 随着同步辐射这一新兴技术的兴起而取得突破性进展, XAFS被广泛应用于物理、化学、生物学、地质、地球化学等领域, 在研究结晶物质、非晶物质与玻璃、液相和气相物质、催化剂、金属原子簇的结构、成键与反应过程等方面显示了不可替代的优势。
- ▶ XAFS也广泛应用于环境矿物学, 在原位研究矿物与不同固液介质条件下的表面化学反应、确定表面反应产物及其在表面上的结合状态, 以及吸附物质特征等方面都有独特的应用价值。

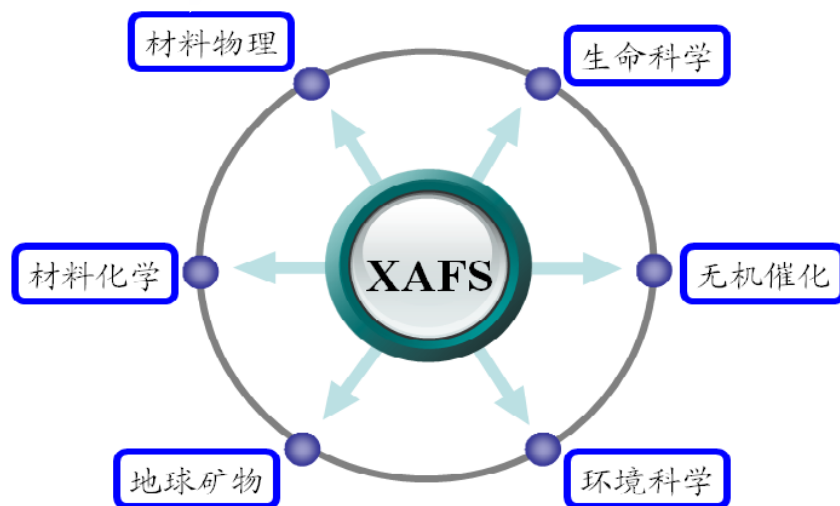
XAFS基本原理简介



XAFS: X射线激发的光电子被周围配位原子散射，导致X射线吸收强度随能量发生振荡，研究这些振荡信号可以得到所研究体系的电子和几何局域结构。

XAFS优点

1. 具有原子识别性
2. 不依赖晶体结构
3. 样品测量浓度低
4. 固液气样品均可测
5. 样品无损分析

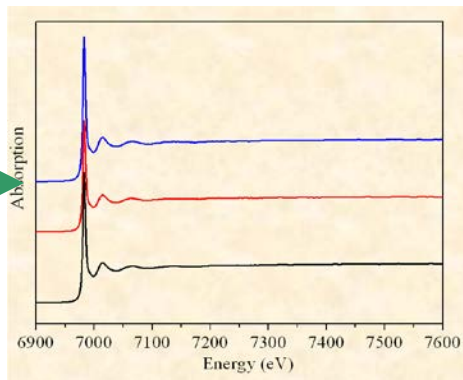


XAFS数据采集、分析、计算

$$\chi(k) = \frac{1}{k} \sum_{j=0}^N \frac{N_j}{R_{0j}^2} f_j(2k) e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda} \sin(\phi_j(k) + 2kR_j)$$

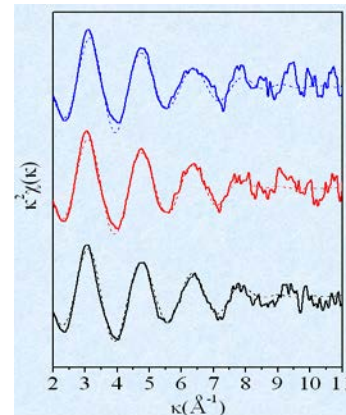


谱图采集装置

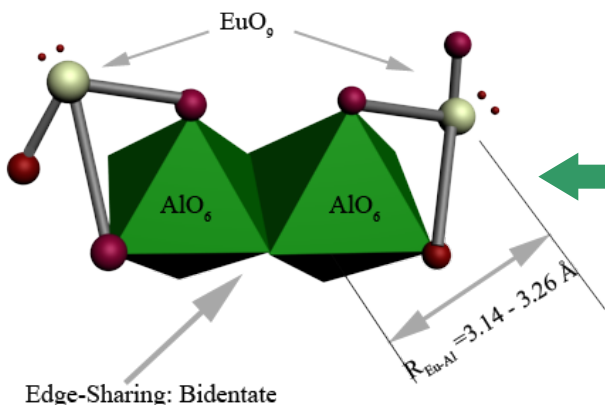


原始谱图

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu(E)}$$



k空间



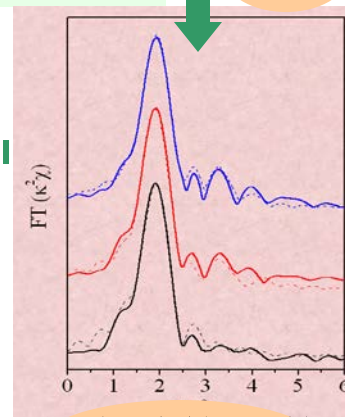
作用机理

$$\tilde{\chi}(R) = FT(\chi(k)) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \chi(k) W(k) e^{i2kR} dk$$

k空间

Second shell (Eu-C/Al/Eu)				
Bond	R(Å)	CN	$\sigma^2(\text{Å}^2)$	R_f
Eu-Al	3.21	0.7	0.006	0.058
Eu-Al	3.21	1.3	0.006	0.056
Eu-Eu	3.49	0.8	0.006	
Eu-Eu	3.61	1.9	0.006	0.049

拟合和计算结果

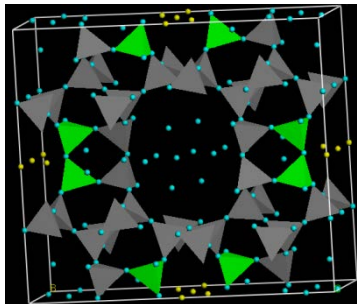


径向结构函数

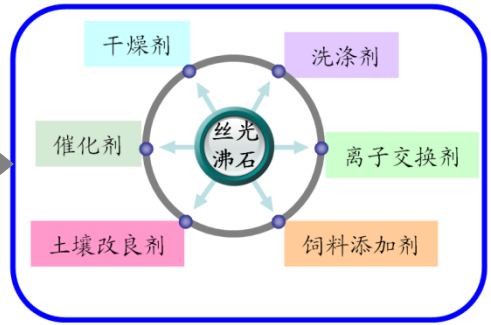
EXAFS谱图进行分析和计算，得到放射性核素的配位数、键长等结构信息，结合计算化学，给出放射性核素的微观结构

1. Ni(II)在丝光沸石/水界面作用机制

研究背景



用途

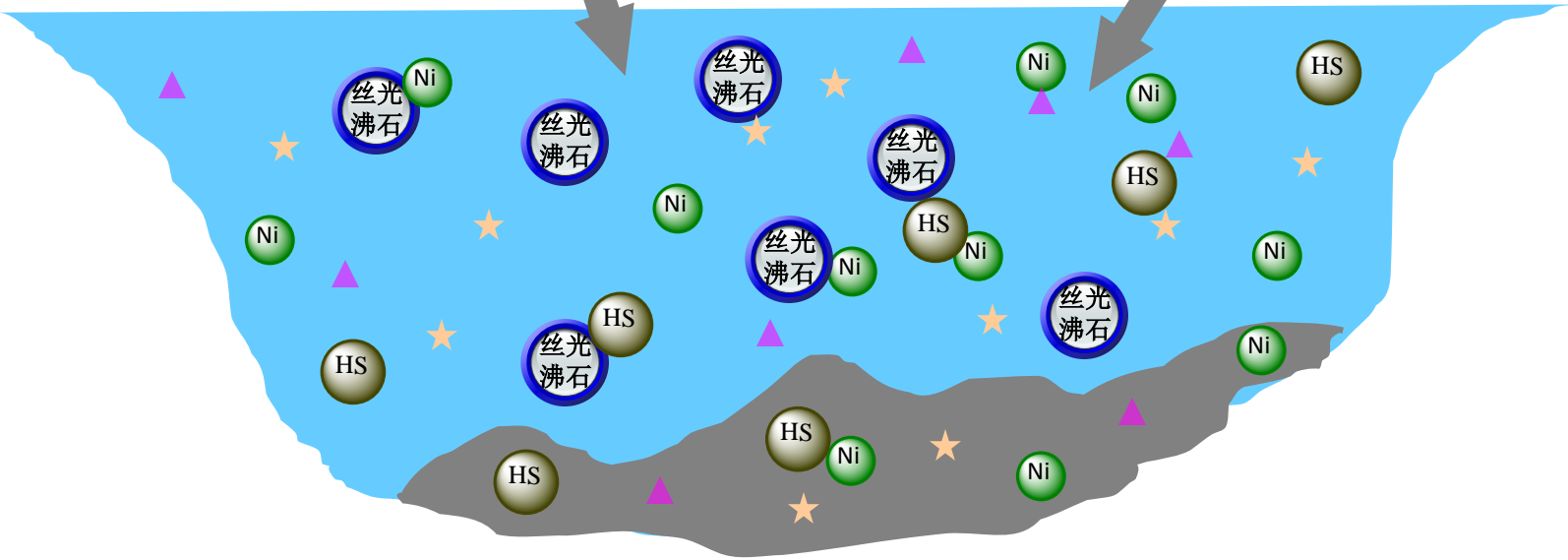


丝光沸石

含水格架状
铝硅酸盐矿物

废弃流失

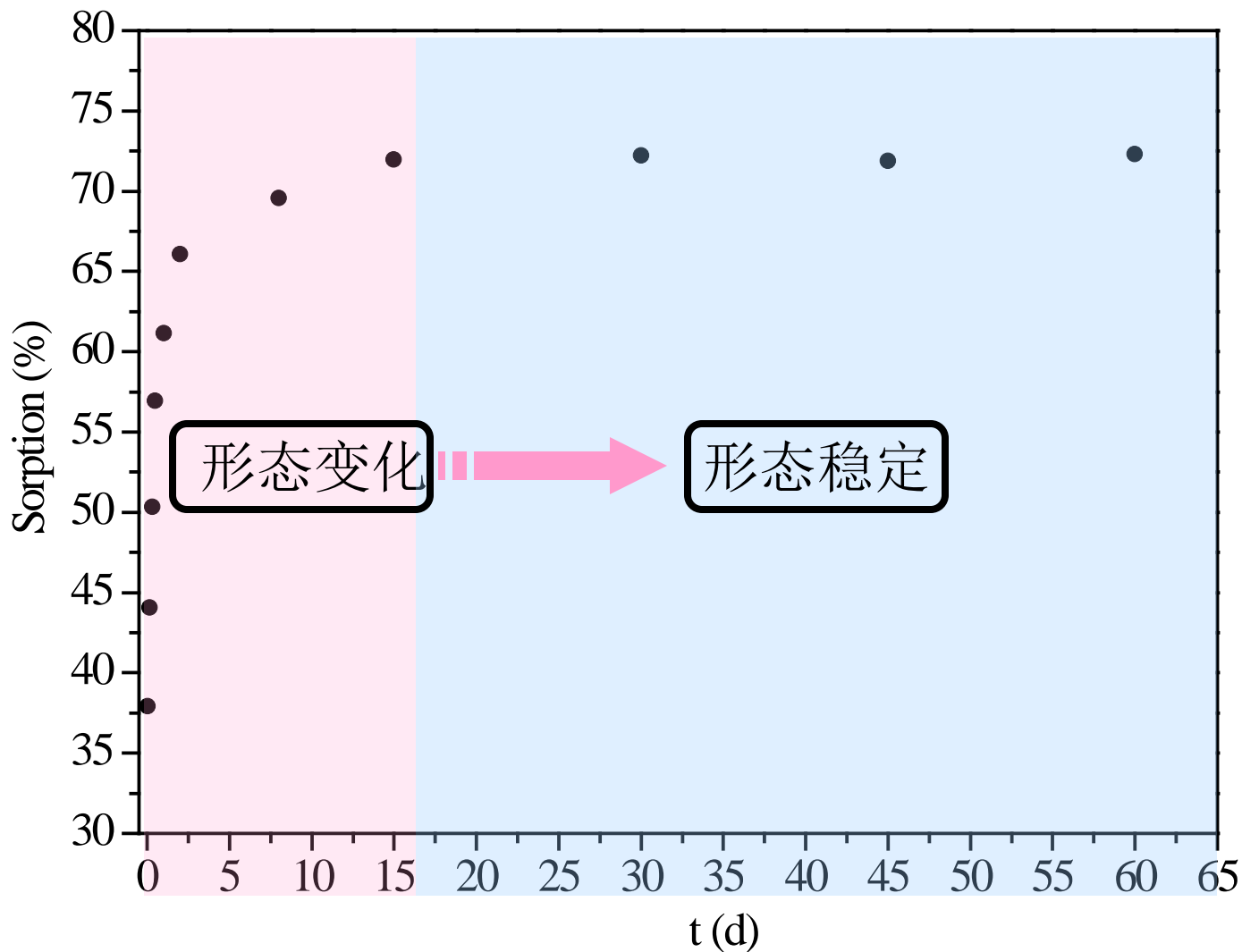
污水排放



重金属离子Ni(II)在水体系统迁移转化示意图

静态实验结果分析

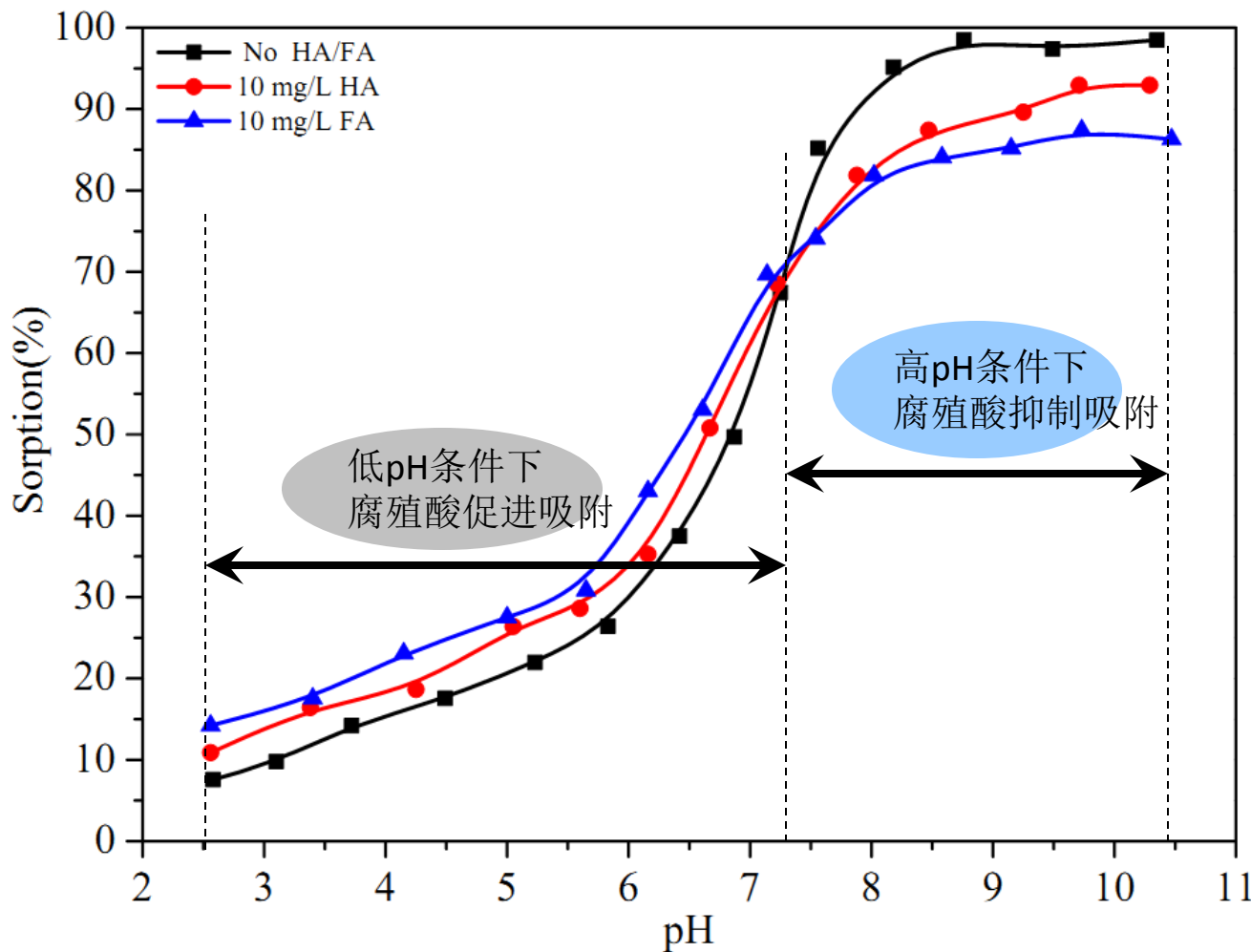
接触时间对Ni(II)宏观吸附行为的影响



pH=7.5, $T=293.15$ K, $m/V=0.5$ g/L, $C_{Ni(II)initial}=10$ mg/L, $I=0.01$ M $NaClO_4$.

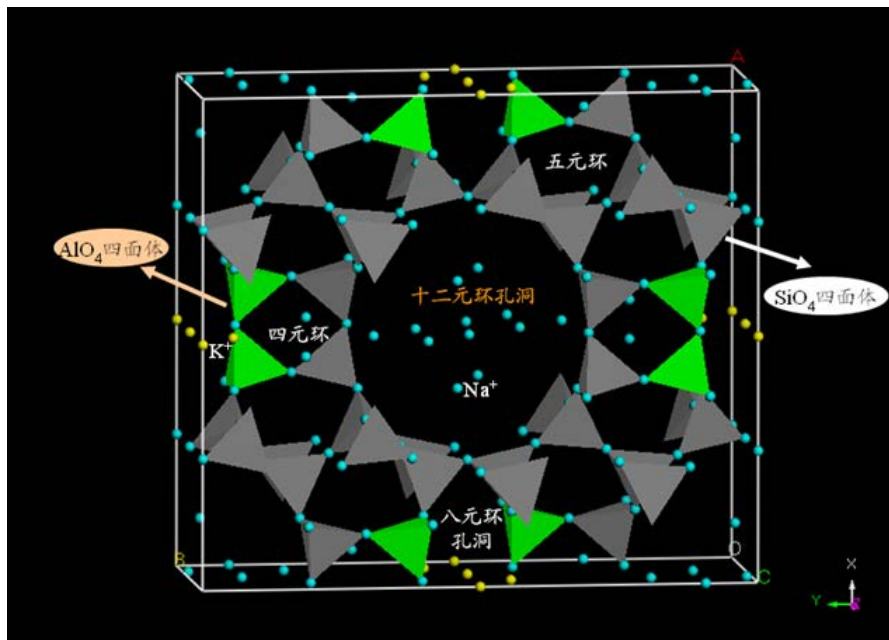
静态实验结果分析

共存腐殖酸对Ni(II)宏观吸附行为的影响



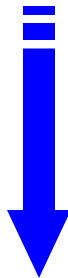
$T=293.15\text{ K}$, $m/V=0.5\text{ g/L}$, $C_{\text{Ni(II)initial}}=10\text{ mg/L}$, $I=0.01\text{ M NaClO}_4$.

几何理论计算推断结构形态



丝光沸石晶体结构

AlO_4 中 $R_{\text{Al-O}}=1.78 \text{ \AA}$, $R_{\text{O-O}}=2.89 \text{ \AA}$
SiO_4 中 $R_{\text{Si-O}}=1.58-1.64 \text{ \AA}$, $R_{\text{O-O}}=2.58-2.67 \text{ \AA}$
NiO_6 中 $R_{\text{Ni-O}}=2.04 \text{ \AA}$, $R_{\text{O-O}}=2.88 \text{ \AA}$



$R_{\text{Ni-O}} \gg R_{\text{Al-O}}, R_{\text{Ni-O}} \gg R_{\text{Si-O}} \implies \text{Ni不能取代Al和Si}$

NiO_6 中 $R_{\text{O-O}} \approx \text{AlO}_4$ 中 $R_{\text{O-O}} \implies \text{Ni能和AlO}_4$ 形成边-边配位结构

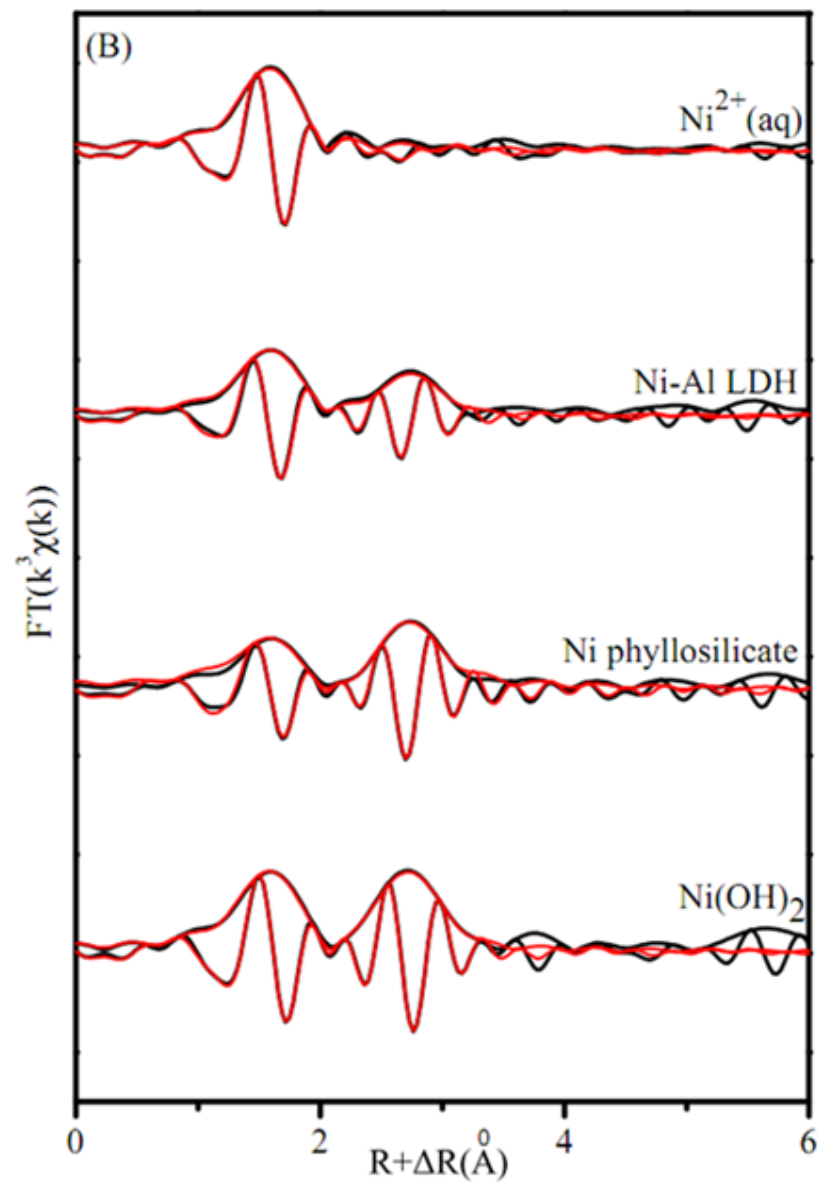
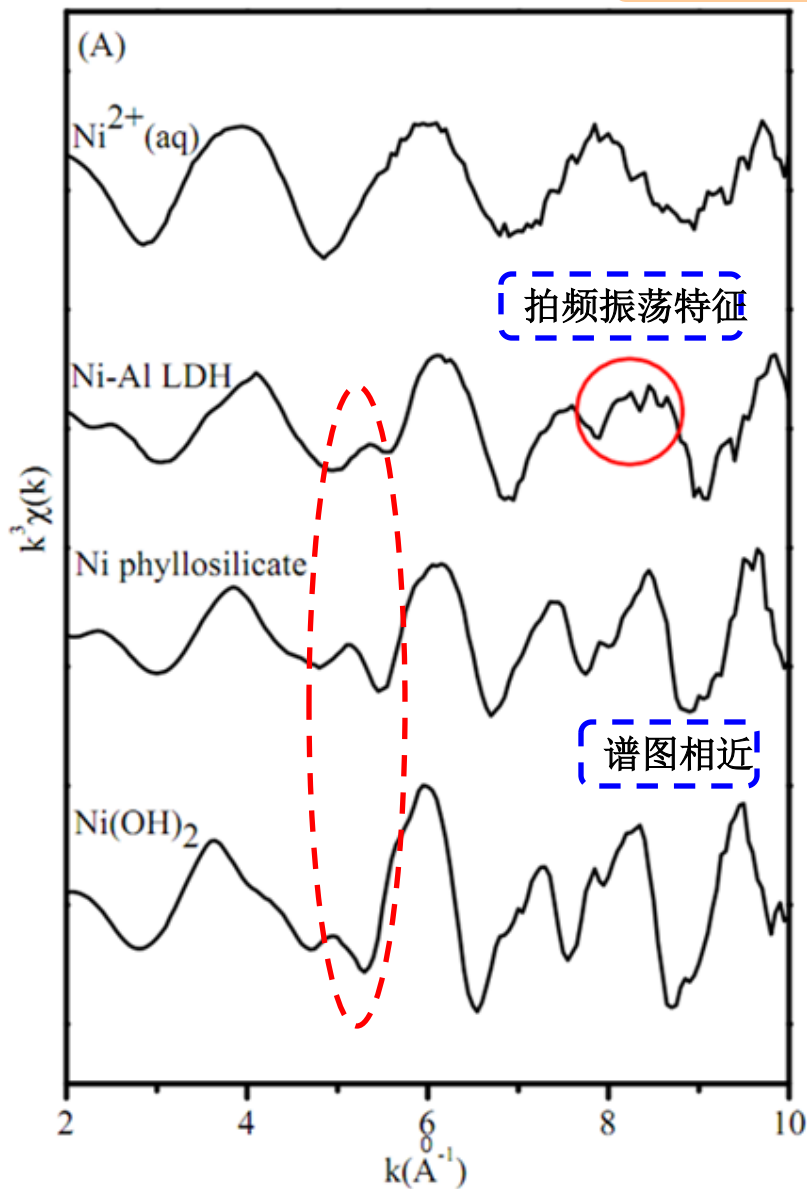
NiO_6 中 $R_{\text{O-O}} \gg \text{SiO}_4$ 中 $R_{\text{O-O}} \implies \text{Ni不能和SiO}_4$ 形成边-边配位结构



Ni 和 $\text{AlO}_4/\text{SiO}_4$ 更为具体的吸附形态(角角结合、边边结合、面面结合)将由立体几何知识结合XAFS谱图分析得到的Ni-Al/Si键长信息综合分析确定

XAFS结果分析

Ni(II)标准样品谱图分析



Ni(II)标准样品EXAFS谱图拟合结果

表 4-3 Ni(II)标准样品的 EXAFS 谱图拟合结果.

Table 4-3 Structural parameters derived from EXAFS analysis for Ni(II) reference samples.

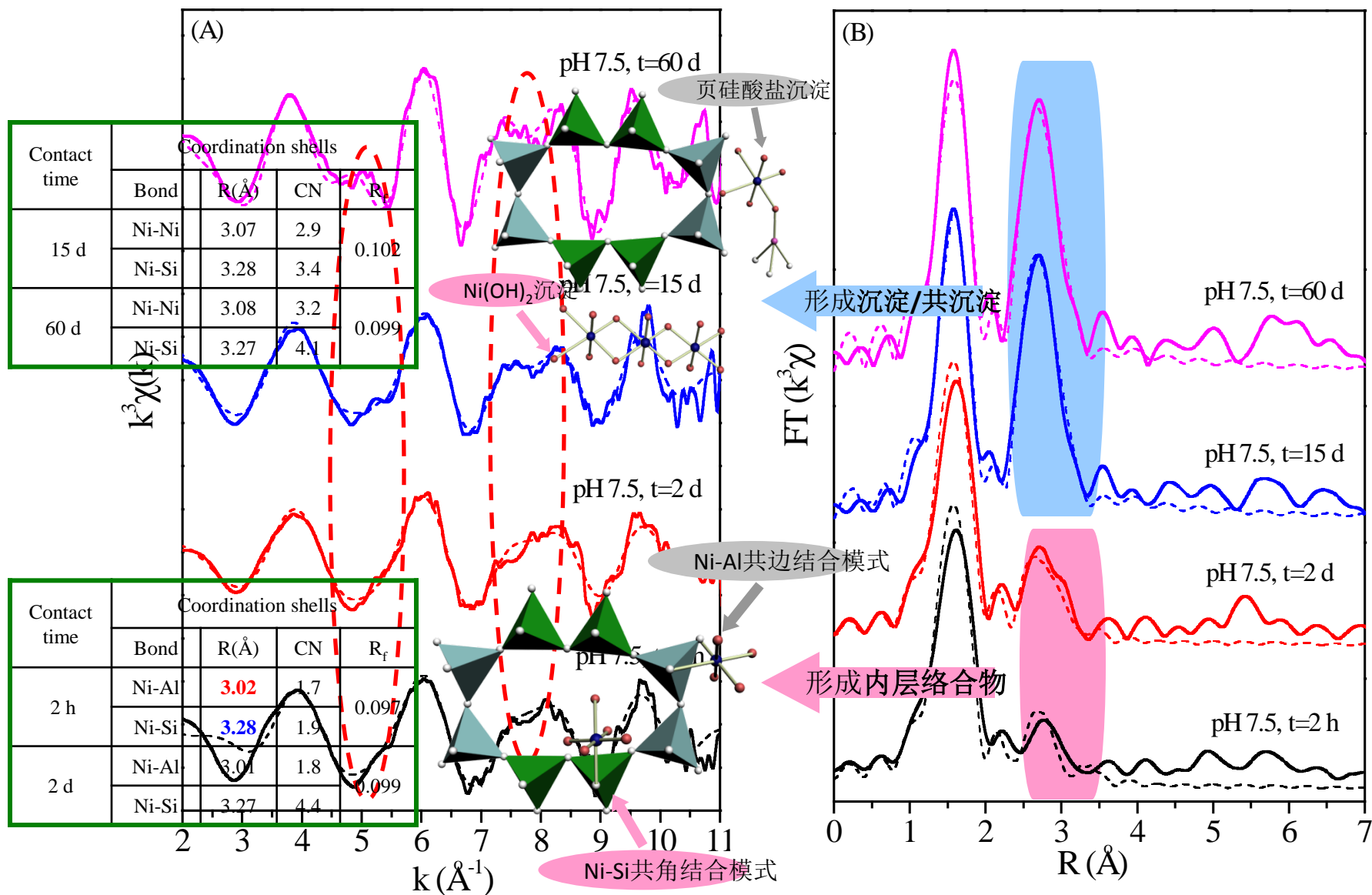
样品	配位壳层	CN	R (Å)	σ^2 (Å ⁻²)	R_f
Ni ²⁺ (aq)	Ni-O	5.70	2.04	0.00648	0.00254
Ni-Al LDH	Ni-O	5.28	2.03	0.00815	0.0156
	Ni-Ni	3.10	3.05	0.00673	
	Ni-Al	1.56	3.08	0.00921	
Ni phyllosilicate	Ni-O	5.40	2.03	0.0106	0.0176
	Ni-Ni	6.42	3.09	0.00936	
	Ni-Si	2.00	3.23	0.00154	
Ni(OH) ₂ (s)	Ni-O	5.76	2.04	0.00637	0.00185
	Ni-Ni	6.11	3.12	0.00780	

R ---键长, CN ---配位数, σ^2 ---德拜-瓦勒因数, R_f ---EXAFS 实验谱图和理论谱图的拟合误差。

依据Ni-Ni键长可以区分吸附样品体系中不同的沉淀形态

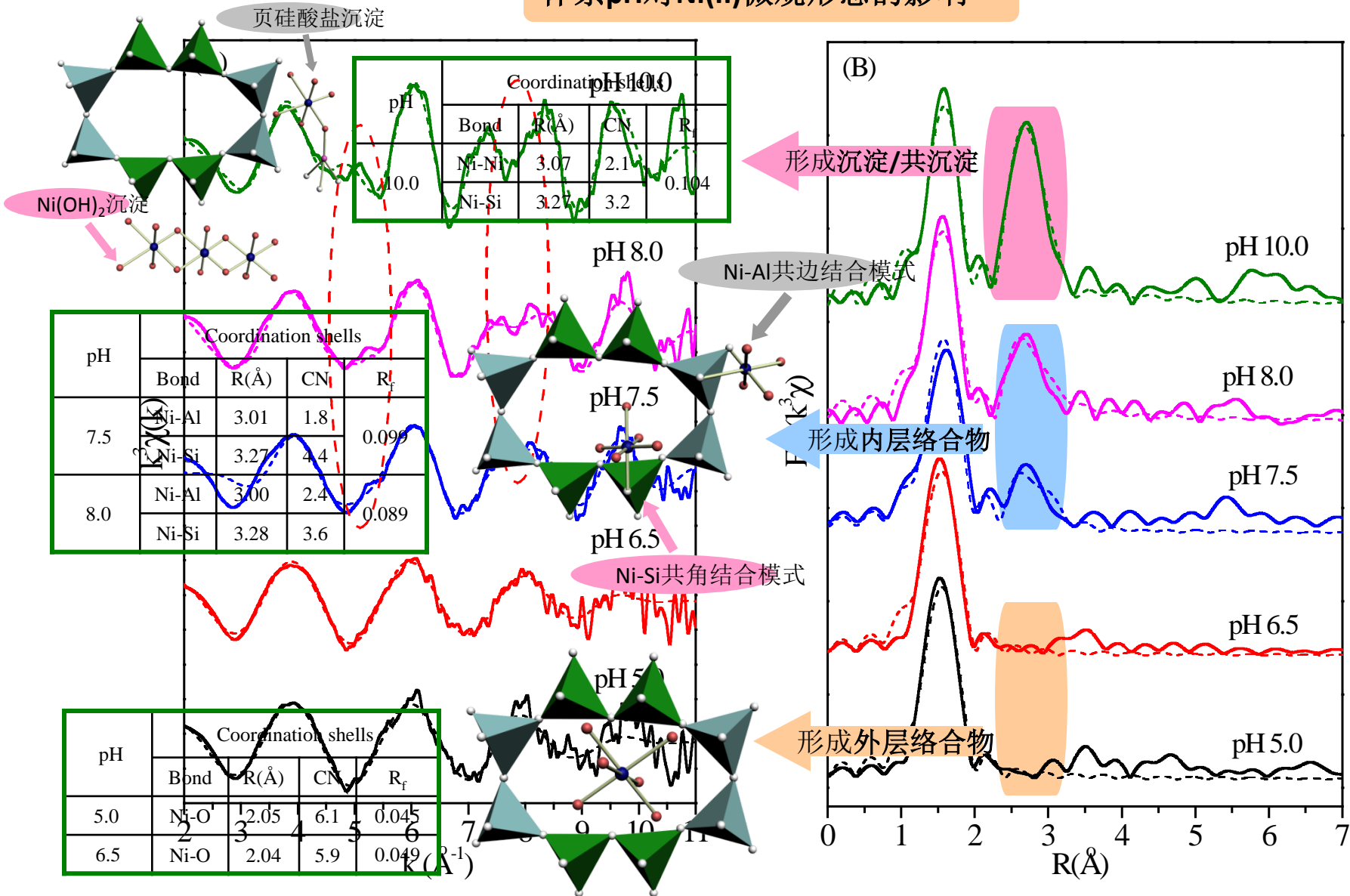
XAFS结果分析

接触时间对Ni(II)微观形态的影响



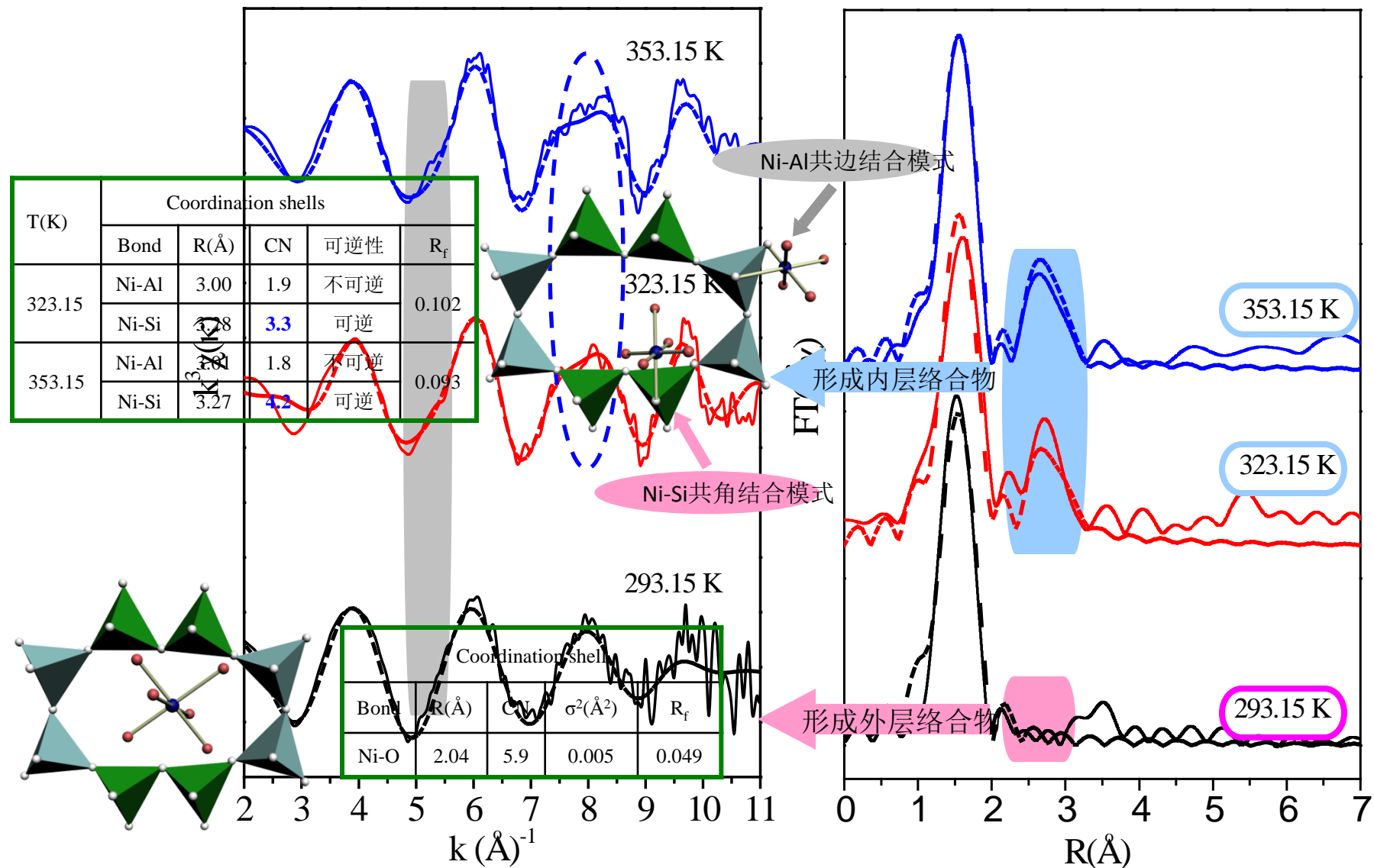
XAFS结果分析

体系pH对Ni(II)微观形态的影响



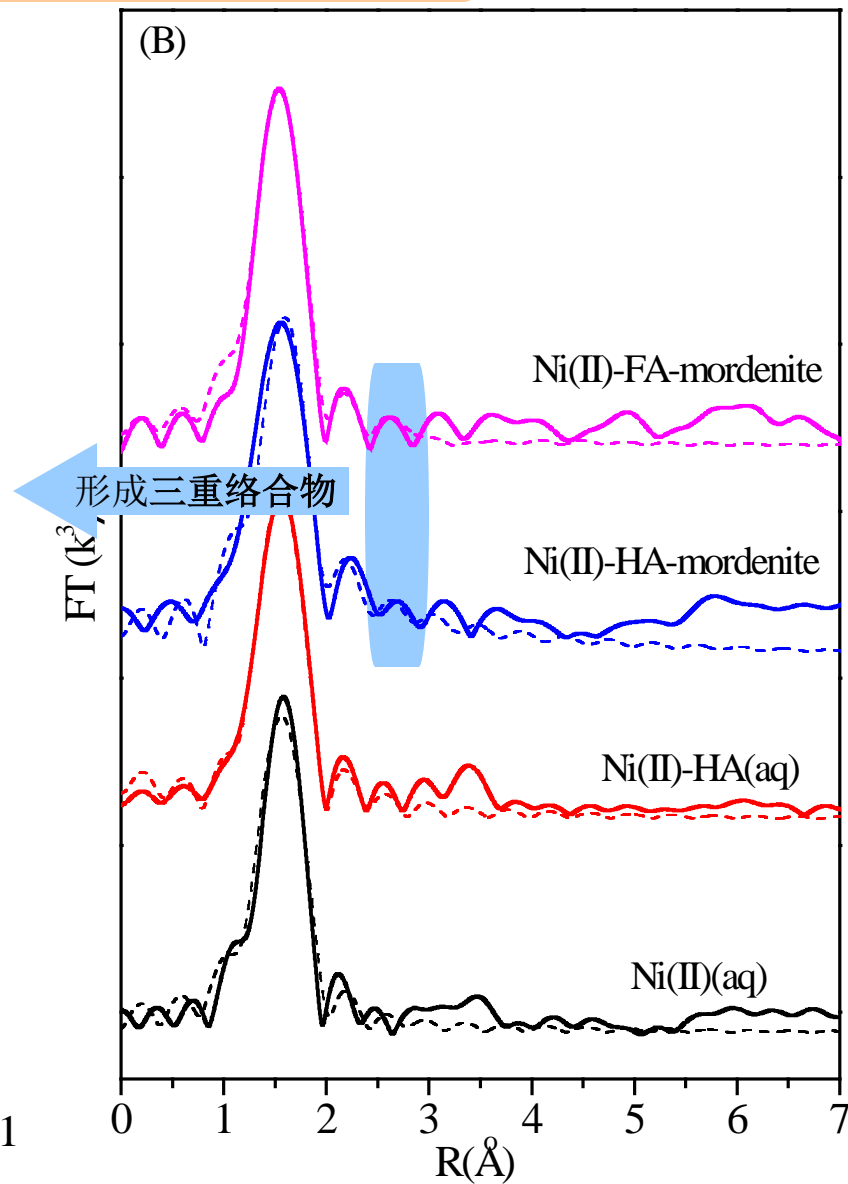
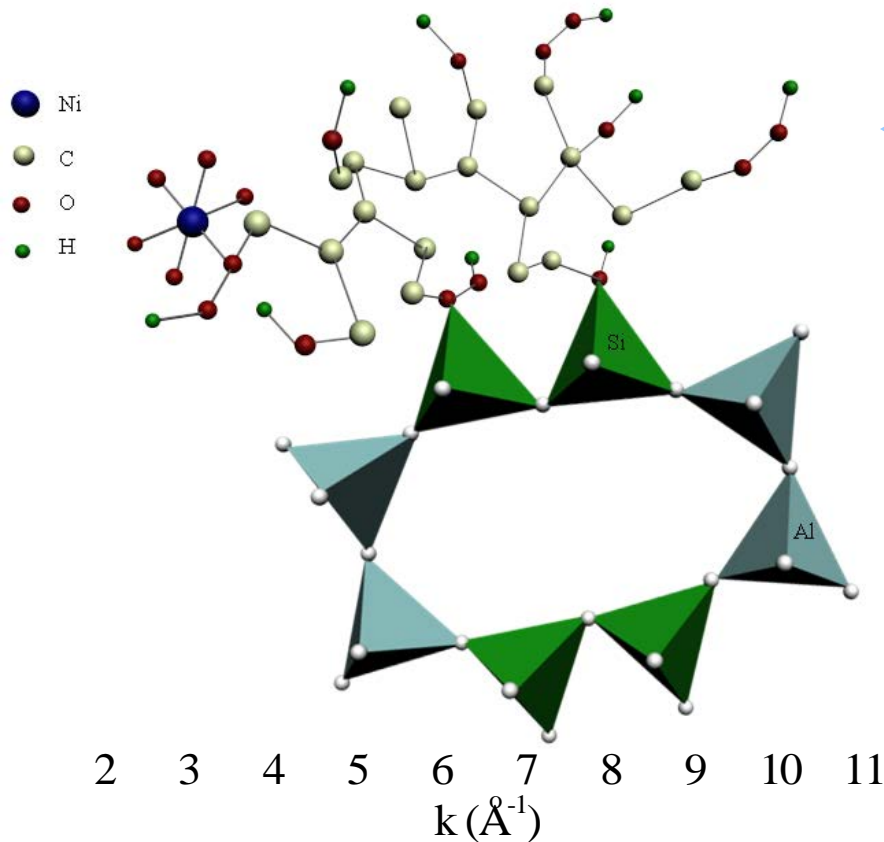
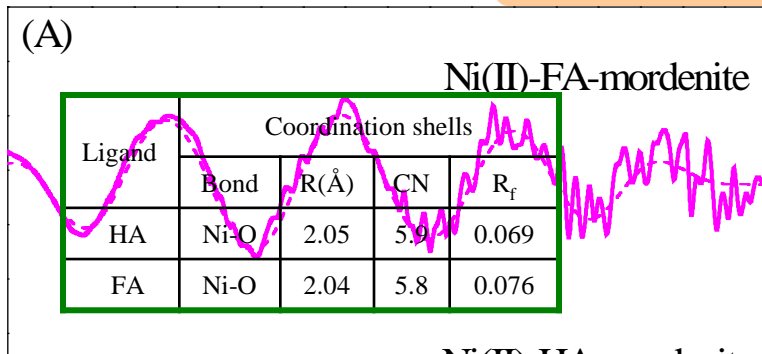
XAFS结果分析

体系温度对Ni(II)微观形态的影响



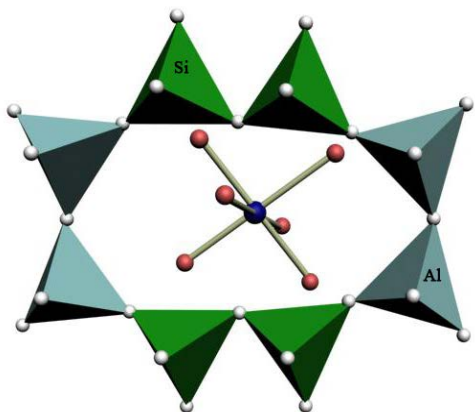
XAFS结果分析

共存腐殖酸对Ni(II)微观形态的影响

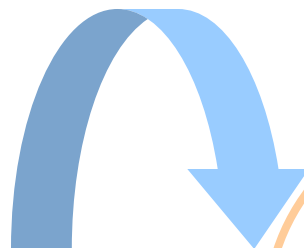


微观作用机理

(A) Ion exchange/Outer-sphere complexation



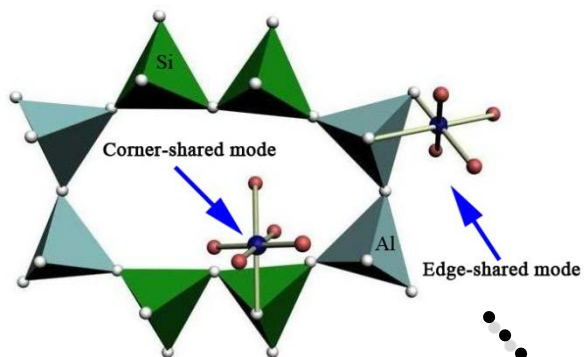
pH < 7.0, T = 293.15 K
作用力微弱，容易解吸



化学迁移性高
生态毒性较高
需要净化处理

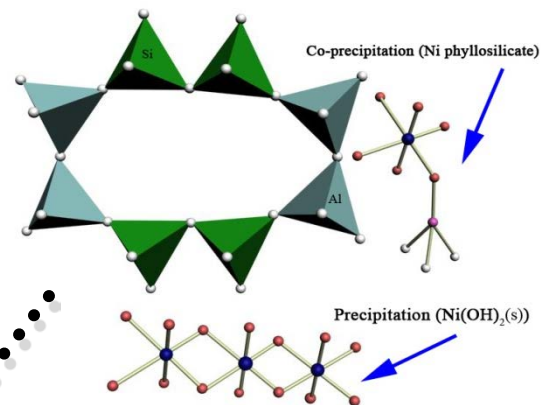
微观作用机理

(B) Inner-sphere complexation



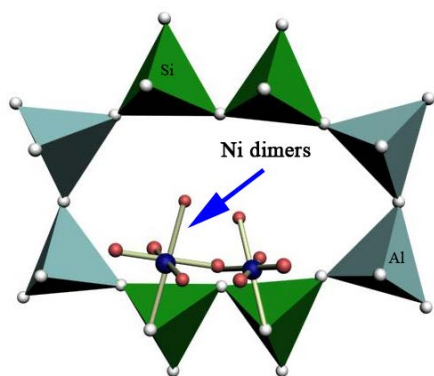
7.0 <math>pH < 8.5</math>,

(C) Precipitation/Co-precipitation



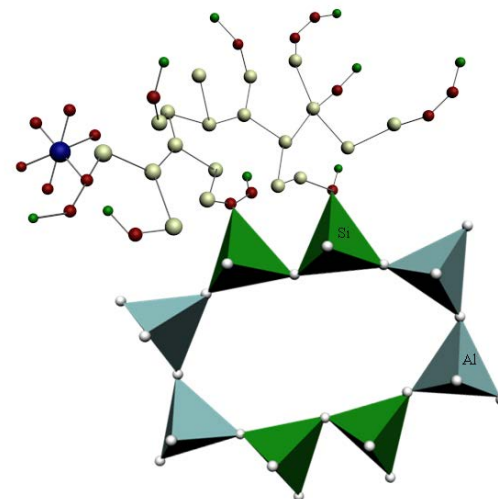
$pH > 8.5$, $t > 15\text{ d}</math>
形态稳定, 降低迁移性$

(D) Surface dimerization



100 mg/L Ni(II)
Ni(OH)₂沉淀前体

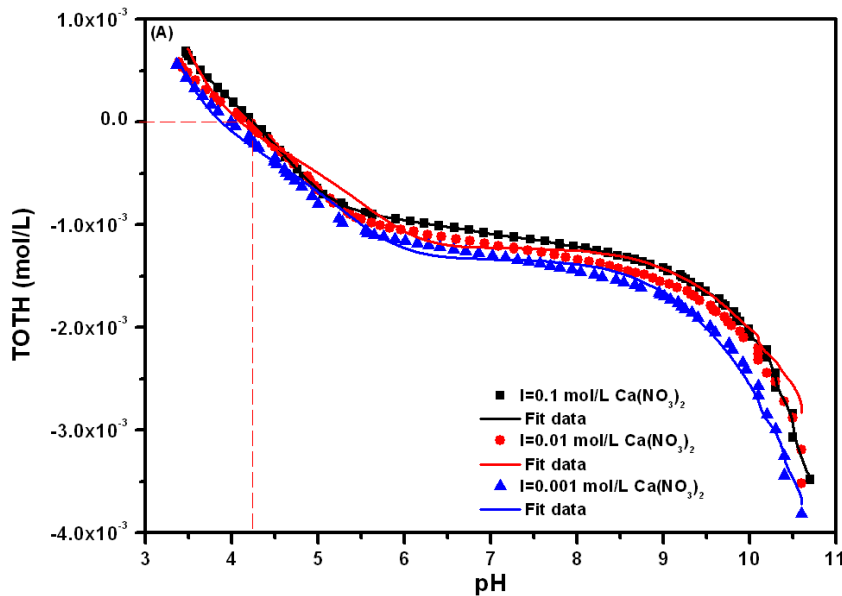
化学迁移性低
沉入水体底泥
生态毒性降低
不需后续处理



$pH < 7.5$, 共存腐殖酸
作用力强, 降低迁移性

Sorption of Ni on montmorillonite

Characterization of montmorillonite



Surface site concentration and constants

表 3-1 钙基蒙脱石表面位浓度和表面质子化常数.

Table 3-1 Surface site concentrations and surface complexation constants of Ca-montmorillonite.

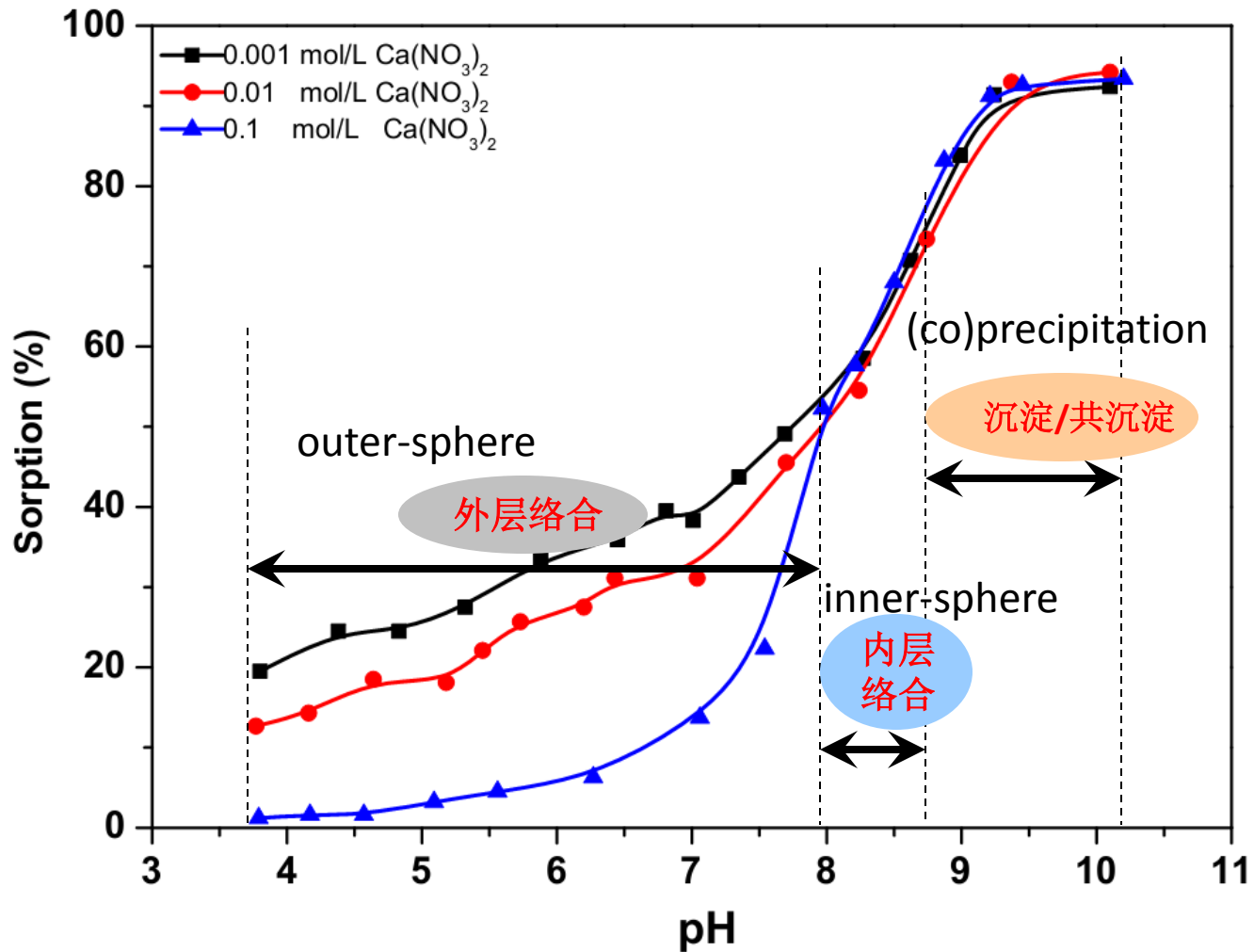
BET=64.4 m²/g, N_{X2Ca}=110 mmol/100g, T=20 °C.

离子强度	位点	浓度(mol/g)	表面反应	logK
0.01 mol/L	≡AlOH	2.96×10 ⁻⁴	≡AlOH + H ⁺ ⇌ ≡AlOH ₂ ⁺	3.21
			≡AlOH ⇌ ≡AlO ⁻ + H ⁺	-5.86
	≡SiOH	2.36×10 ⁻⁴	≡SiOH ⇌ ≡SiO ⁻ + H ⁺	-1.99
			≡X ₂ Ca + 2H ⁺ ⇌ ≡2XH + Ca ²⁺	4.98
	WSOS/DF			19.09

酸碱滴定数据及其拟合曲线

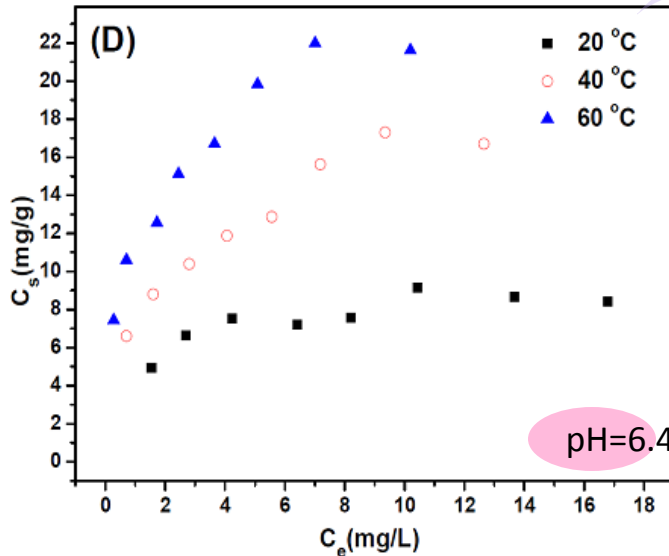
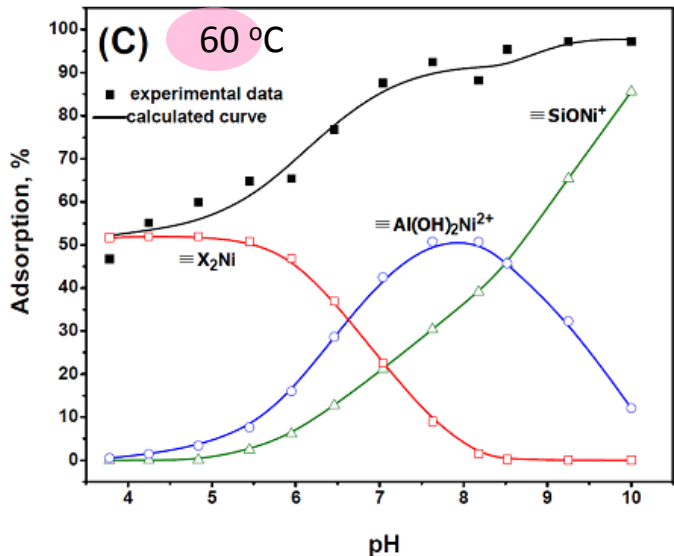
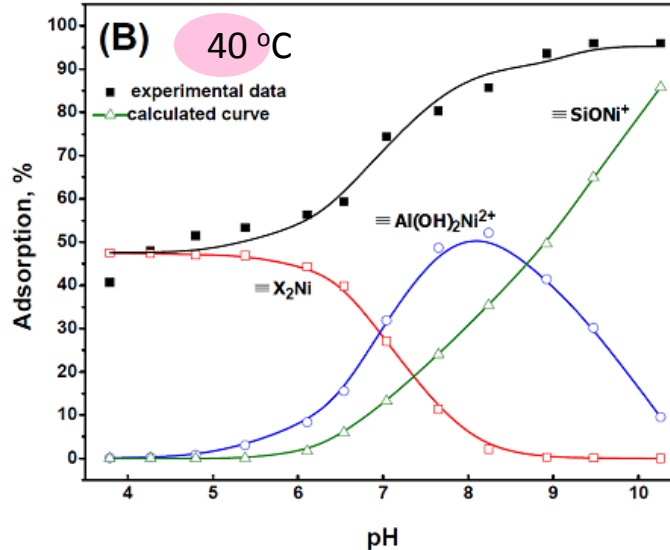
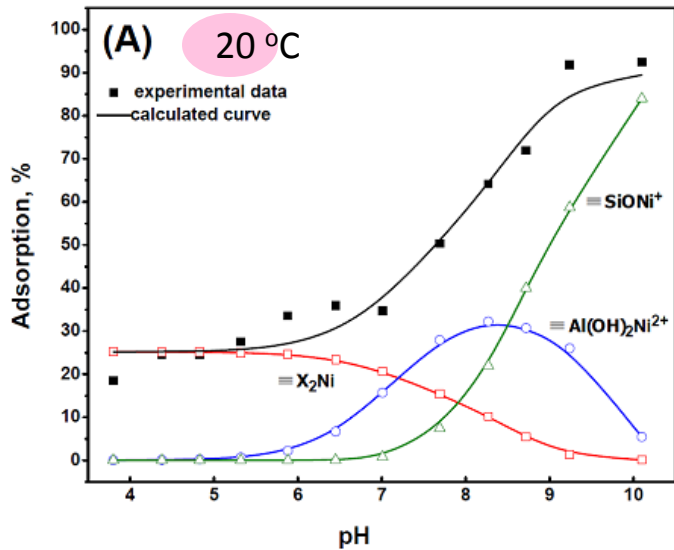
二元体系静态实验结果分析

体系pH和离子强度对Ni(II)宏观吸附行为的影响



$T=20\text{ }^{\circ}\text{C}$, $m/V=0.5\text{ g/L}$, $C_{\text{Ni(II)initial}}=10\text{ mg/L}$.

体系温度对Ni(II)宏观吸附行为和吸附形态的影响



pH < 7.0
离子交换形态 X₂Ni

pH > 7.0
内层络合形态

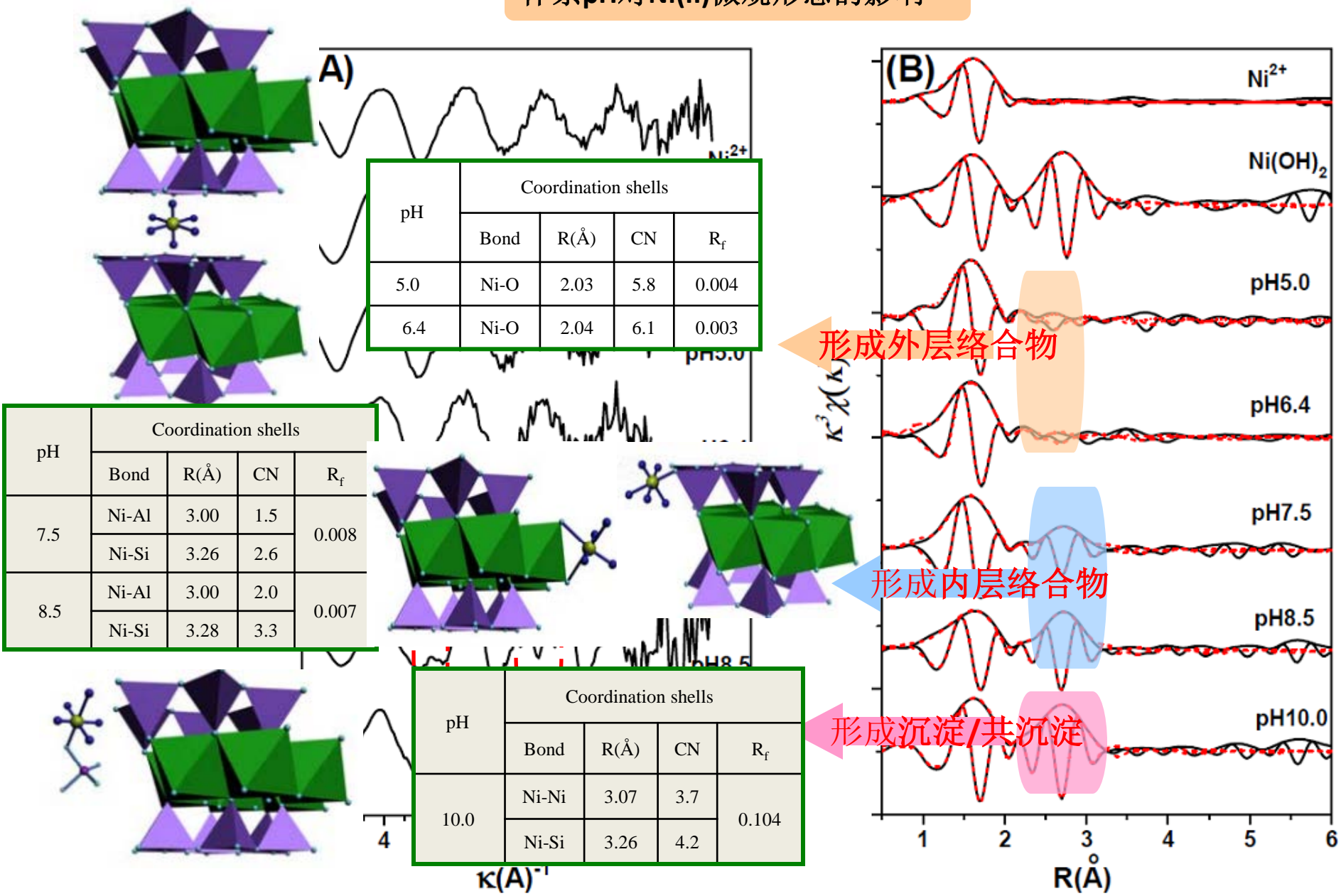
7.0 < pH < 8.5
双齿形态 Al(OH)₂Ni²⁺ 为主

pH > 8.5
单齿形态 SiONI⁺ 为主

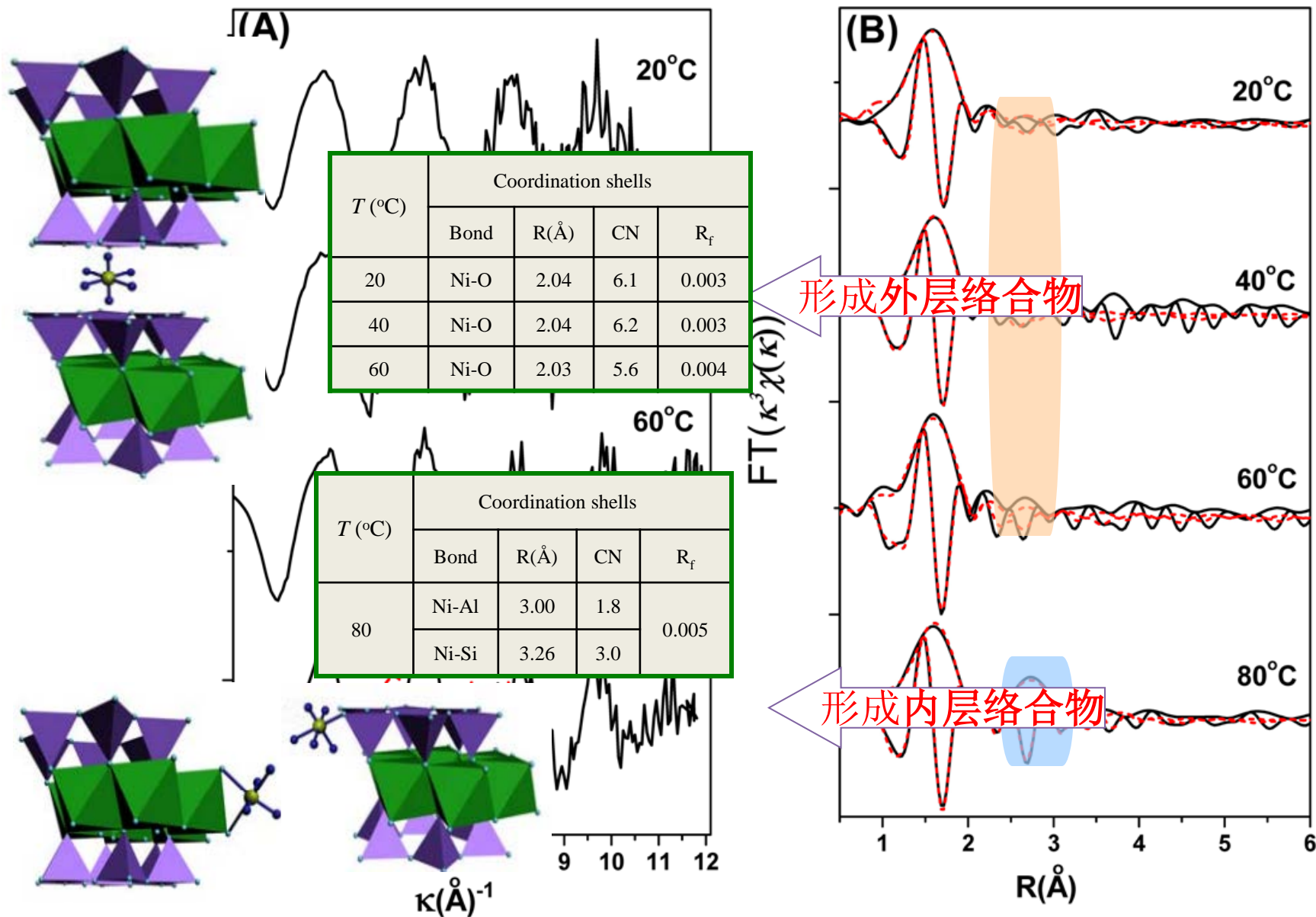
1. 孔径大小
2. 可用位点
3. 表面电势

二元体系XAFS结果分析

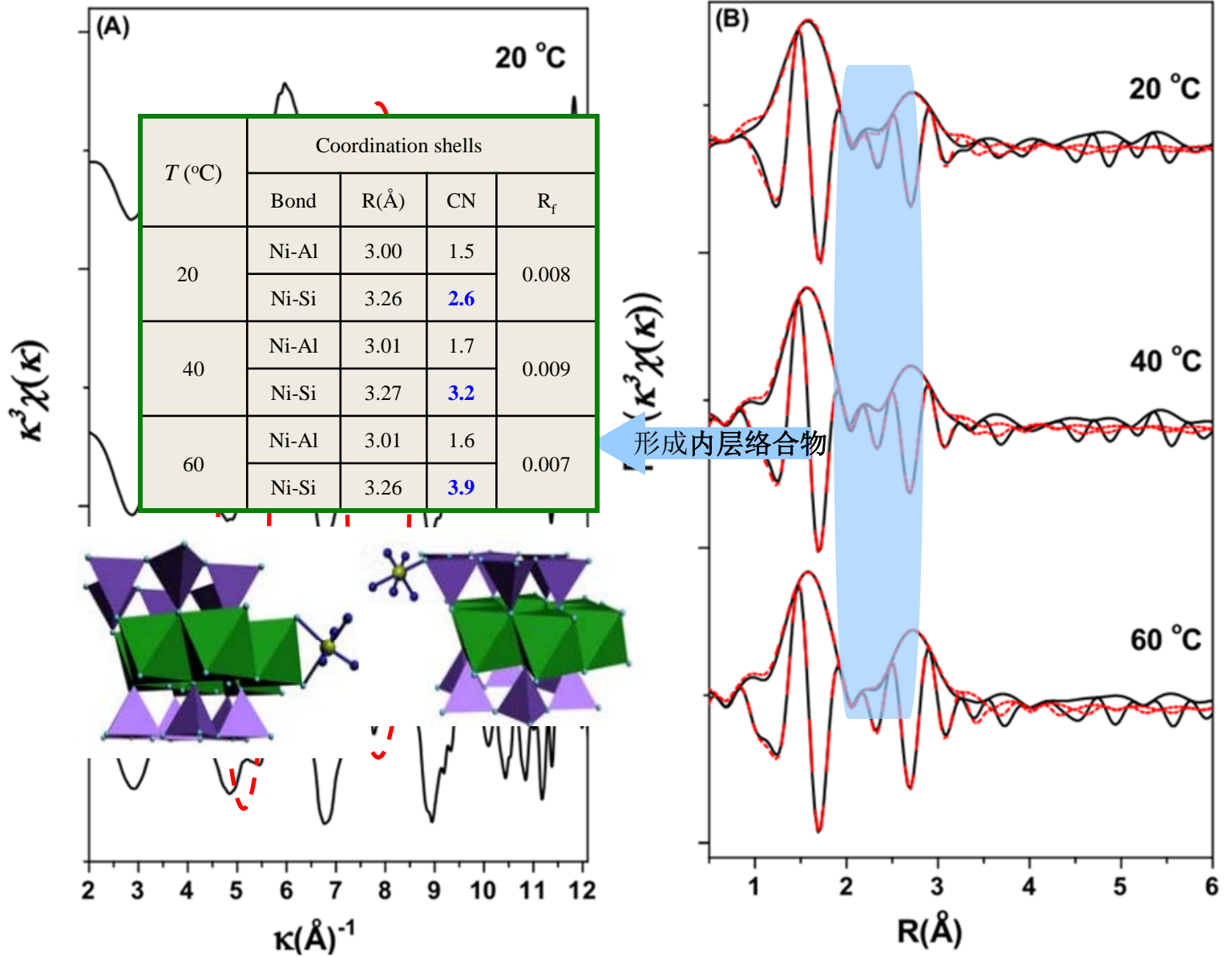
体系pH对Ni(II)微观形态的影响



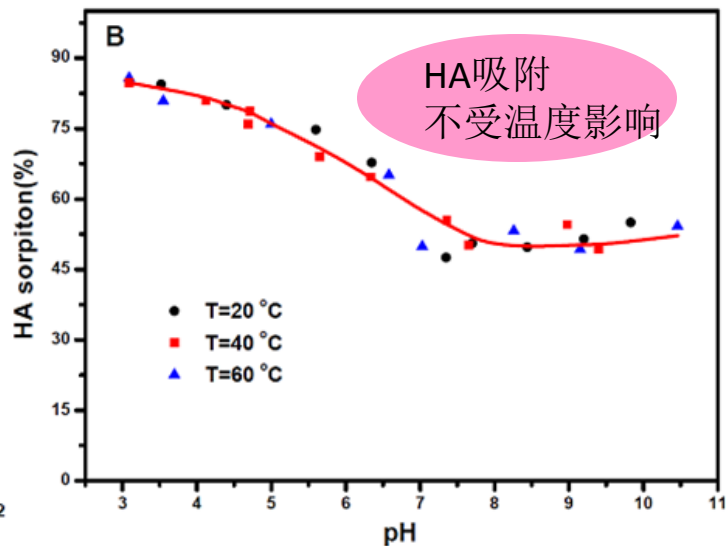
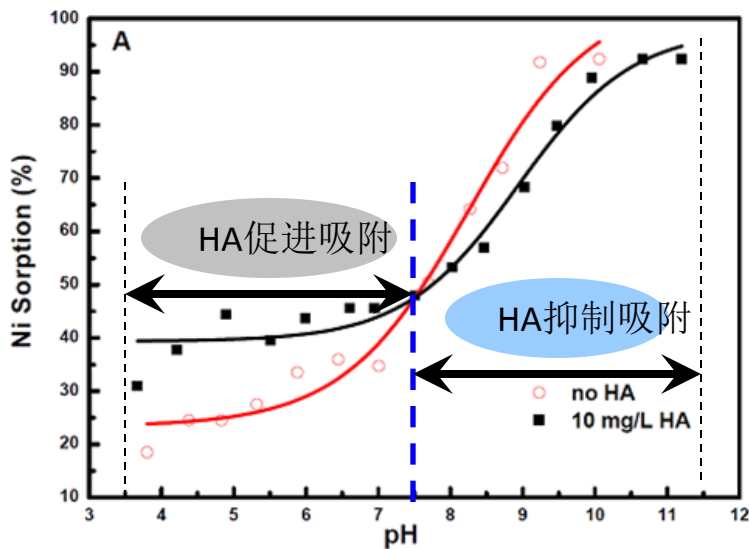
体系温度对Ni(II)微观形态的影响, pH=6.4



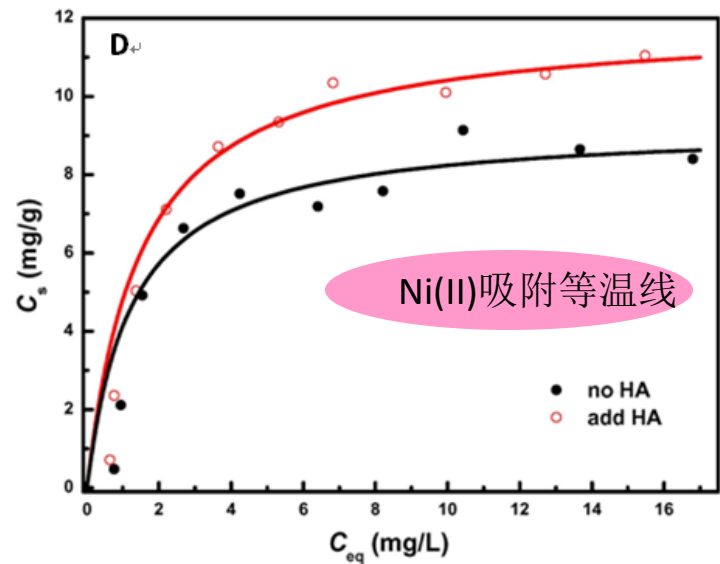
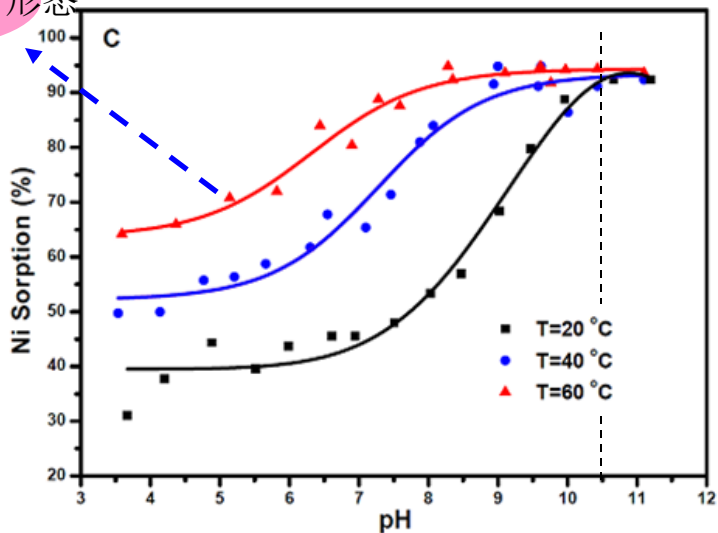
体系温度对Ni(II)微观形态的影响, pH=7.5



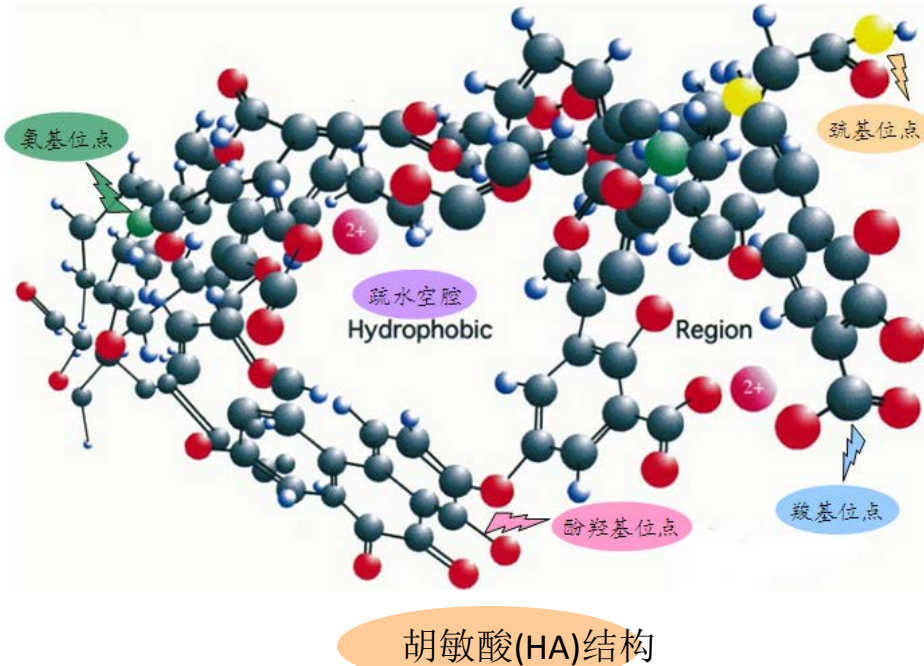
三元体系静态实验结果分析



二重结合形态



表面位浓度比较



运用模型: Model VI

HA羧基浓度: 3.3 mmol/g

HA酚羟基浓度: 1.7 mmol/g

HA分子中C含量: 60.44%

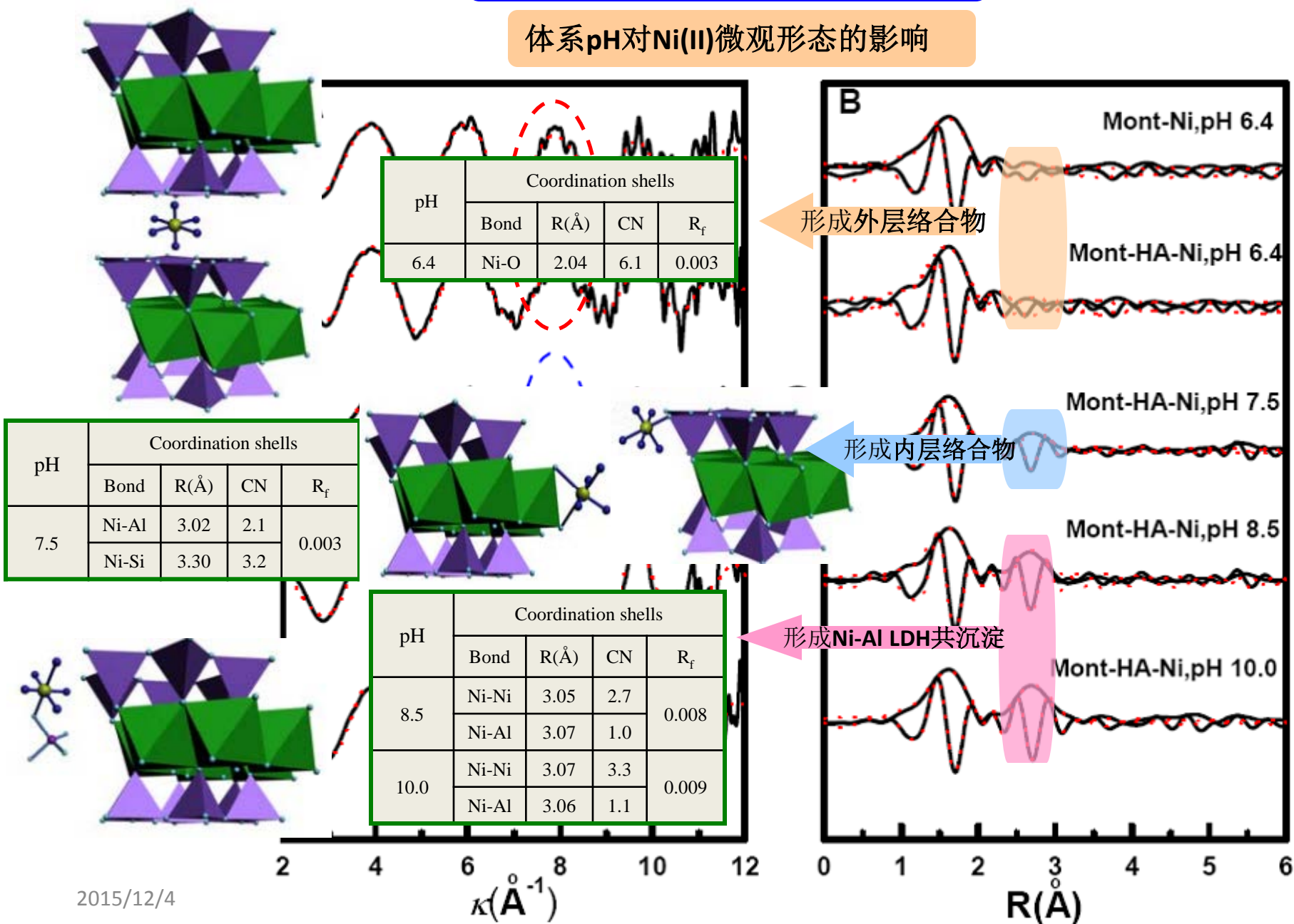
pH 7.5条件下HA吸附率: 50%

HA初始浓度 **10 mg/L**: 吸附在钙基蒙脱石上的HA所能提供的结合位点浓度: $3.23 \times 10^{-5} \text{ mol/L}$, 此条件下Ni(II)被吸附浓度: $1.59 \times 10^{-4} \text{ mol/L} \times 48\% = 7.62 \times 10^{-5} \text{ mol/L}$, **HA对Ni(II)吸附的贡献比例为42%**, **58%的Ni(II)会直接结合在钙基蒙脱石表面位点上**, 形成表面络合物或沉淀/共沉淀形态

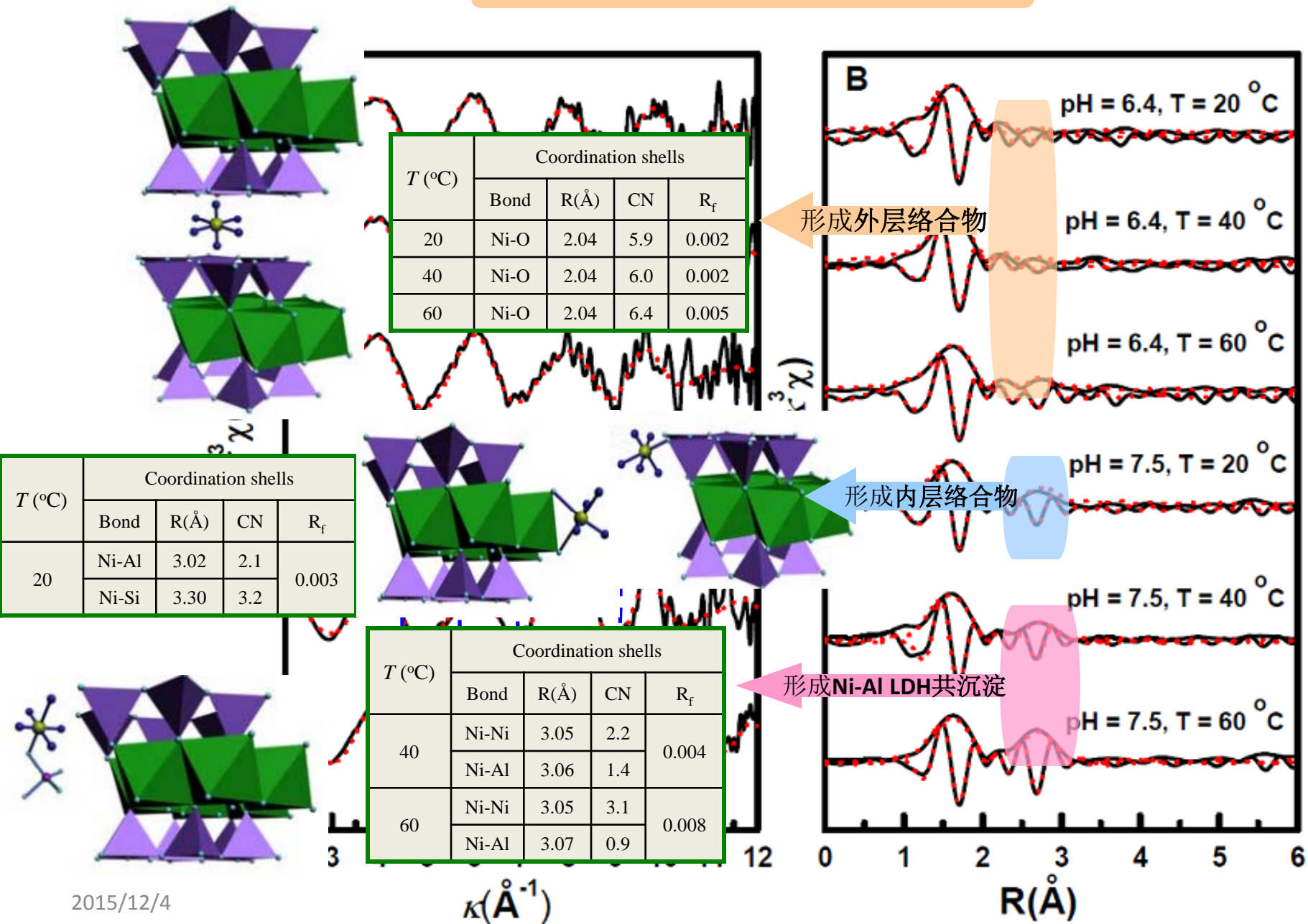
Ni(II)更为具体的吸附形态将由XAFS谱图分析进一步确定

三元体系XAFS结果分析

体系pH对Ni(II)微观形态的影响

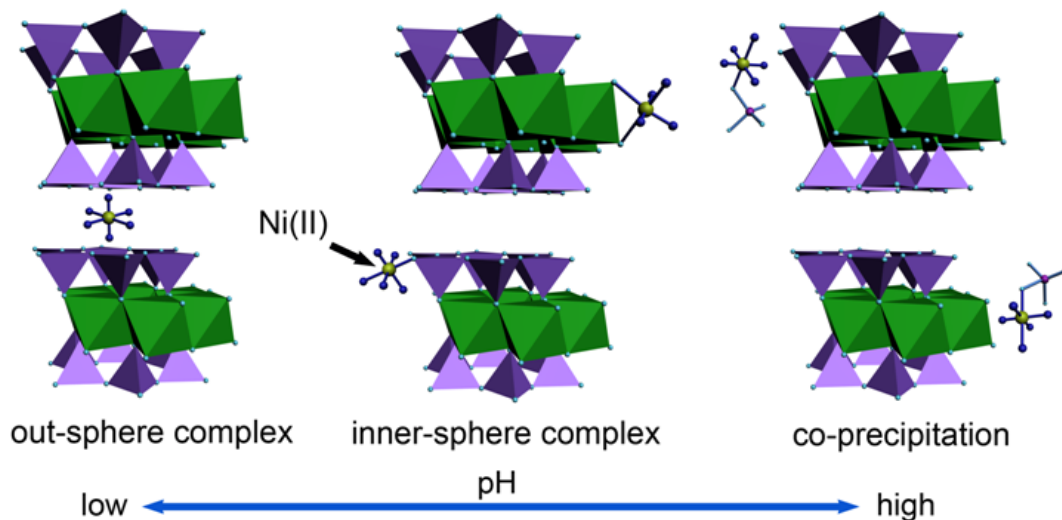


体系温度对Ni(II)宏观吸附行为的影响



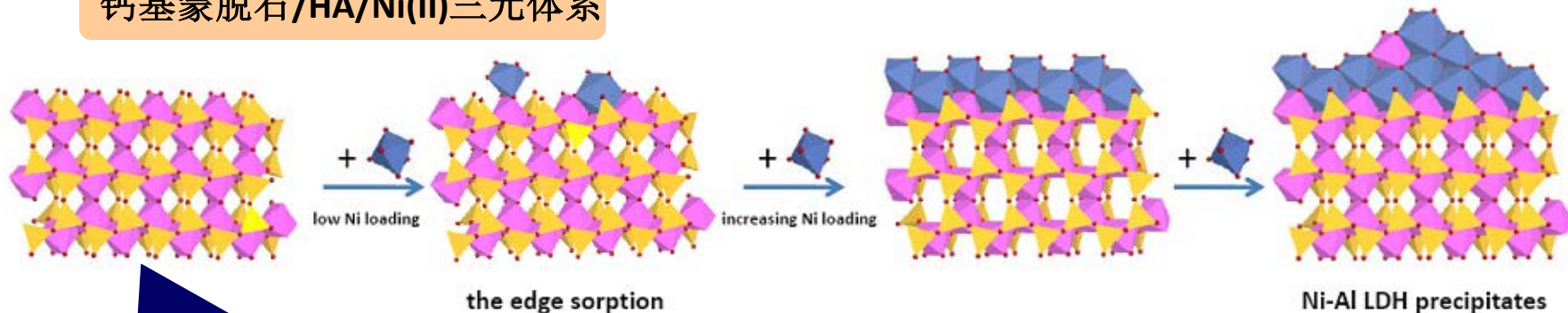
微观作用机理

钙基蒙脱石/Ni(II)二元体系



Ni(II)吸附形态的稳定性
随体系pH的升高而增强

钙基蒙脱石/HA/Ni(II)三元体系

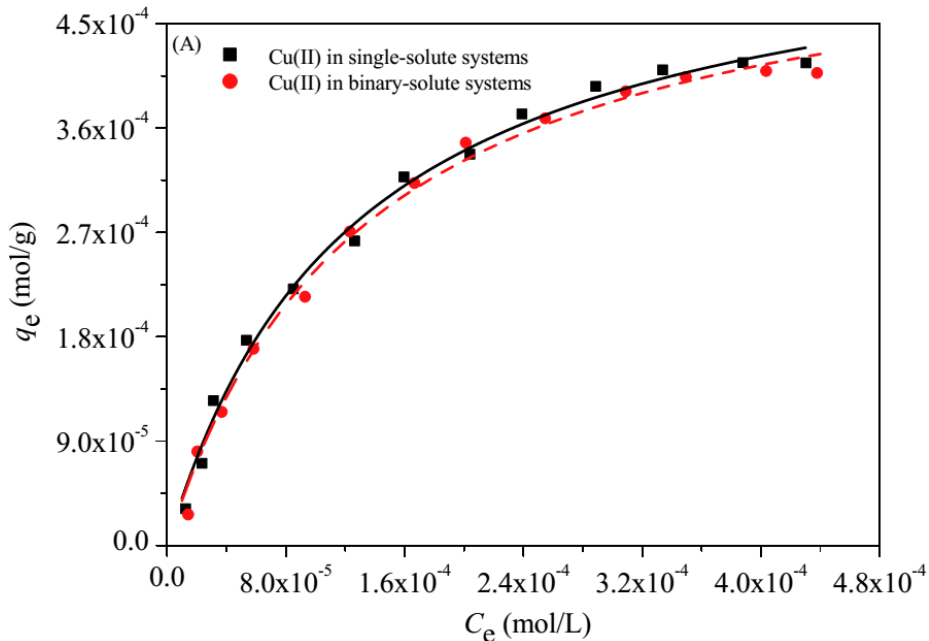


共存HA促使较高温度和体系pH条件下Ni(II)在钙基蒙脱石上形成热力学稳定性良好的Ni-Al LDH共沉淀，降低了吸附可逆性和Ni(II)的化学迁移性及生态毒性

Simultaneous sorption of Cu and Ni on montmorillonite

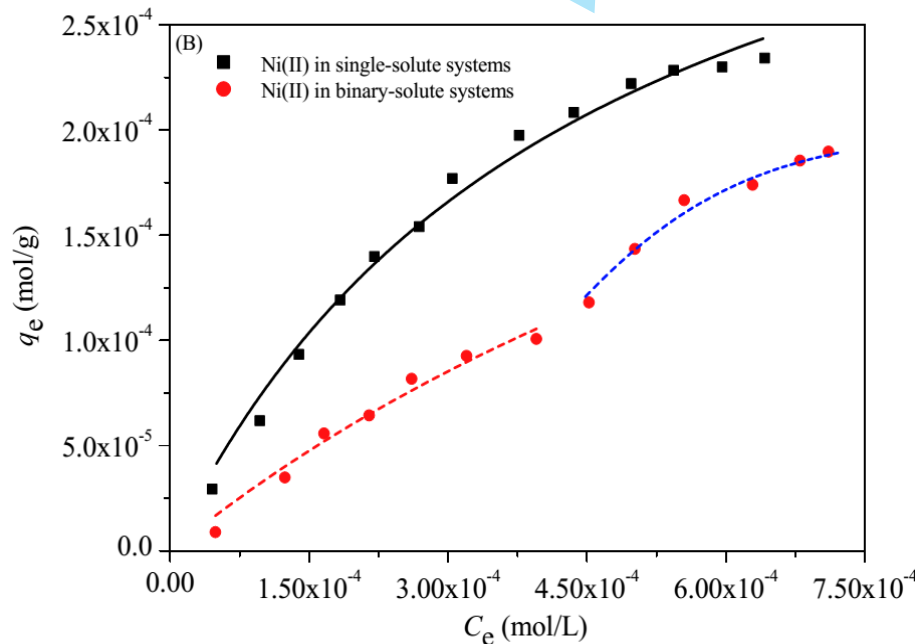
Competitive Sorption Cu(II) and Ni(II) on Montmorillonite

Macroscopic sorption behaviors

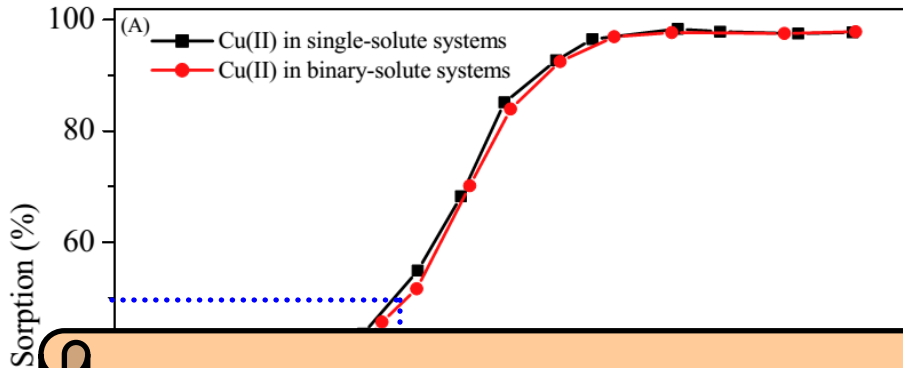


The coexisting Ni(II) has no influence on Cu(II) sorption

The coexisting Cu(II) significantly changes Ni(II) sorption behavior



Macroscopic sorption behaviors



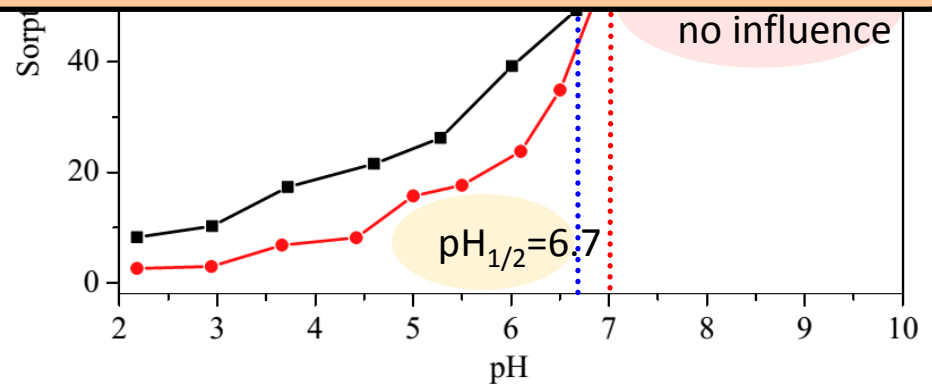
The $\text{pH}_{1/2}$ value for Cu(II) sorption (4.9) is lower than that (6.7) for Ni(II) sorption

Cu(II) has a higher affinity than Ni(II) for sorption on Mont

2 3 4 5 6 7 8 9 10

pH

The coexisting Ni(II) has no influence on Cu(II) sorption

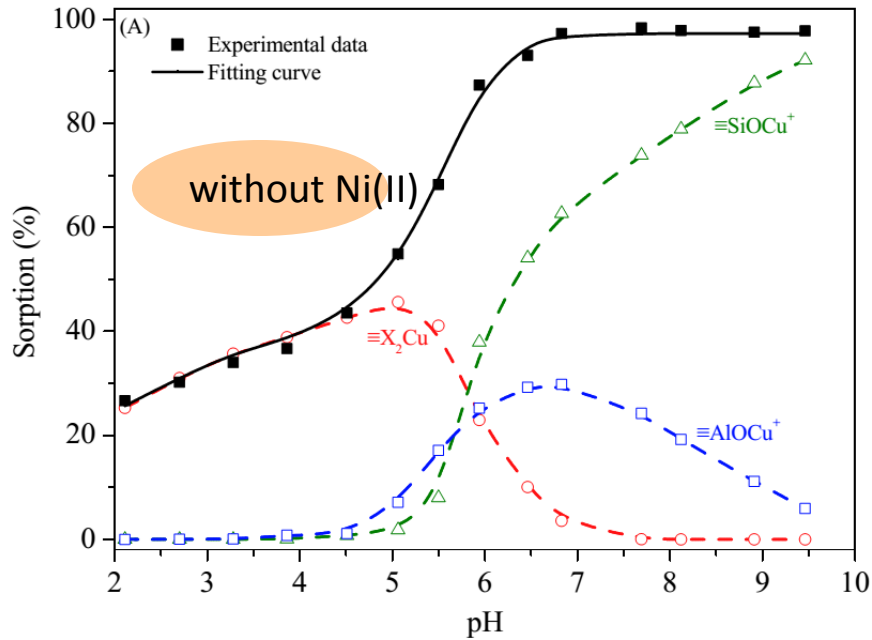


$\text{pH}_{1/2}=6.7$

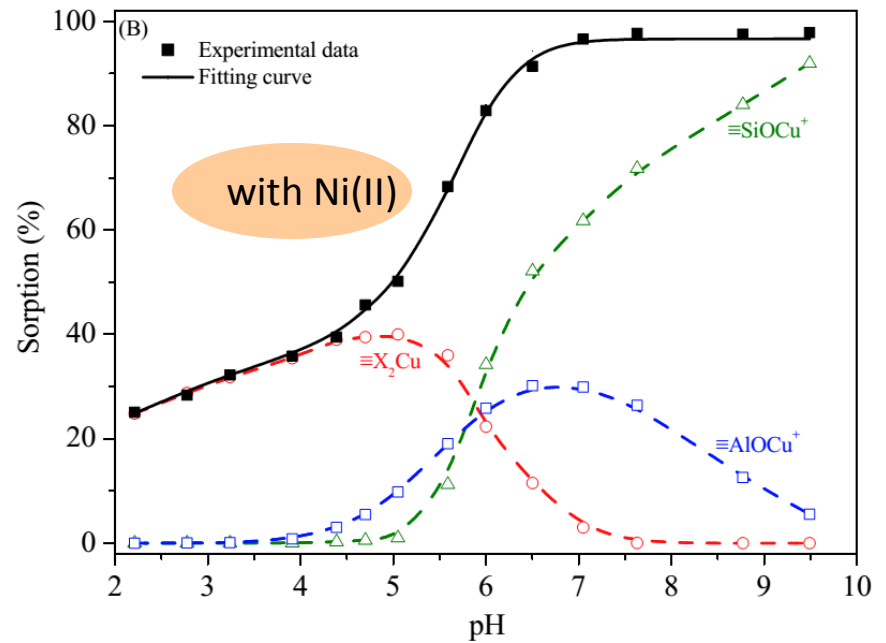
no influence

Surface complexation modeling

Cu(II) in single-solute system



Cu(II) in binary-solute system



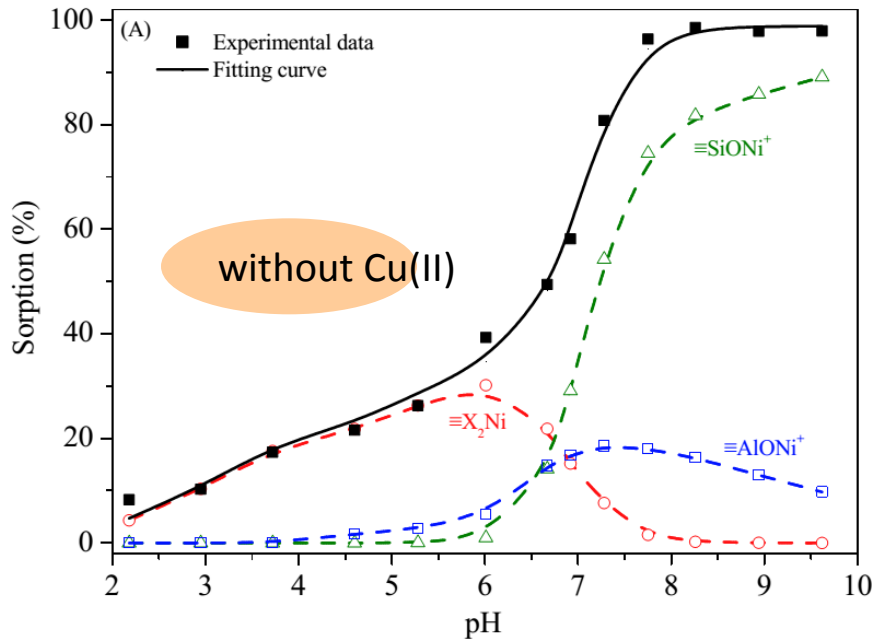
The presence of Ni(II) has no obvious influence on the sorption species of Cu(II)

pH < 5.5, $\equiv X_2Cu$ species, cation exchange reaction

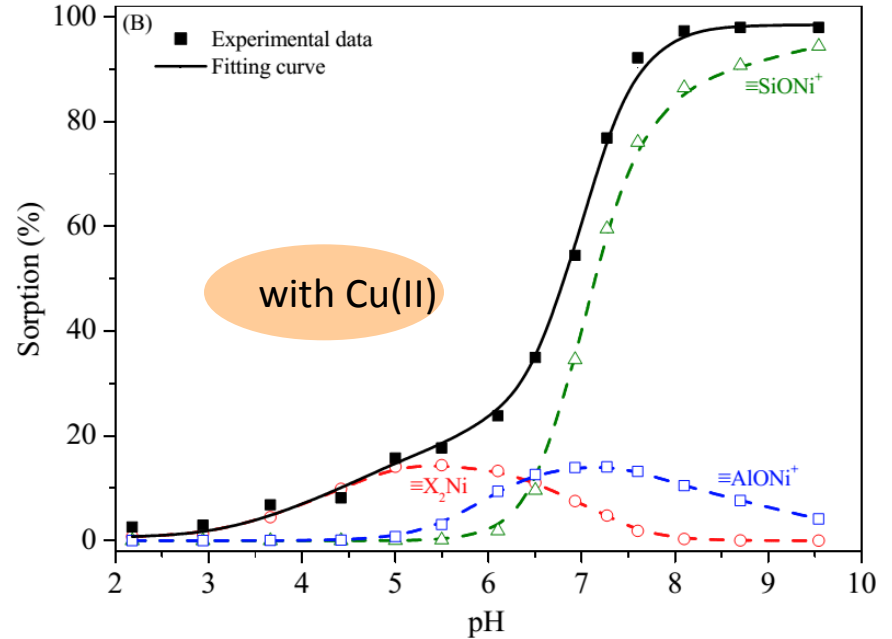
pH > 5.5, $\equiv SiOCu^+$ and $\equiv AlOCu^+$ species, inner-sphere complexation

Surface complexation modeling

Ni(II) in single-solute system



Ni(II) in binary-solute system



The presence of Cu(II) alters the sorption species of Ni(II)

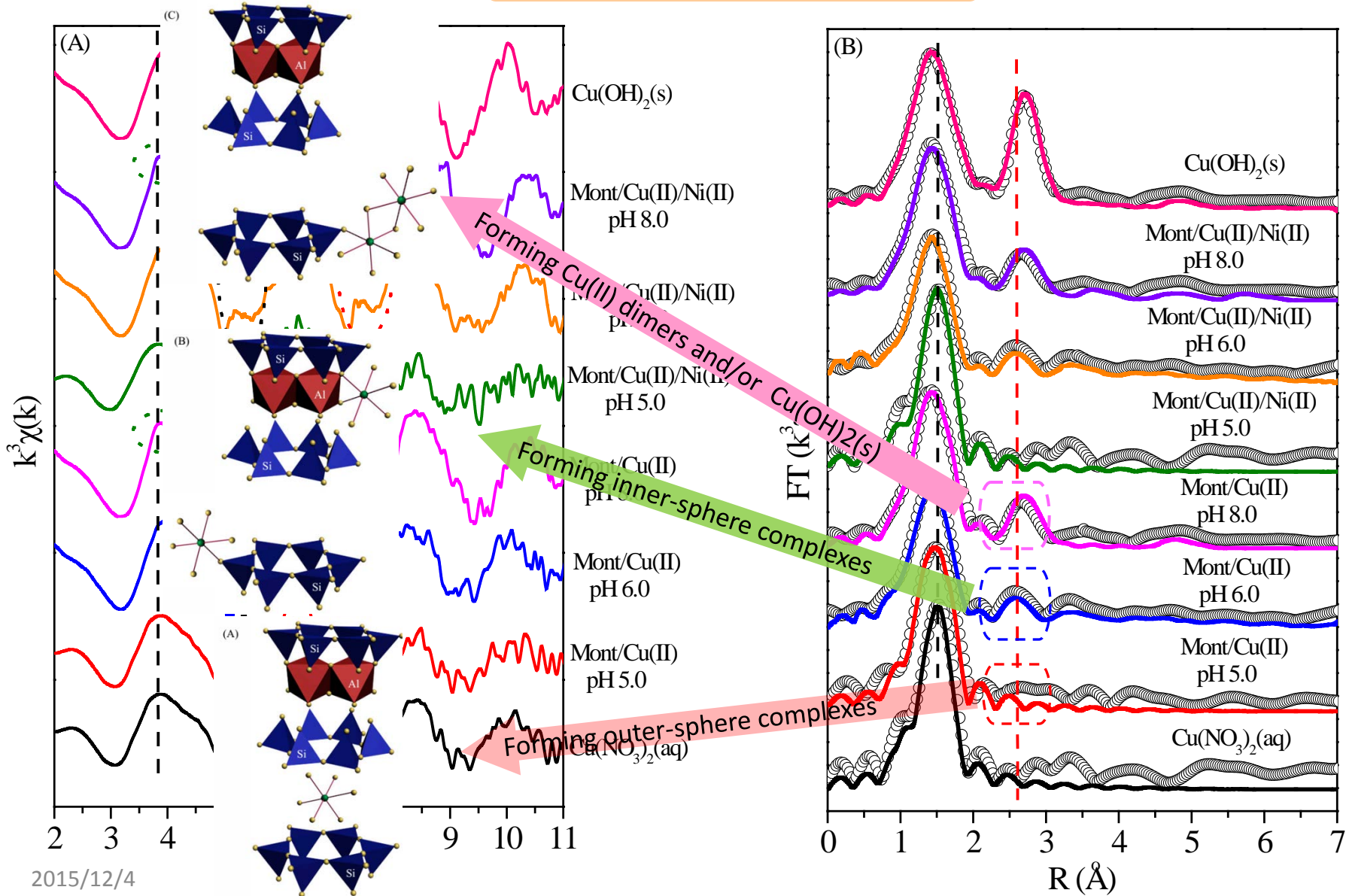
pH=6.0, single-solute system: $\equiv\text{X}_2\text{Ni}$ species, cation exchange reaction

binary-solute system: 50% $\equiv\text{X}_2\text{Ni}$ and 50% $\equiv\text{AlONi}^+$ species,

cation exchange and inner-sphere complexation

XAFS analysis

Cu(II) sorption species



吸附选择性Cu(II)>Ni(II)的原因

1

电负性: Cu(II) (2.00) > Ni(II) (1.91)
电负性越大, 吸附亲和力越强

2

一级水解常数: Cu(II) (8.0) < Ni(II) (9.6)
一级水解常数越低, 越容易被吸附

3

软度系数: Cu(II) (0.284) > Ni(II) (0.252)
软度系数越大, 越倾向于被吸附

4

电子构型: Cu(II) ($3d^9$) vs Ni(II) ($3d^8$)
Cu(II)的Jahn-Teller形变效应增强了其在蒙脱石上的吸附亲和力

5

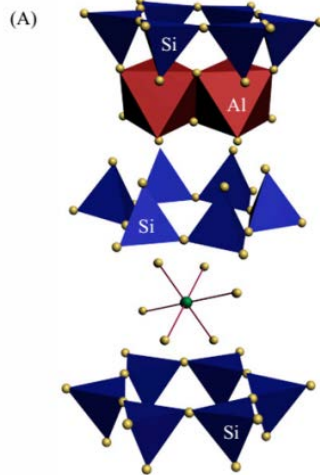
蒙脱石结构: 八面体空位
蒙脱石不对称的八面体基面有利于形变的Cu(II)O₆八面体结合

XAFS谱图的采集和解谱分析结果验证了表面模型拟合的推断

没有Cu(II)共存条件下

Ni(II)进入蒙脱石层间，
保持水合离子形态

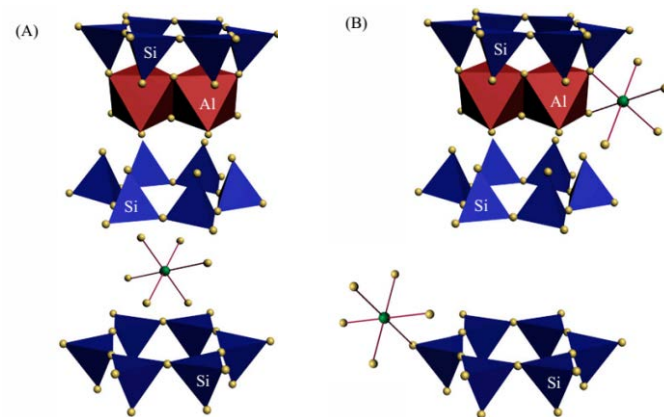
pH 6.0



自由离子
高迁移性
高生物有效性
高生态毒性

Cu(II)共存条件下

部分Ni(II)和蒙脱石发生表面络合



结合紧密
热力学稳定性高
化学迁移性低
生态毒性低

部分代表性相关论文

Environ. Sci. Technol. 42(2008) 6532; 43 (2009) 2362; 43(2009) 3115.
43(2009) 5776; 45(2011) 3621; 45(2011) 7718;
45(2011) 10454; 46(2012) 6020; 47(2013) 9904;
48(2014) 5493; 48(2014) 13138; 49(2015) 4255;
49(2015) 9168; 49(2015) 11721. In revision

Geochim. Cosmochim. Acta 75(2011) 6520; 121 (2013) 84;
140 (2014) 621; 165(2015)86;
166(2015) 129; (2015) in press

Chem Soc Rev 42(2013) 8821; **Adv. Mater.** 23(2011) 3959.

Chem. Sci. 3 (2012) 433; **ACS Nano** 7 (2013) 3589

J. Phys. Chem. B,C 113 (2009) 860; 114 (2010)6779; 113(2009)7659;
114 (2010) 12948; 114(2010)13846; 115(2011) 22025.
115(2011)25234; 118 (2014)8440

J. Mater. Chem. A 1(2013)11691; 2(2014)944; 2(2014) 4391;
3 (2015) 297; 3(2015)6073; 3(2015)10119; 3(2015)...

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2015/12/4



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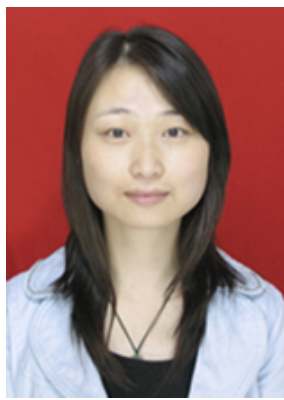
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宋文成



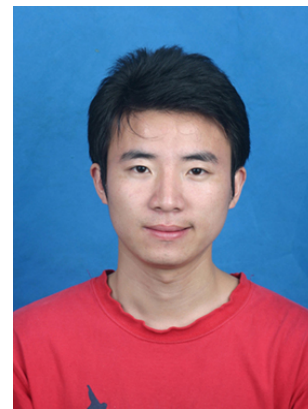
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