

金属表面のXAFS測定

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謝辞

放射光利用に関して

- 高エネルギー加速器研究機構

BL-9A,9C,11B,12C

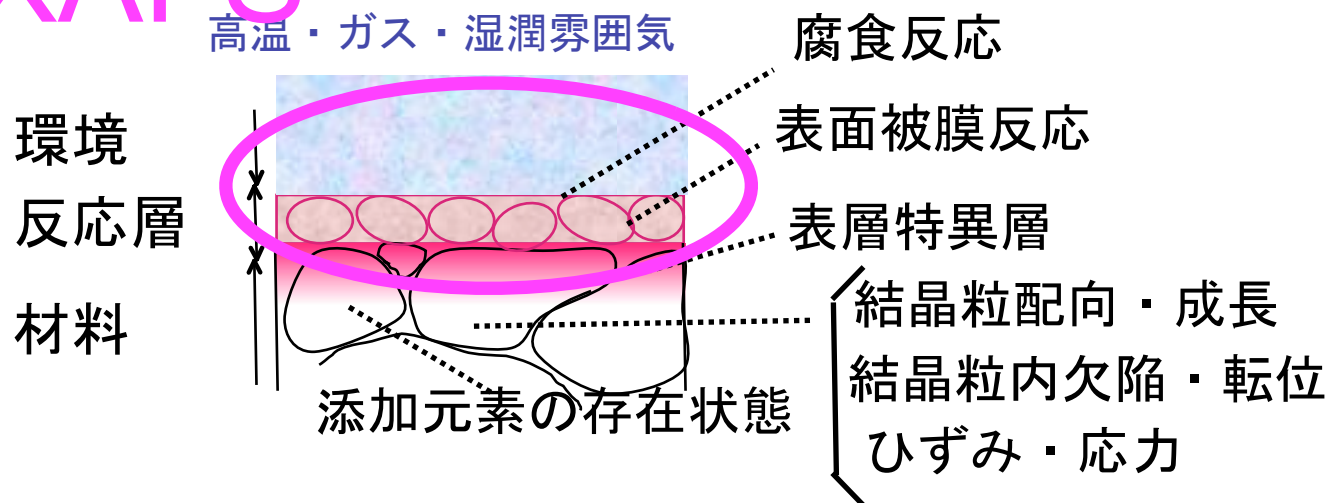
北島義典、丹羽尉博、稲田康宏、野村昌治

実験に関して（新日鉄）

- 低合金鋼の大気腐食：紀平寛
- 放射光実験：太田典明
- 低合金鋼の大気腐食：紀平寛
- ステンレス孔食：金子道郎

金属系材料で特に重要な構造情報

蛍光XAFS



観察したい現象 ×

放射光を活用した
in situ 技術の開発

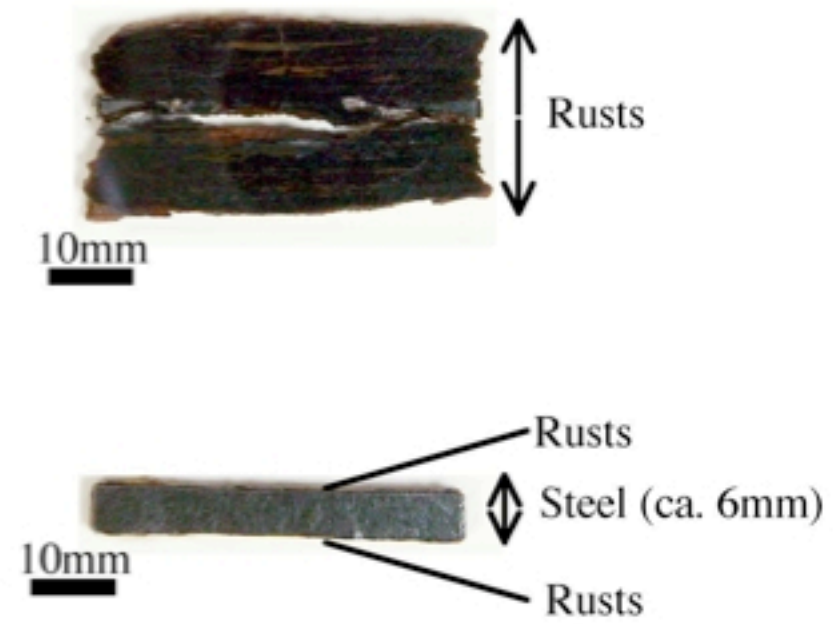
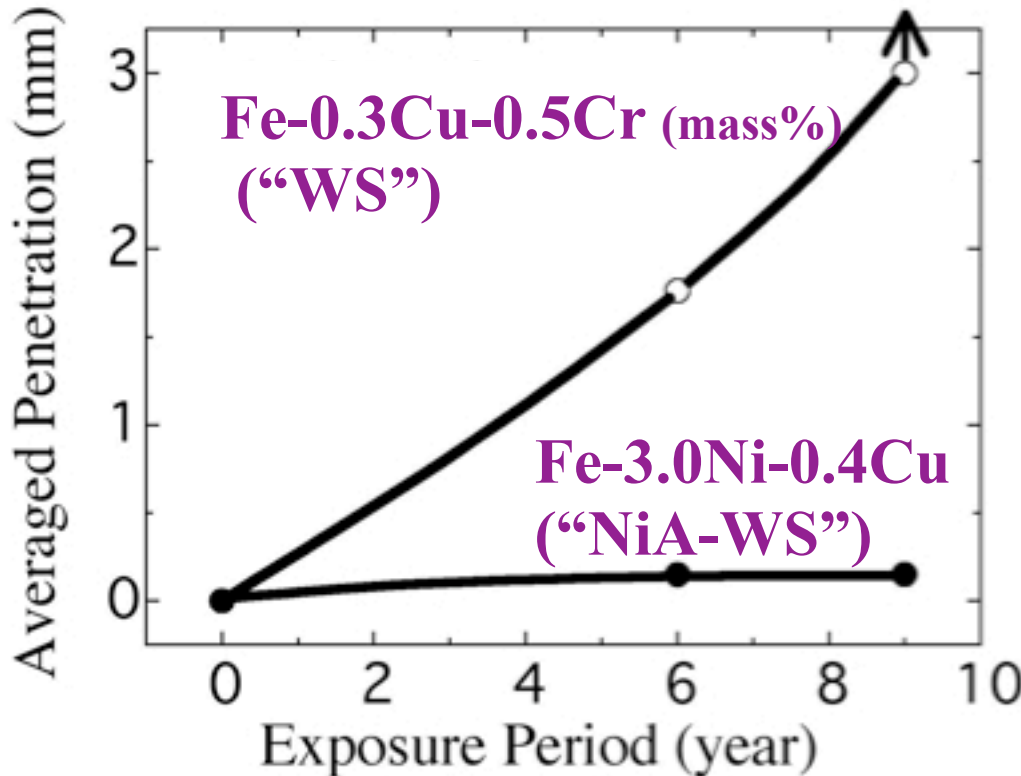
Development of advance weathering steel

H. Kihira et al., (1999,2000)

- Maintenance cost
- Environment issue



Needs for atmospheric corrosion resistance
w/o coating and/or painting



Corrosion test at a coastal area
(1.3 mdd NaCl,... 10 km from the beach, Chiba, in Japan)

Rusts formed on weathering steel

Objective

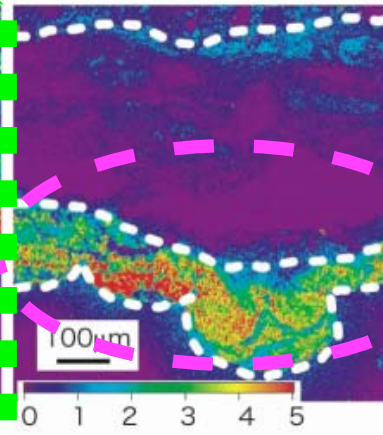
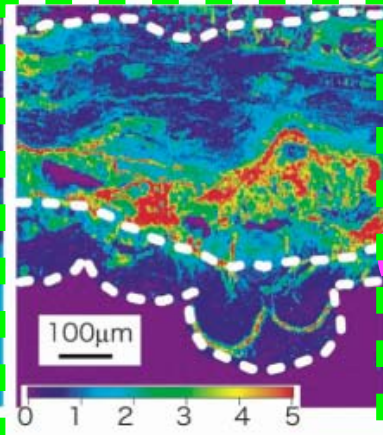
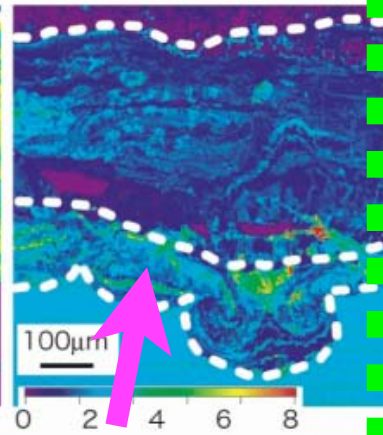
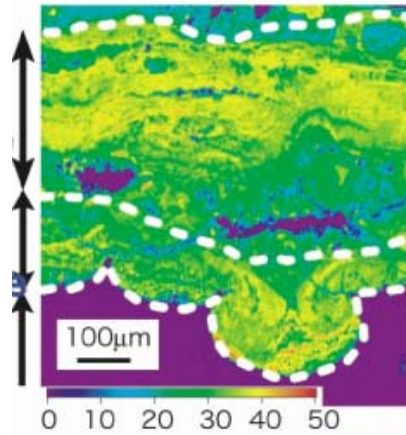
States of chloride in rust ?

NiA-WS

How does the protective rust function?



Rusts
Outer
Rust
Inner
Steel

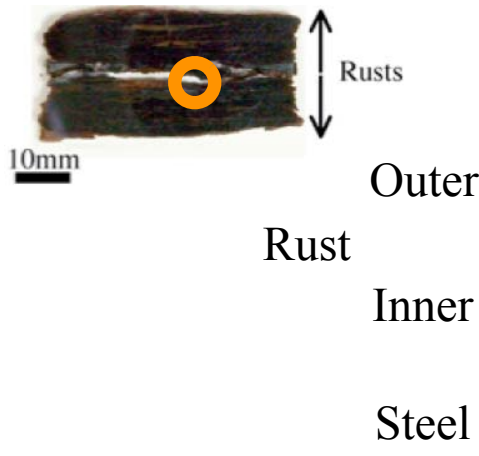


cation-selective

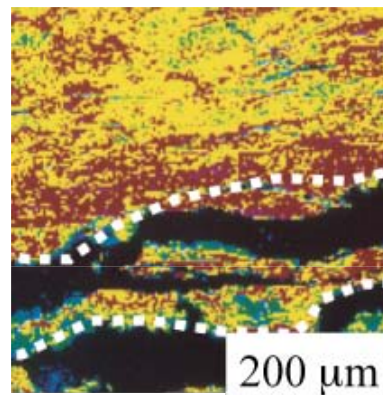
compositional mapping



WS



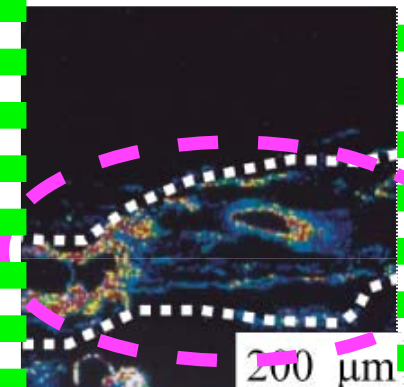
Outer
Rust
Inner
Steel



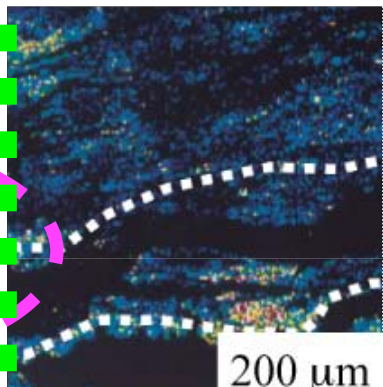
O

Ni

anion-selective



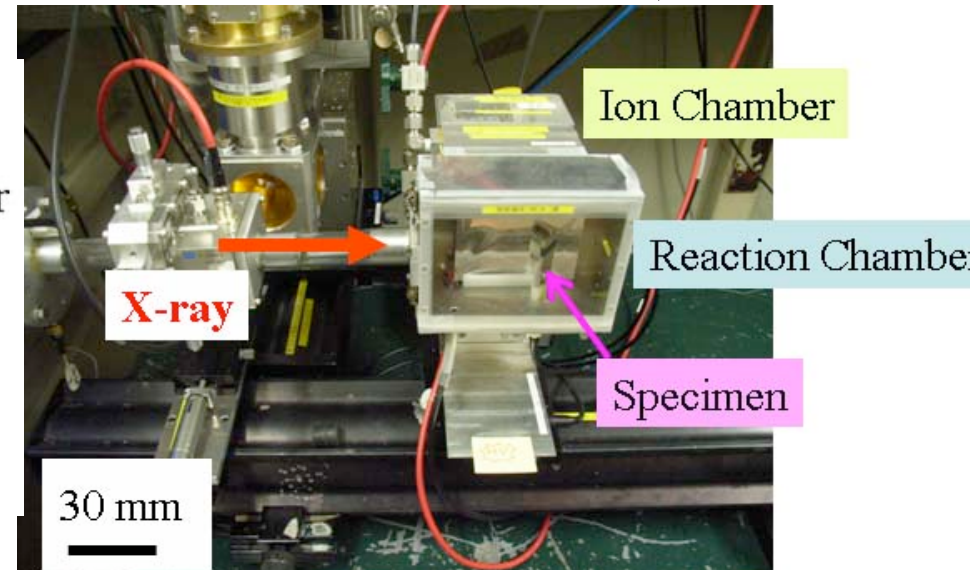
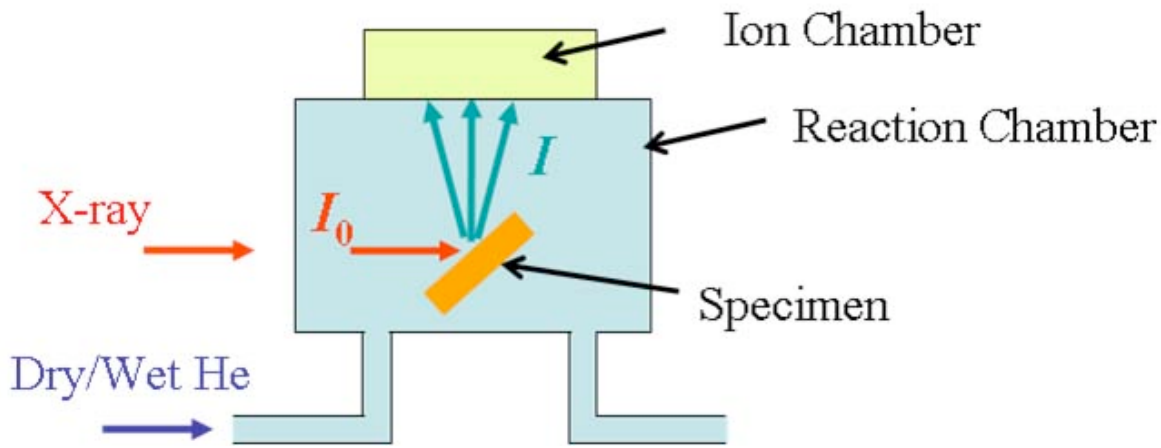
Cl



Na

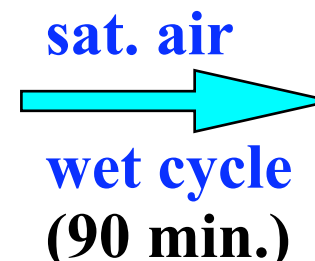
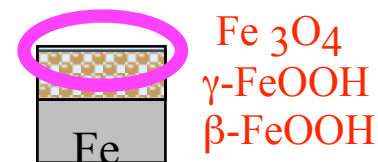
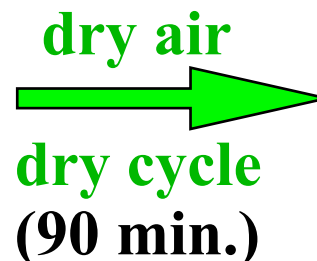
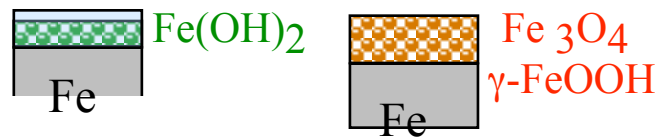
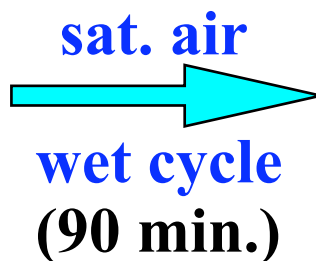
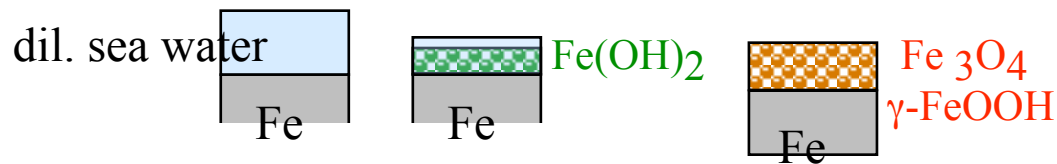
In situ XAFS observation during wet-dry cycles

PF, BL-9A



PF, BL-9C, 11B, 12C

wet-dry cycles



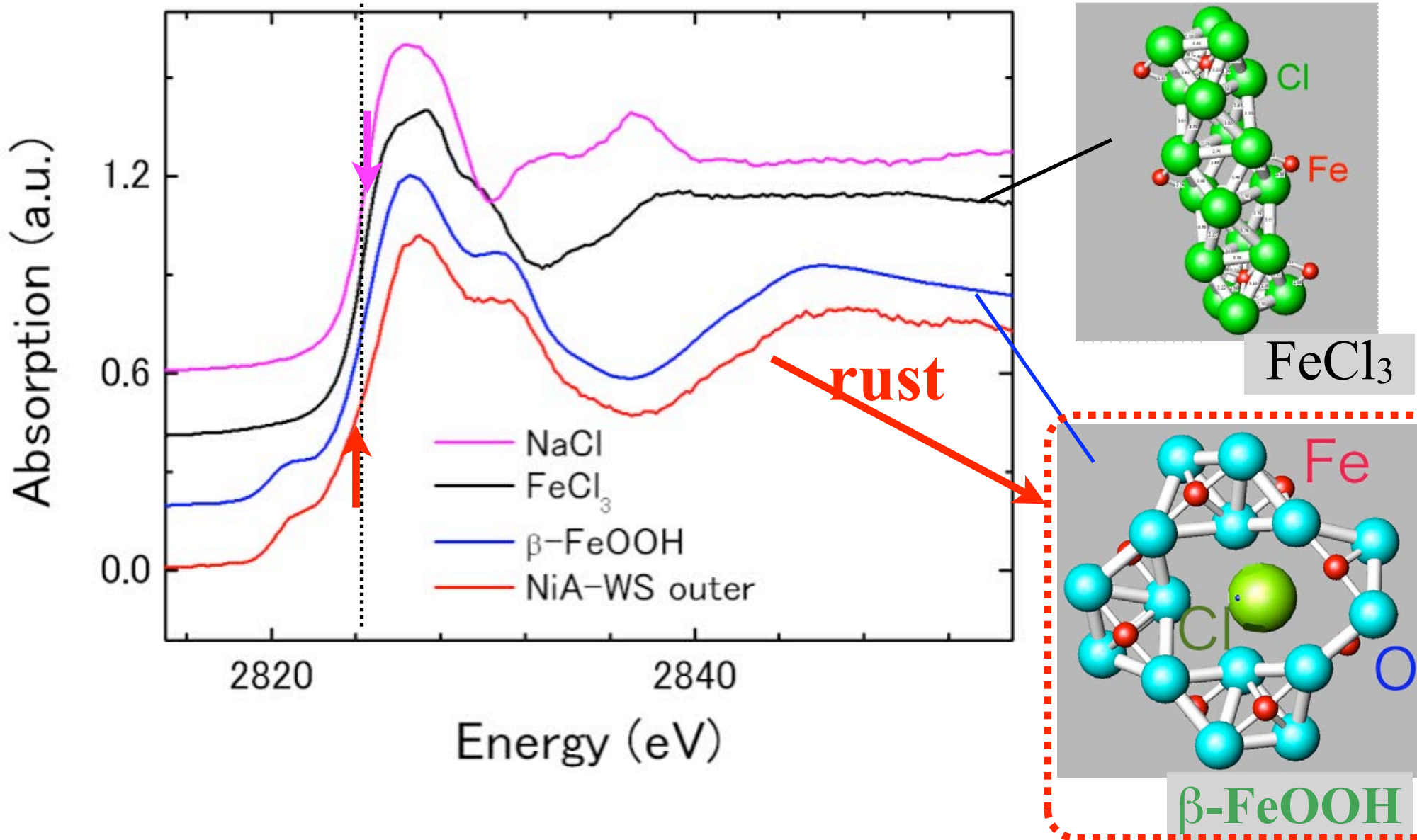
蛍光XAFS

Cl & Ni

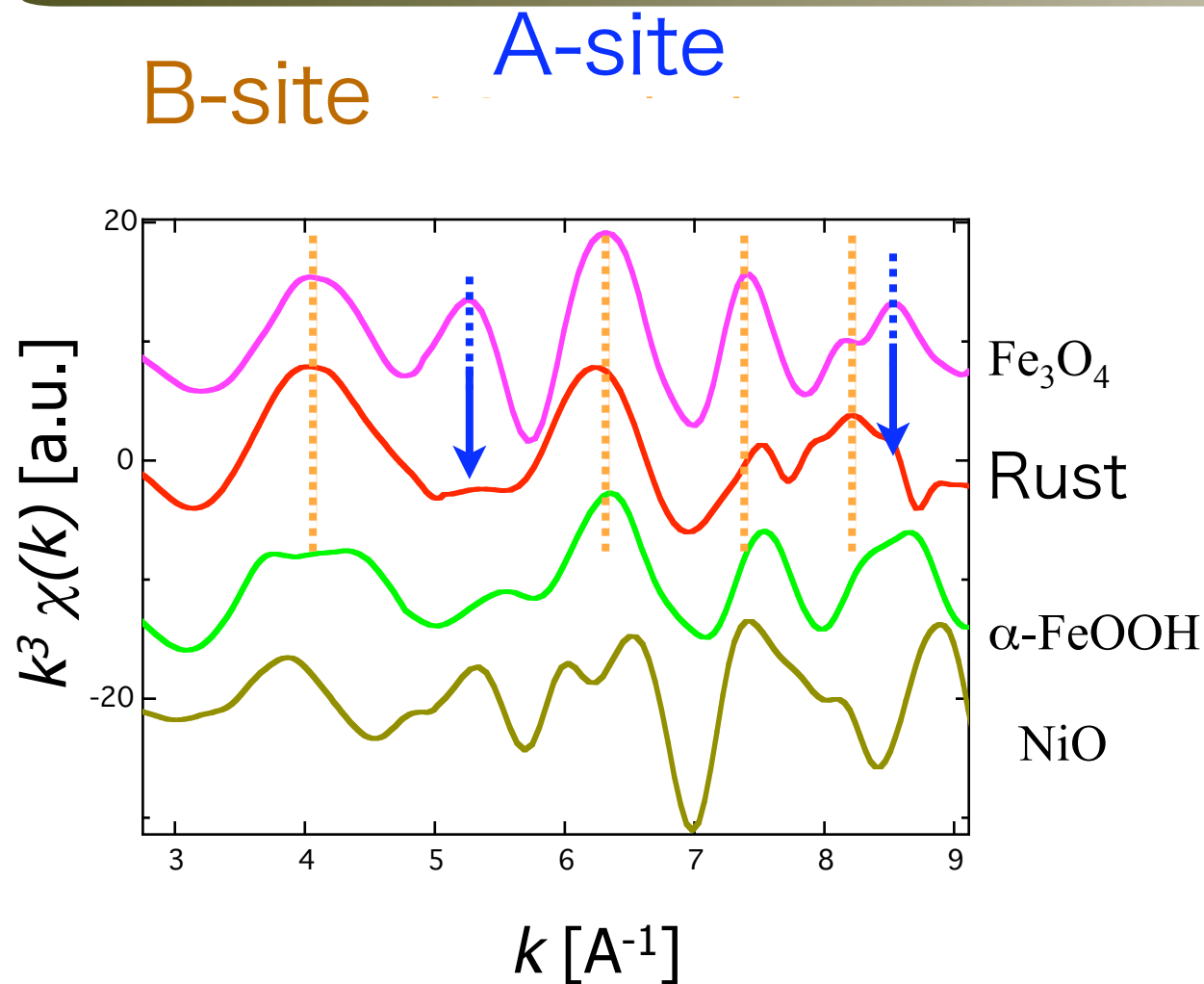
K-edge

XAFS spectra of rust and references (Cl K-edge) (9 y's at a coastal area)

→ *slight but significant difference*



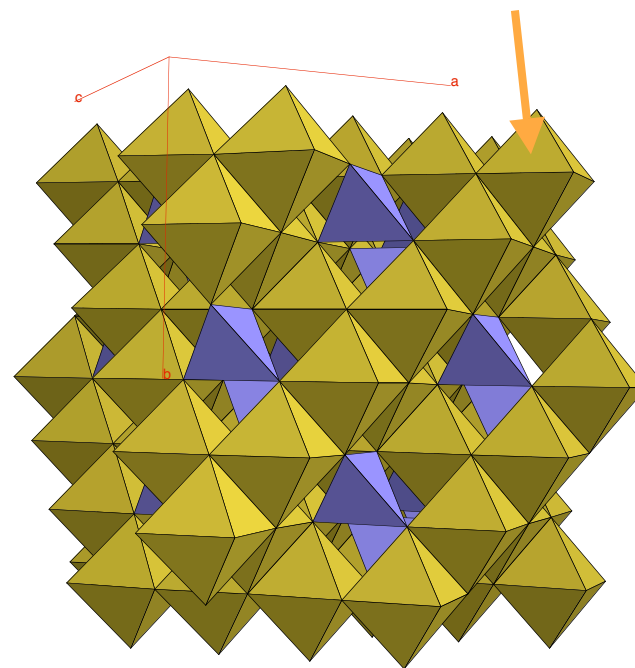
Ni-state in the rust by XAFS (X-ray Absorption Fine Structure)



Inverse Spinel

8a(A-site)
 Fe^{3+}

16d(B-site)
 Fe^{3+} Fe^{2+}
 Ni^{2+}



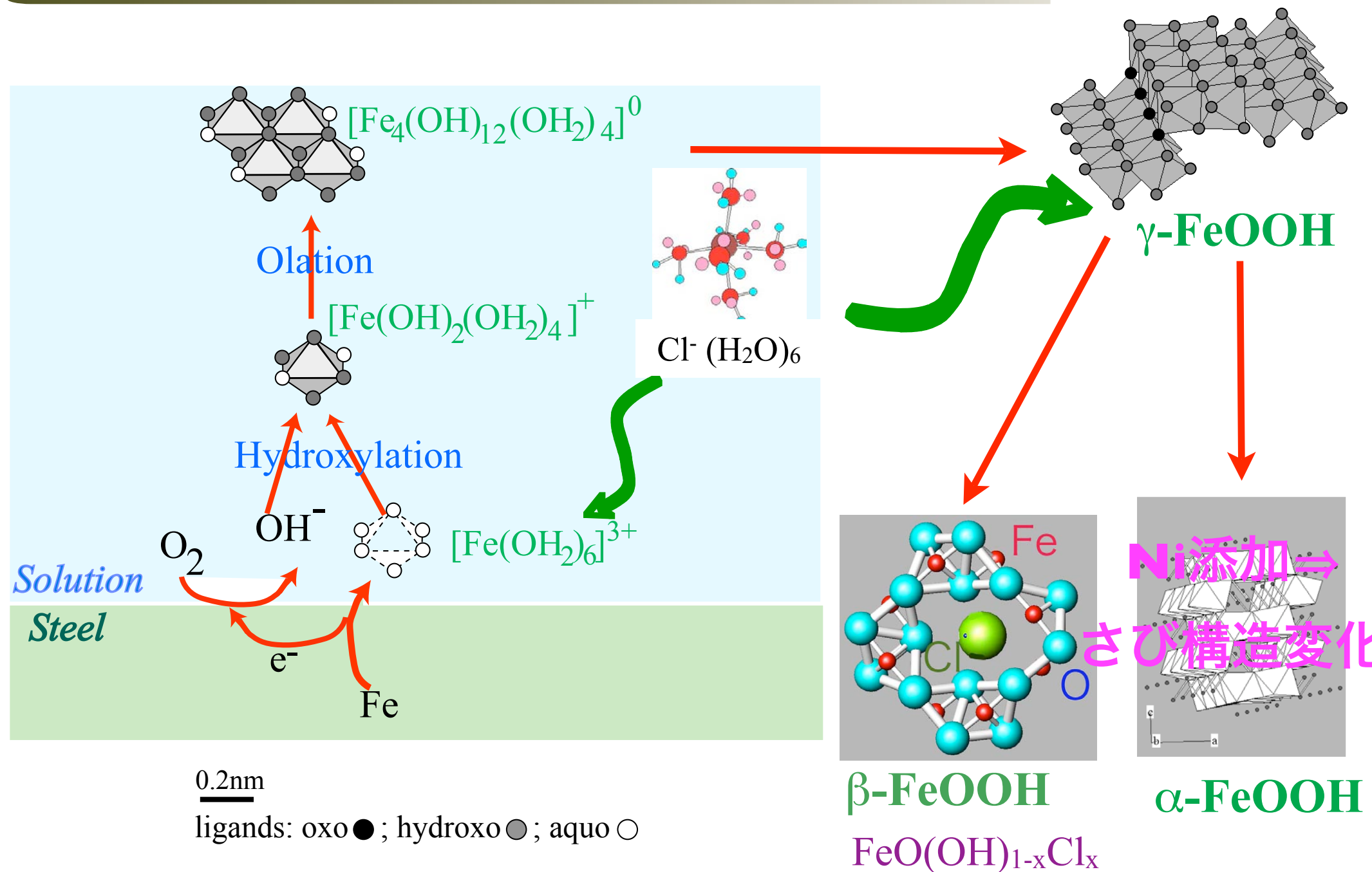
Ni substitute Fe^{2+} in Fe_3O_4

: formation of Fe_2NiO_4

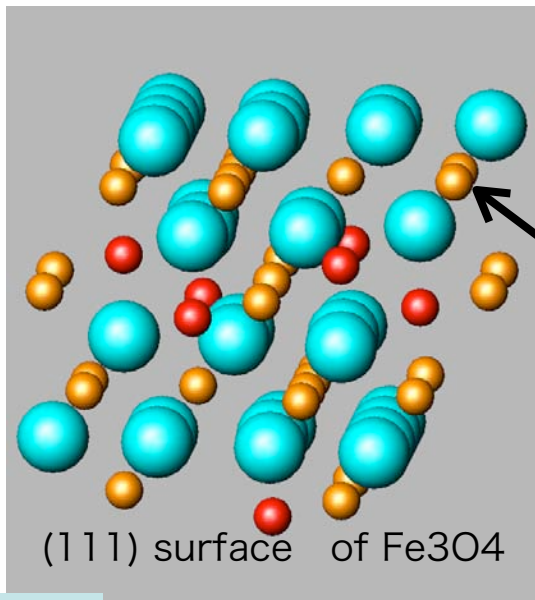
Reactions during wet-dry cycles

by XAFS,

Evolution of “ $Fe(O,OH)_6$ nano-network” 斜入射X線回折,



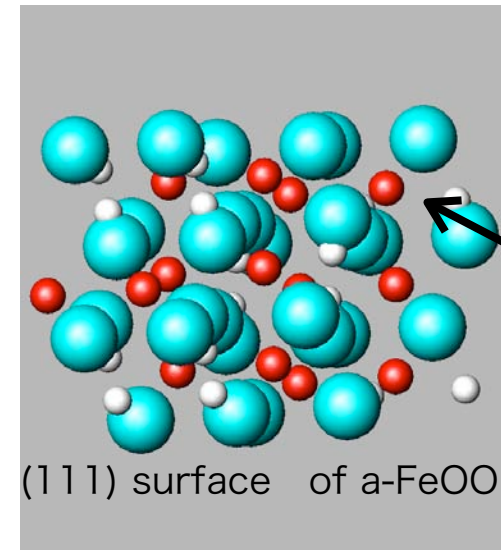
Reaction at Liq./Rust interface



Layer of
 $\text{Ni}^{2+} + \text{Fe}^{3+}$



NiA-WS
(protective rust)



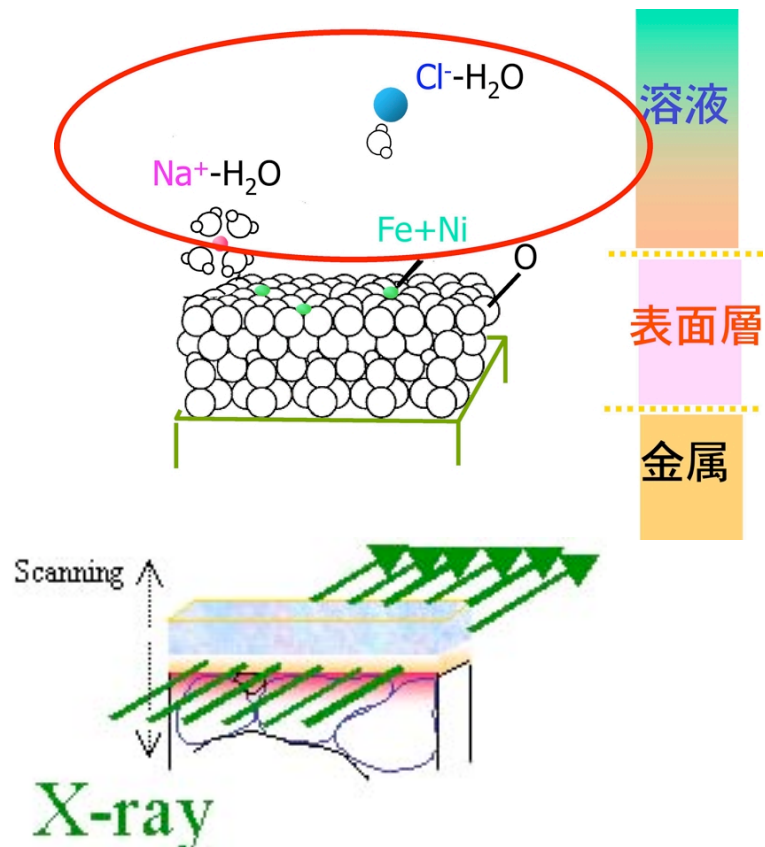
Layer of
 Fe^{3+}



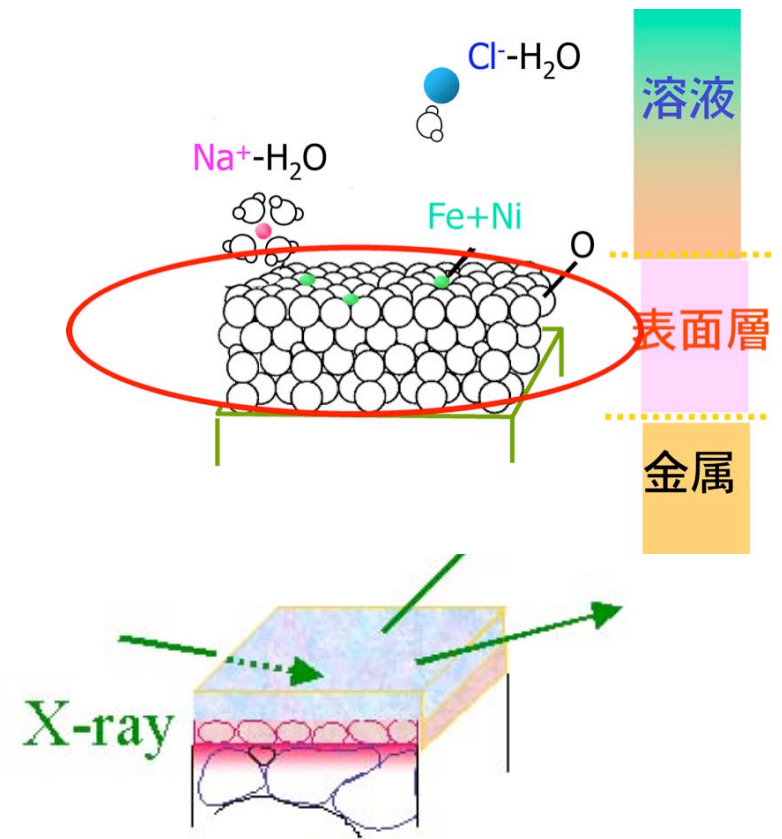
Conventional WS
(no protective rust)

固体/液体界面の in situ 観察

A. 液体中反応

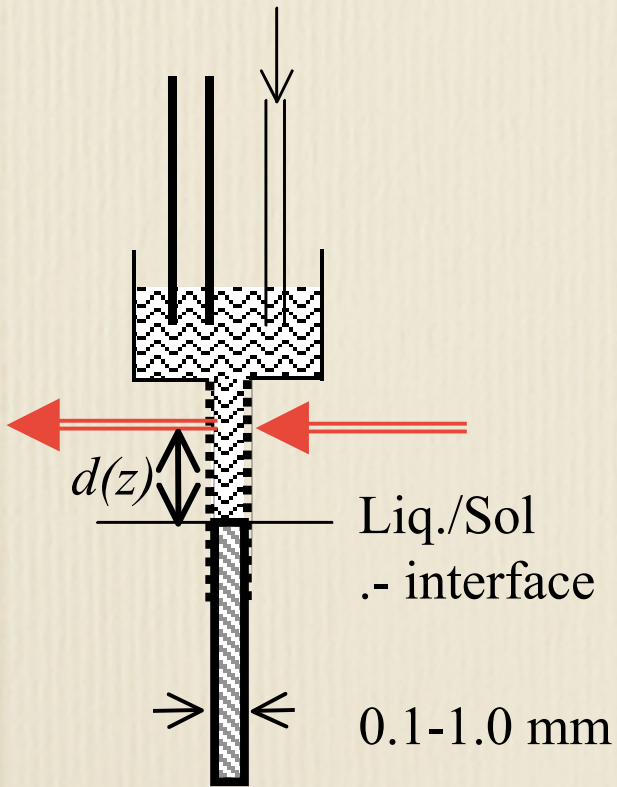


B. 表層への析出反応



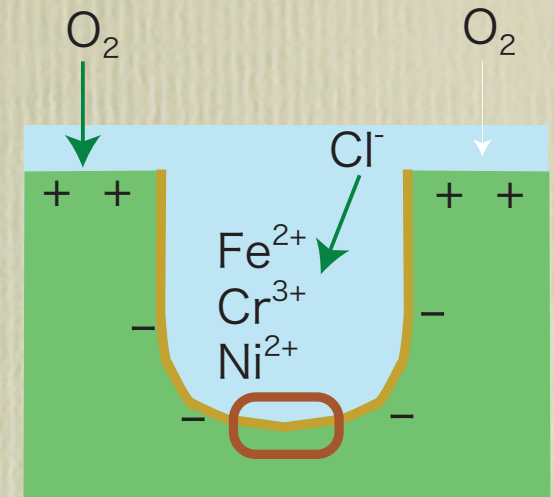
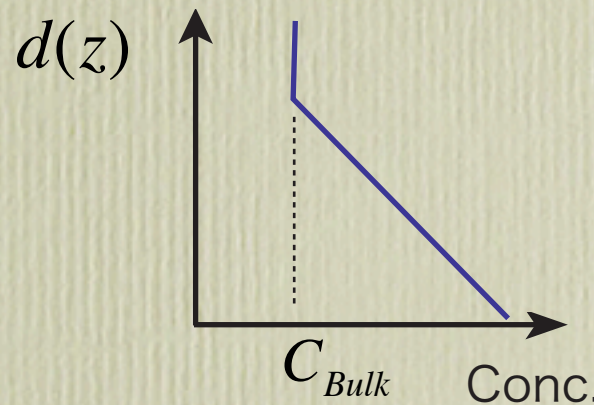
How can we observe the interface ?

Idea for the system



$d(z)$ range \approx mm

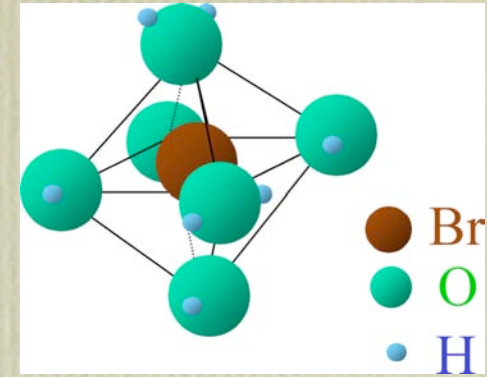
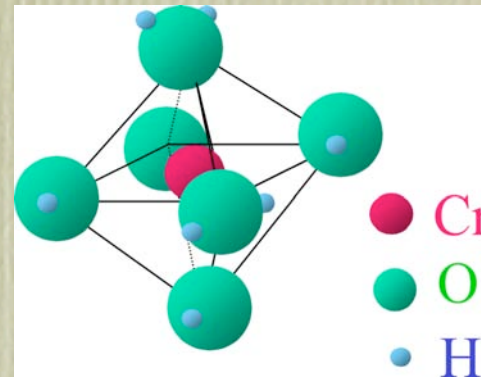
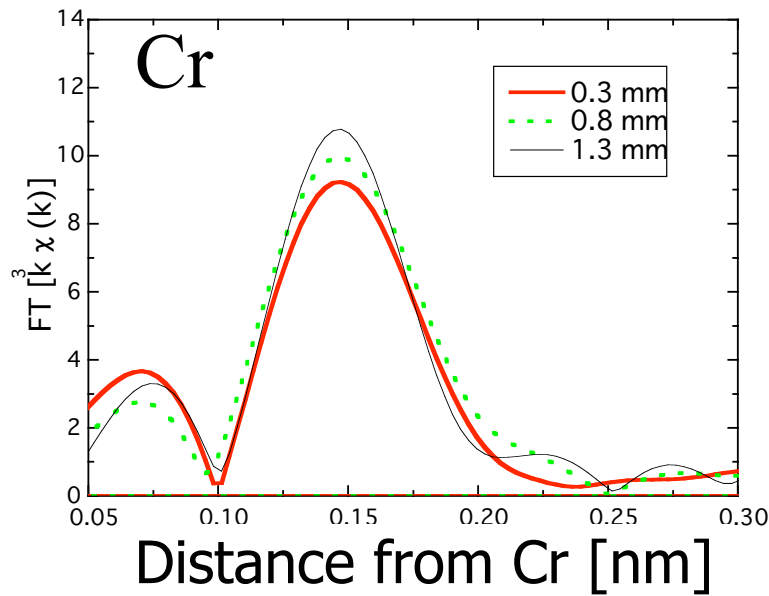
Disrace from
the interface



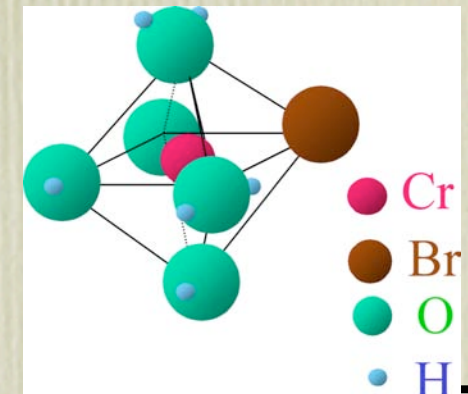
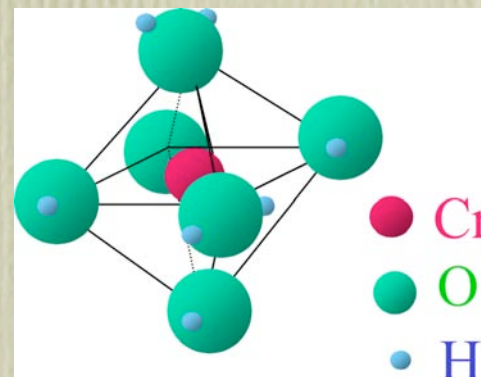
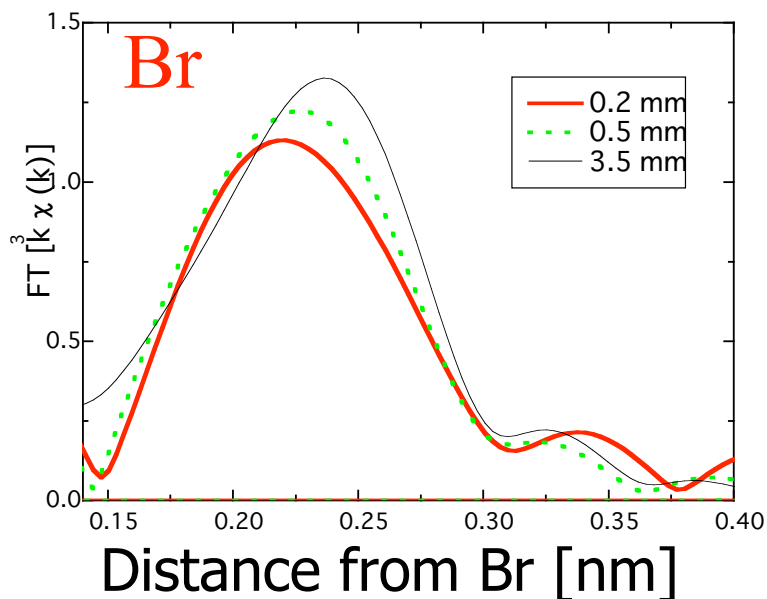
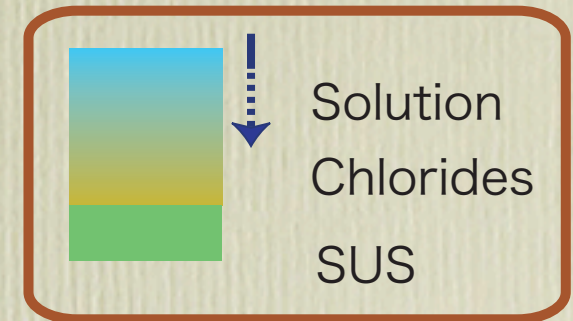
$d(z)$ range $\approx \mu m$

Change of Structure Near Interface

Fe-18Cr-12Ni-2Mo, 1M LiBr, $E=0.8V(Ag/AgCl)$



In the bulk sol.
Near interface

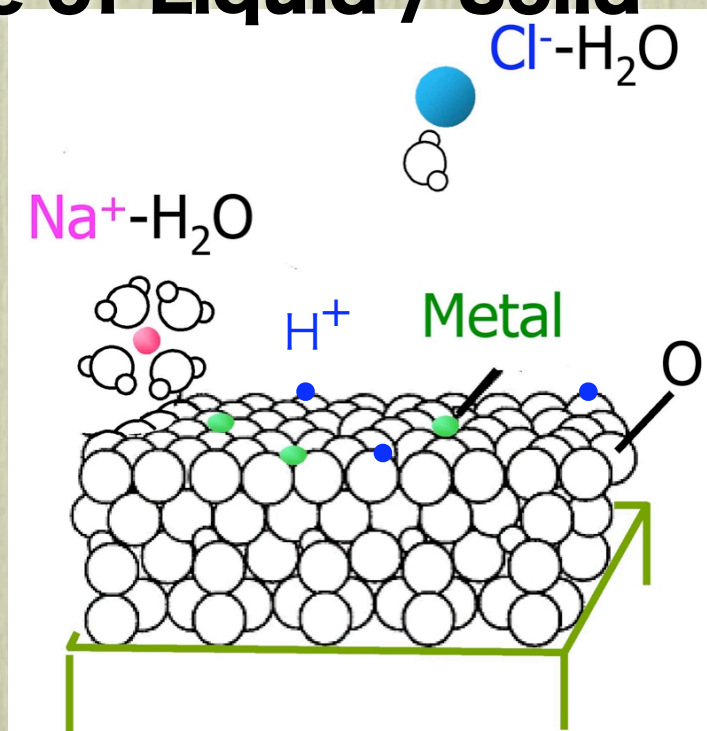


界面反応のその場観察 ← 蛍光-XAFS

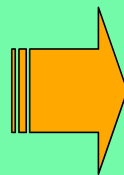
(耐候性鋼の大気腐食)

← 透過-XAFS, 斜入射X線回折,..

Interface of Liquid / Solid



Electro-chemical reactions
(corrosion, batteries,..)
Metal-solution reactions
Catalysis



*Understanding of Mechanism
&
Control of the reactions*