Accelerated Discovery of Advanced RedOx Materials for STWS to Produce Renewable Hydrogen

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Project: PD120
NSF CBET-1433521

Overview

Timeline

- Start: 9-1-2014
- End: 8-31-2017
- 25% completed as of 5/31/2015
- 2 PhD students started 1/1/2015

Budget

- Total Project Funding

  2014-2017: $525,371K NSF

- Funds received in FY15

  $58,000 (to be updated)

Partners

Prof. Alan Weimer (CU Boulder)

Barriers

X. (to be updated)

Relevance

Overall Objectives:

1. Develop a computationally accelerated and experimentally validated materials-by-design approach to discover materials with optimum STWS properties and that can be tailored for materials discovery for other technologies;

2. Use our accelerated materials discovery approach to screen metal oxide materials for STWS and the reactor developed in the DOE effort and provide a rank ordered list of promising redox materials;

3. Address fundamental and broad materials chemistry questions in accomplishing tasks 1 and 2.

Objectives This Period:

1. Develop theoretical models that predict promising STWS thermodynamics and kinetics based on fundamental materials properties (descriptors).
2. Develop a computational materials screening approach based on 1 to identify materials with promising thermodynamic and kinetic properties for STWS.
3. Apply screening approach to binary oxides and validate its predictions.

Approach

Project Technical Approach

- Computational prototyping of hercynite & related materials integrating theory and experimentation
- Using both thermodynamic and kinetic filters in optimization of materials for quasi-isothermal solar water splitting

In Silico Materials Testing

Experimental Materials Validation

Efficient STWS Materials

Thermodynamic Filters

Kinetic Filters
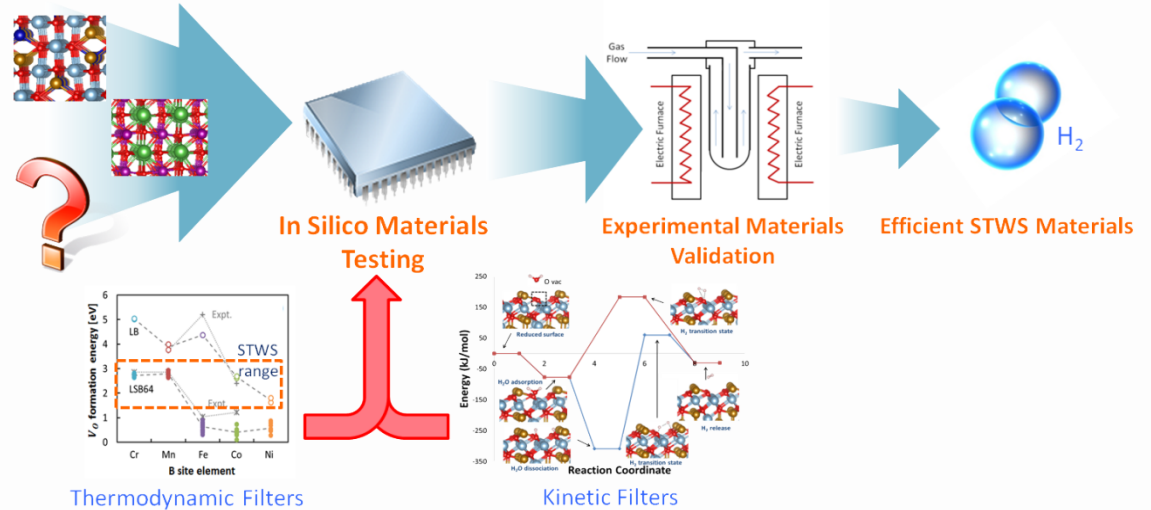
Apply fundamental materials science, chemistry and physics to develop materials design rules and discover promising materials using state-of-the-art electronic structure theory. For this objective, quantum simulations require careful, expert application due to limits of the methods, effects of spin and complexity of detailed mechanisms.
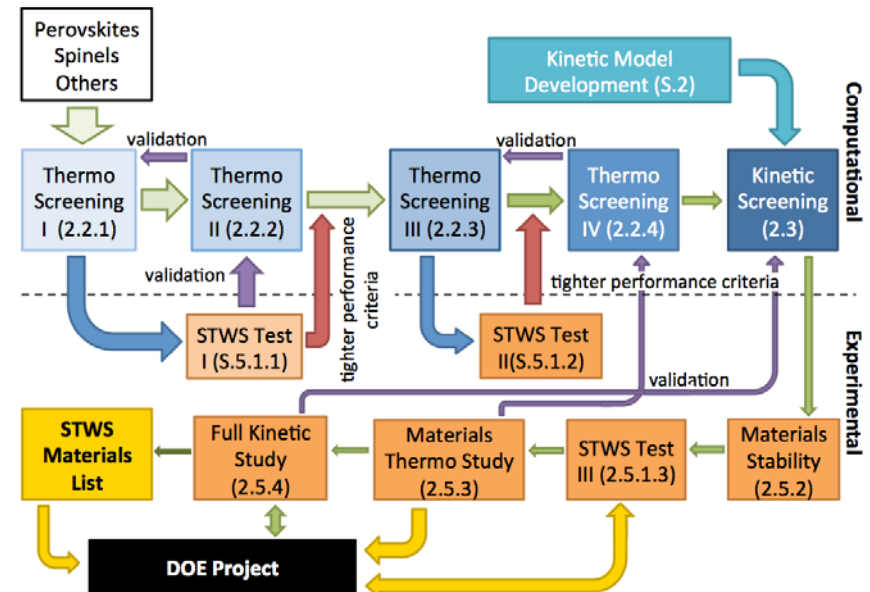
Criteria for Materials Assessment

$\Delta H_{red} < 0$ kJ/mol $\qquad\qquad\qquad \Delta H_{red} > 286$ kJ/mol
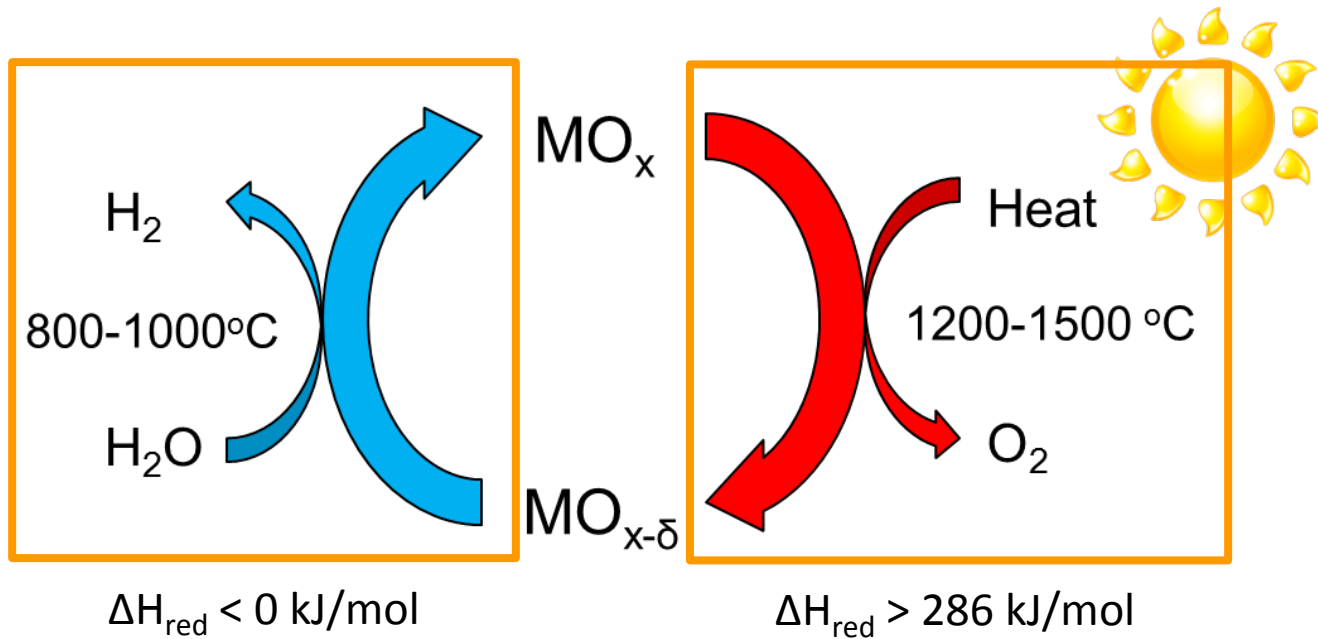
Overall: $H_2O \rightarrow H_2 + 1/2\ O_2$ ($\Delta H_{ws} = 286$ kJ/mol)

Oxidation: $\Delta S < 0$ therefore ΔH must be ≤ 0

Reduction: $\Delta H_{red} + \Delta H_{ox} \geq \Delta H_{ws}$ therefore ΔH_{red} must be ≥ 286 kJ/mol

If $\Delta H_{red} < 286$ kJ/mol, the material is unlikely to drive water splitting, and can be eliminated from screen.
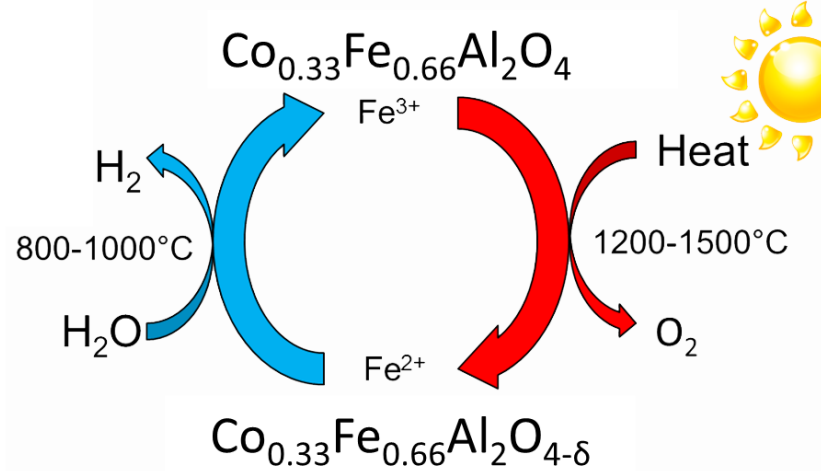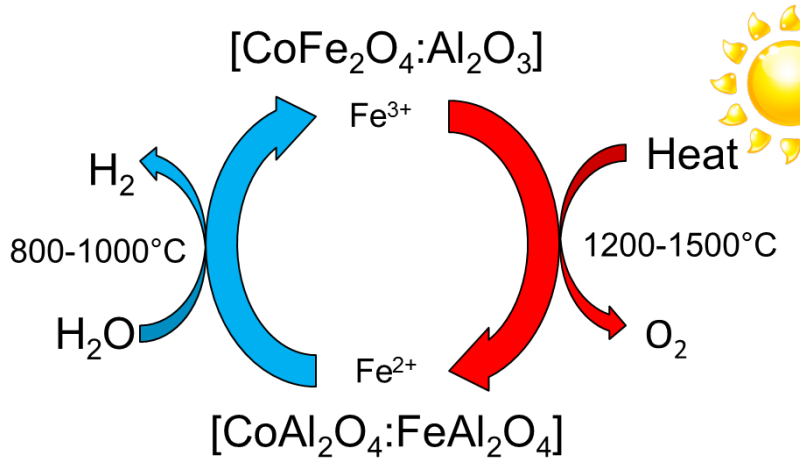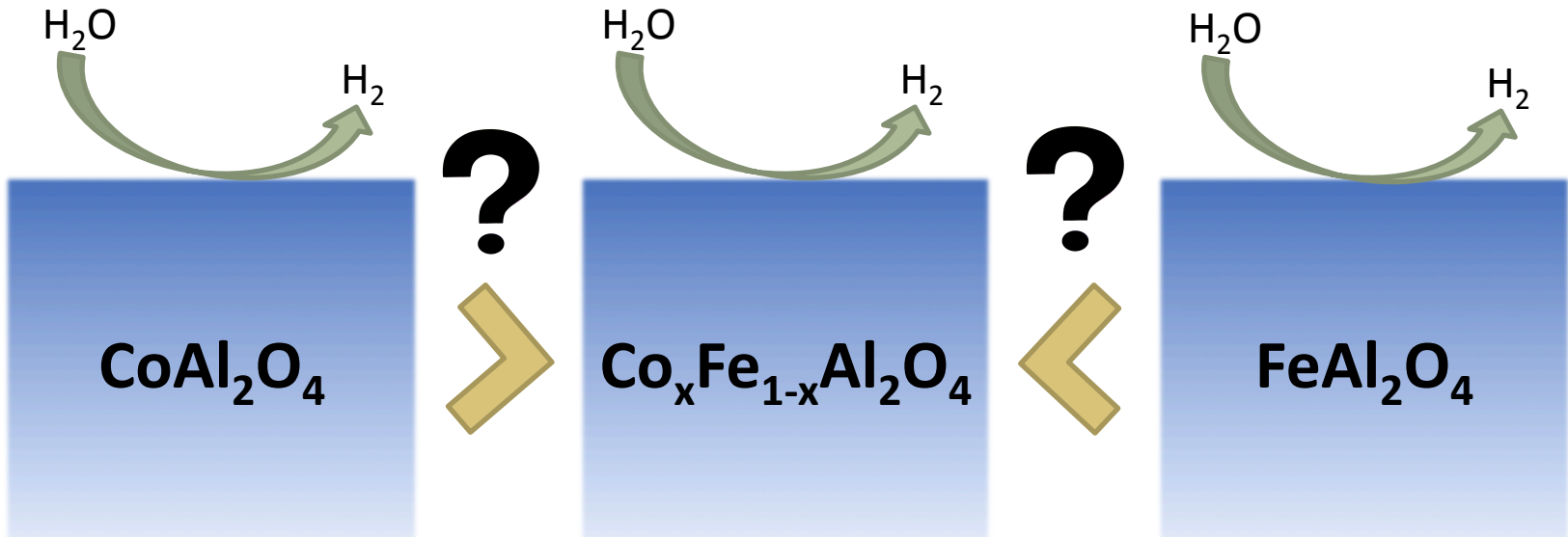
A Case Study: Metal Aluminates

Determine doped hercynite cycle mechanism

Stoichiometric Mechanism

$[CoFe_2O_4:Al_2O_3]$
Fe^{3+}
Heat
H_2
800-1000°C
1200-1500°C
H_2O
Fe^{2+}
O_2
$[CoAl_2O_4:FeAl_2O_4]$

O-vacancy Formation mechanism

$Co_{0.33}Fe_{0.66}Al_2O_4$
Fe^{3+}
Heat
H_2
800-1000°C
1200-1500°C
H_2O
Fe^{2+}
O_2
$Co_{0.33}Fe_{0.66}Al_2O_{4-\delta}$

Determine predictive ability with novel aluminate STWS materials

H_2O → H_2

$CoAl_2O_4$? **$Co_xFe_{1-x}Al_2O_4$** ? **$FeAl_2O_4$**
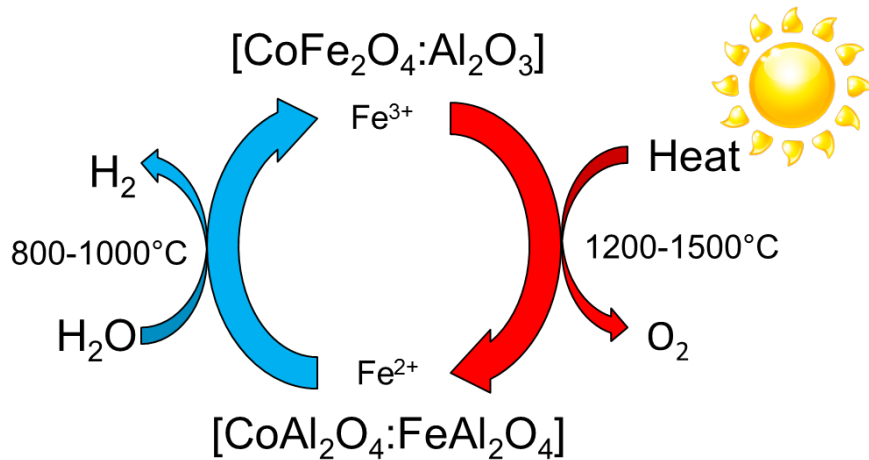
Hercynite Stoichiometric Rxn Has Insufficient Reduction Power, but O-vacancy Rxn Can Reduce Water
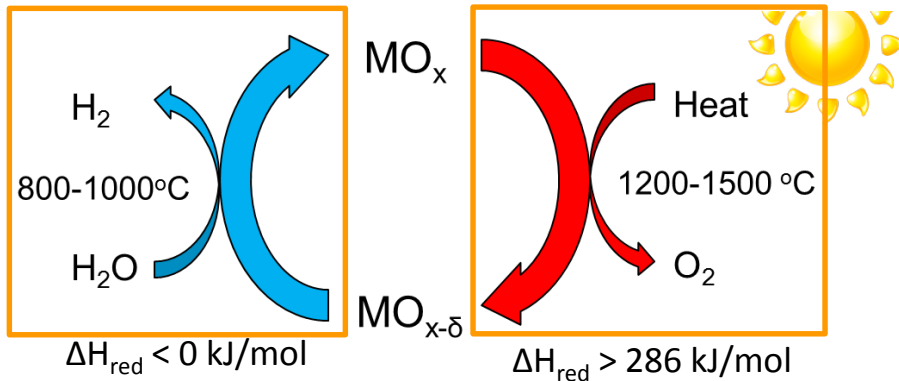
$\Delta H_{red} < 0$ kJ/mol

$\Delta H_{red} > 286$ kJ/mol

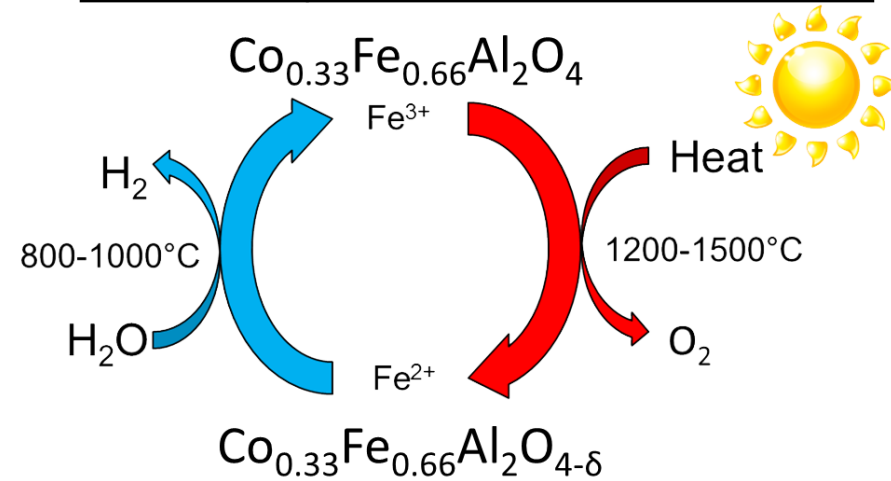If ΔH_{red} <286 kJ/mol, the material is unlikely to drive water splitting, and can be eliminated from screen.

Stoichiometric Mechanism

ΔH_{red} = 150 kJ/mol
ΔH_{ox} = 138 kJ/mol

Not thermodynamically viable

O-vacancy Formation Mechanism

ΔH_{red} = 384 to 621 kJ/mol
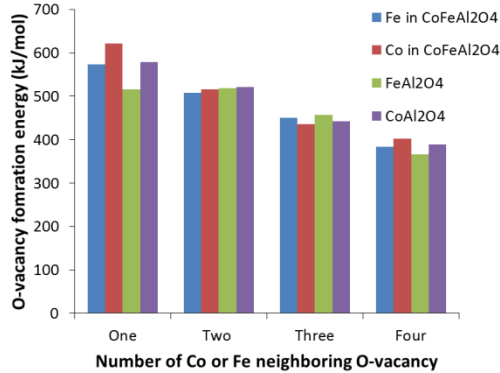ΔH_{ox} = -102 to -335 kJ/mol
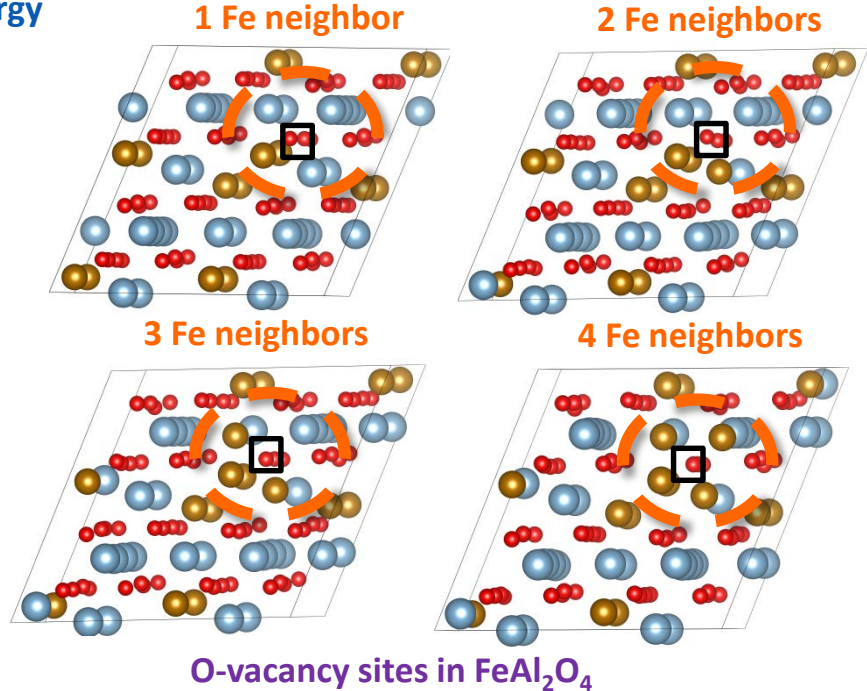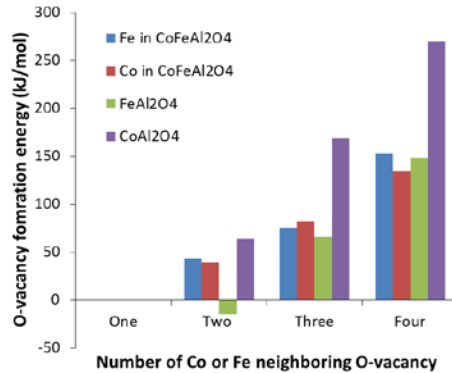
Thermodynamically viable

Predicted H$_2$ Generation of MAl$_2$O$_4$
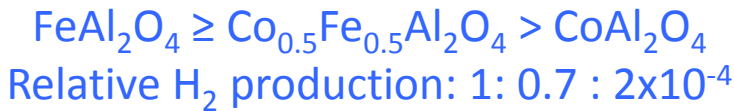
Predicted O-vacancy relative H$_2$ production capacity:

O-vacancy formation energy

O-vacancy site formation energy

1 Fe neighbor

2 Fe neighbors

3 Fe neighbors

4 Fe neighbors


O-vacancy sites in FeAl$_2$O$_4$

Assuming full reduction of all reducible sites at 1500 C and using the relative availability of the sites, we predict the relative H$_2$ generation capacity of the aluminates operating via O-vacancy mechanism to be:

$$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$$

Relative H$_2$ production: 1: 0.7 : 2x10^{-4}

Predicted Stoichiometric Reaction Relative H$_2$ Production Capacity:
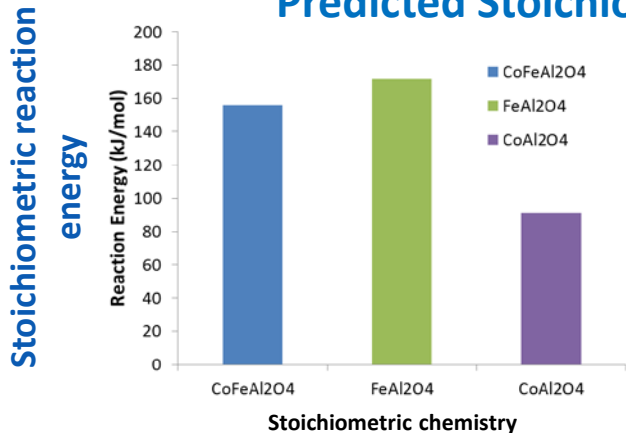
If we assume that the STWS criterion (ΔH > 286 kJ/mol) does not hold, and therefore any material can split water, we predict a relative H$_2$ generation capacity for the aluminates operating via a stoichiometric reaction mechanism to be:

$$CoAl_2O_4 > Co_{0.5}Fe_{0.5}Al_2O_4 > FeAl_2O_4$$

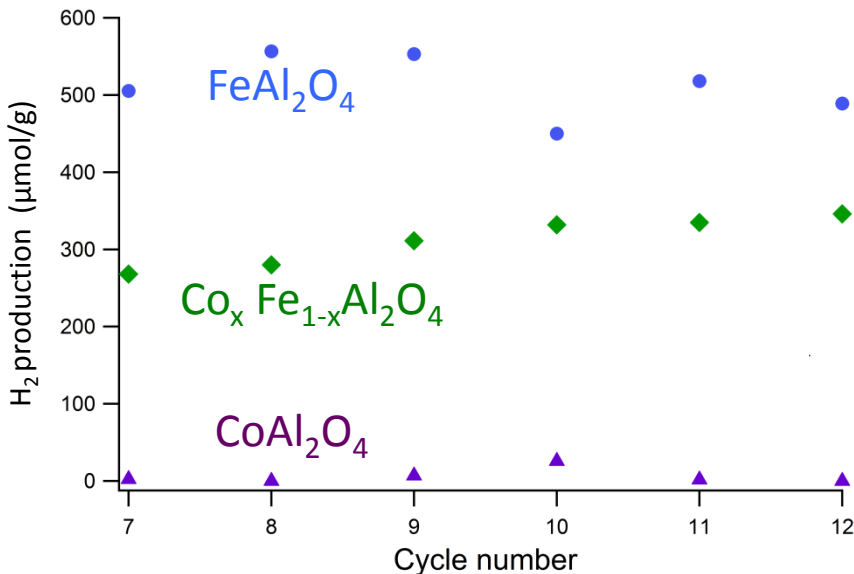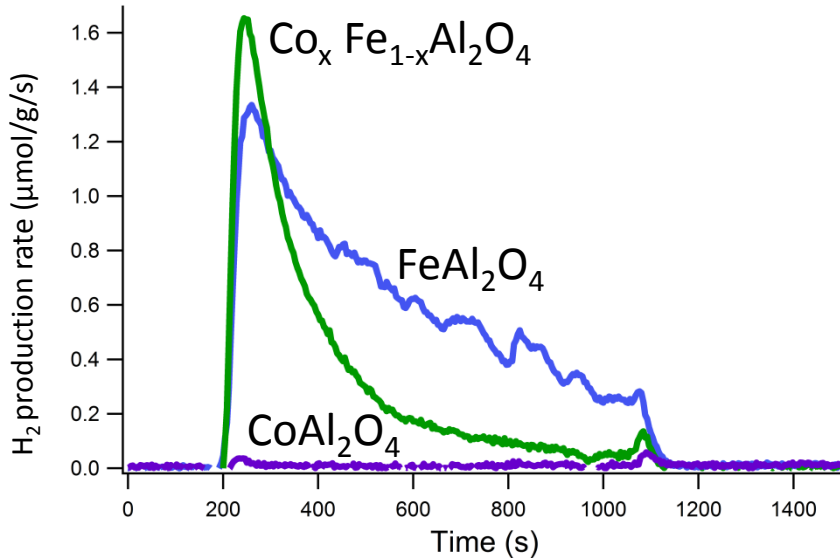Relative H$_2$ production: 1: 0.13: 0.004
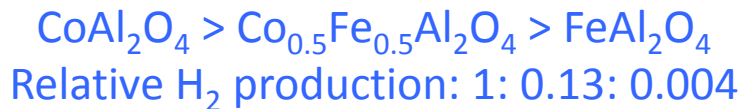
Experimental Validation of Predicted STWS Behavior and Mechanism

1500/1350°C Near-isothermal Water Splitting

Relative H$_2$ production capacity:

FeAl$_2$O$_4$ ≥ Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ > CoAl$_2$O$_4$
Relative H$_2$ production: 1: 0.6 : 0

Predicted O-vacancy H$_2$ production capacity:

FeAl$_2$O$_4$ ≥ Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ > CoAl$_2$O$_4$
Relative H$_2$ production: 1: 0.7 : 2X10^{-4}

Predicted stoichiometric H$_2$ production capacity:

CoAl$_2$O$_4$ > Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ > FeAl$_2$O$_4$
Relative H$_2$ production: 1: 0.13: 0.004

Experimental H$_2$ generation matches our predicted O-vacancy mechanism H$_2$ generation values. Therefore, the aluminates likely operate via an O-vacancy mechanism and the thermodynamic criteria developed for assessing STWS materials and mechanism is valid. Additionally, a new STWS material FeAl$_2$O$_4$ has been shown to be active.

Simple Descriptor Model Predicts ΔH_f(O vac)

- Vacancy formation energy predicted using descriptor model.
- Errors in predicting band gap by DFT methods are systematic (as determined by GW_0) and scaled in model.
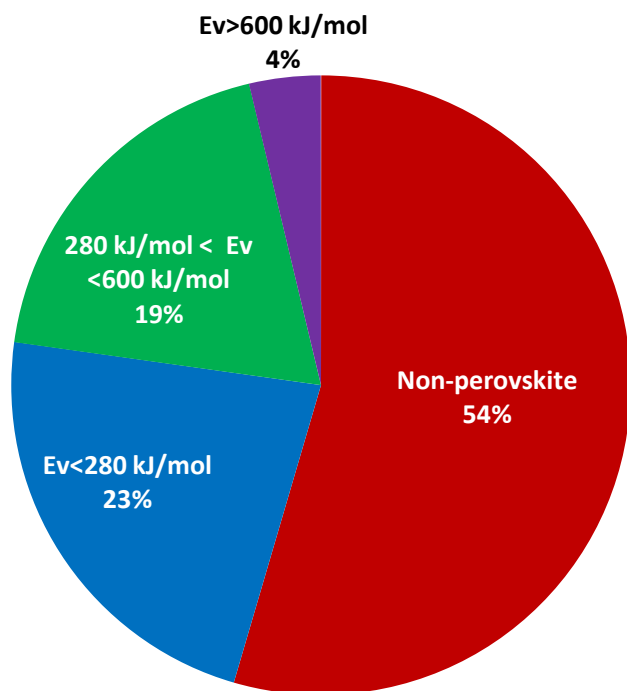- Descriptor model applies to a broad range of
- metal oxides.

a GW E_g, MAE = 0.19 eV

perovskite, ABO_3

corundum, M_2O_3

rutile, MO_2

antifluorite, M_2O

rock salt, MO

spinel, AB_2O_4

$|\Delta H_f| + 0.60\left(E_{O2p} + \frac{1}{2}E_g^{GW}\right) + 2.6\langle\Delta\chi\rangle$

b DFT+U E_g, MAE = 0.21 eV

MAE = 0.39 eV

calculated E_V [eV]

predicted E_V [eV]

$HgTiO_3$

$|\Delta H_f| + 0.60\left(E_{O2p} + \frac{1.5}{2}E_g^{DFT+U}\right) + 2.6\langle\Delta\chi\rangle$

c

½ O_2

2e$^-$

E_V

M + O_2

MO_x

ΔH_f

E

2e$^-$

$\left(E_{O2p} + \frac{1}{2}E_g\right)$

δ^- δ^+

$\langle\Delta\chi\rangle$

antifluorite, M_2O
corundum, M_2O_3
rock salt, MO
rutile, MO_2
perovskite, ABO_3
spinel, AB_2O_4

GW

DFT+U

E_g^{calc} [eV]

E_g^{expt} [eV]

a Main group metal oxides

E_g^{DFT+U} [eV]

Magnetic transition metal oxides

Predicted E_V [eV]

$|\Delta H_f|$ [eV/atom]

Deml, Holder, O'Hayre, Musgrave and Stevanovic, Submitted 2015.

Binary Novel Perovskite Screening

Binary Perovskite Screening Results

Pie chart:
- Non-perovskite 54%
- Ev<280 kJ/mol 23%
- 280 kJ/mol < Ev <600 kJ/mol 19%
- Ev>600 kJ/mol 4%

1045 materials screened
As of 4/10/2015

Elements Considered for Use in Redox Materials

- Calculated predicted E_{O-vac} for 1045 possible binary perovskites using method developed in our group by Deml *et al.*

- 570 materials spontaneously phase transitioned out of the perovskite structure

- 237 materials have reduction enthalpies too low to drive STWS ($E_{O-vac} < 280$ kJ/mol)

- 199 materials are potentially capable of driving STWS*
    (280 kJ/mol $<E_{O-vac} < 600$ kJ/mol)

- 39 materials have reduction enthalpies too high for practical use as STWS materials ($E_{O-vac} > 600$ kJ/mol)

Materials were not analyzed for thermal stability or fabrication practicality

Spin Considerations

Relative energies in kJ/mol of the spin states for inverse and normal aluminate and ferrite spinels.

| Configuration		Co_3O_4	$CoAl_2O_4$	$CoFe_2O_4$	Fe_3O_4	$FeAl_2O_4$
Inverse[a]	All up[c]	135	**0.0**	71	52	**0.0**
	Alternating layers[d]	57	0.7	19	**0.0**	0.3
	Tetrahedral and octahedral[e]	83	N/A	**0.0**	8	N/A
	Other	**0.0**[f]	N/A	N/A	N/A	N/A
Normal[b]	All up[c]	N/A	19	34	N/A	**0**
	Alternating layers[d]		**0**	**0**		54
Inversion energy[g]			85	-14		33
Inversion parameter (x) at 1200 °C			0.02	0.85		0.23

[A,b]Energy differences in kJ/mol
[c]All electrons for Co and Fe atoms initially set to spin up
[d]Electrons in every other layer of Co and/or Fe atoms initially set to alternate spin up & spin down.
[e]Electrons of all tetrahedral atoms initially set to spin up. Electrons of all octahedral atoms initially set to spin down.
[f]Electrons of tetrahedral Co atoms initially set to high spin states (μ=3) and octahedral Co atoms initially set to low spin states (μ=0.1).
[g]The energy difference, in kJ/mol, between the lowest energy inverse structure and normal structure. A positive number indicates that the normal structure is energetically preferred, while a negative number indicates that the inverse structure is preferred.
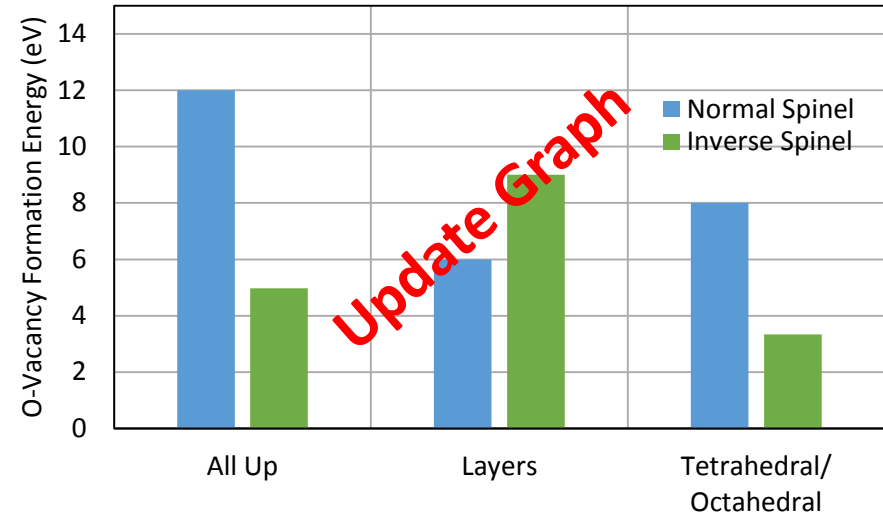
Considerations:
- Lowest energy spin state may vary between normal and inverse structure
- Lowest energy spin states may vary between host structure and O-vacancy defect structure
- Finding spin states currently requires manually testing of multiple configurations followed by multiple runs near minimum for verification

Possible Opportunities:
- Develop script for 'smart' testing of spin states
- Incorporate spin effects into O-vacancy model

Both spin and inversion can significantly affect the predicted STWS behavior of candidate materials - requires added complexity in O-vacancy formation energy models

# Approach to Kinetic Determination

Stable Intermediates Along Reaction Path for Water Splitting on Hercynite
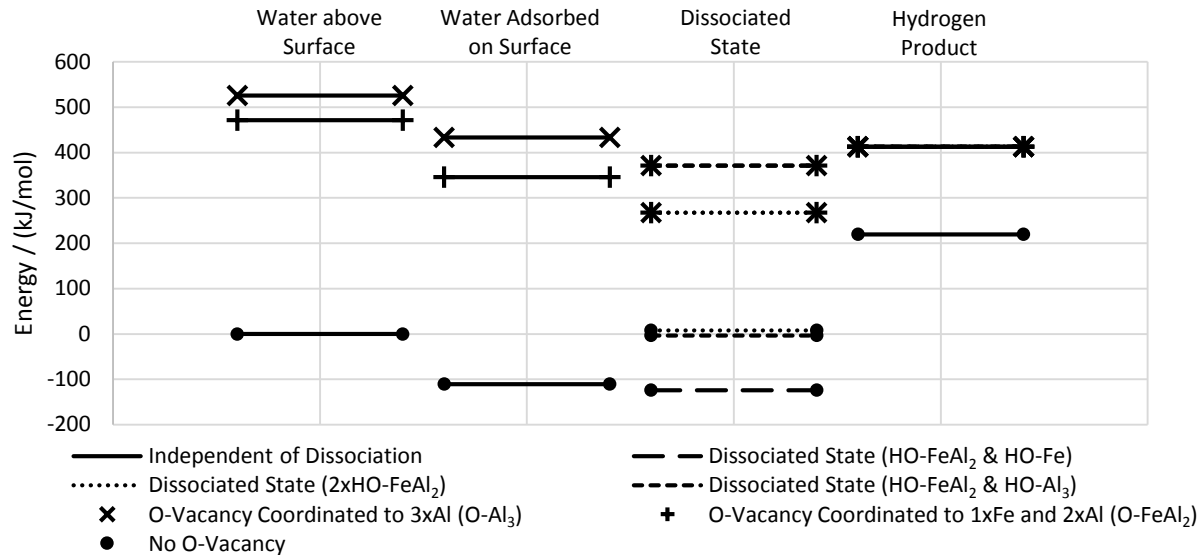
Started analysis with stable adsorbed intermediates for water splitting on hercynite with and without oxygen vacancies.

Hydrogen formation appears unfavorable without the oxygen vacancies. The activation barriers along this pathway will not be calculated.
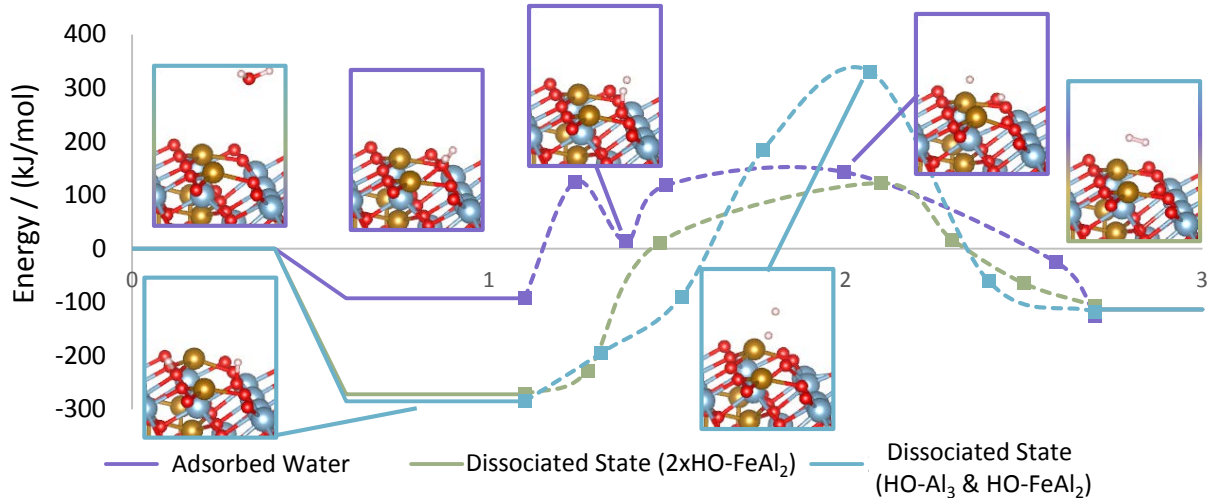
On ceria, the formation of hydrogen is the rate limiting process in the water splitting reaction.[*] We expect that it will be the most important activation barrier for other materials as well.
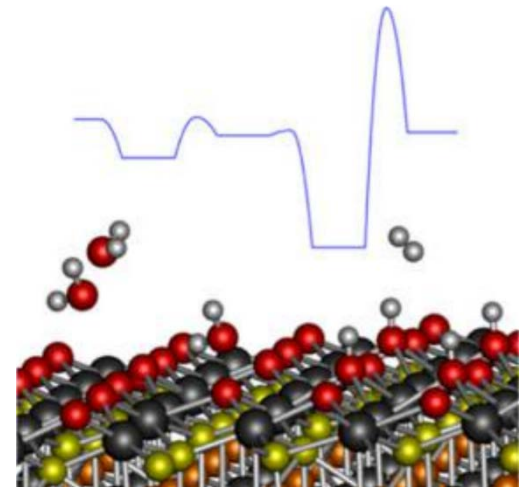
[*]Hansen, H. A., & Wolverton, C. (2014). Kinetics and Thermodynamics of H2O Dissociation on Reduced CeO2(111). *The Journal of Physical Chemistry C, 118*(47), 27402-27414. doi: 10.1021/jp508666c

# Preliminary Kinetics Results

O-Vacancy Coordinated to 3xAl (O-Al$_3$)

Legend: Adsorbed Water — Dissociated State (2xHO-FeAl$_2$) — Dissociated State (HO-Al$_3$ & HO-FeAl$_2$)

O-Vacancy Coordinated to 1xFe and 2xAl (O-FeAl$_2$)

Legend: Adsorbed Water — Dissociated State (2xHO-FeAl$_2$) — Dissociated State (HO-Al$_3$ & HO-FeAl$_2$)

NEB method is being used to identify the transition state of the hydrogen evolution reaction on hercynite (in progress)
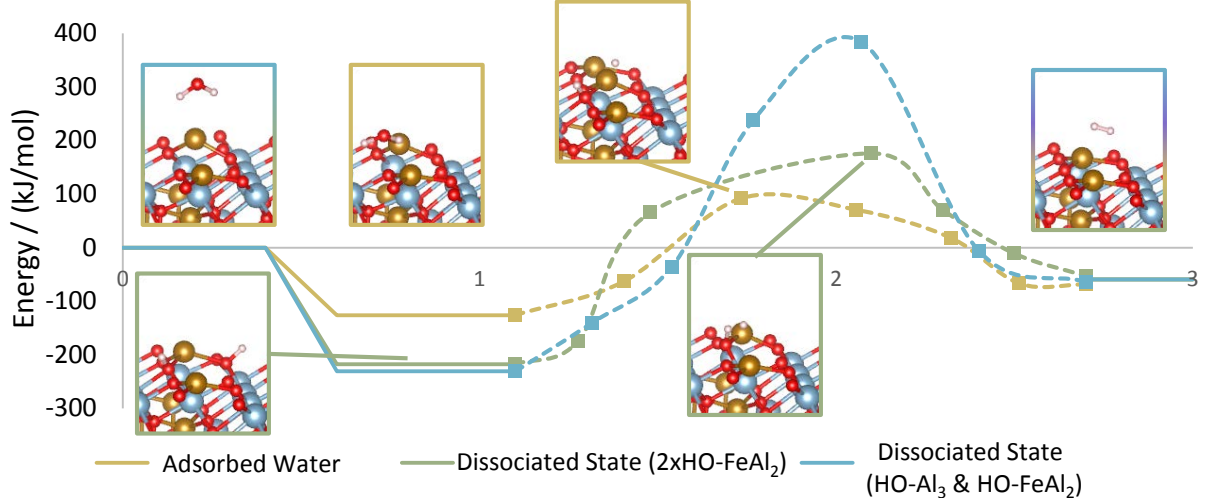
Iron hydrogen interactions appear to stabilize points around the transition state

Transition State (in progress)

Fe-H Atom Distance / Å vs Normalized Reaction Coordinate
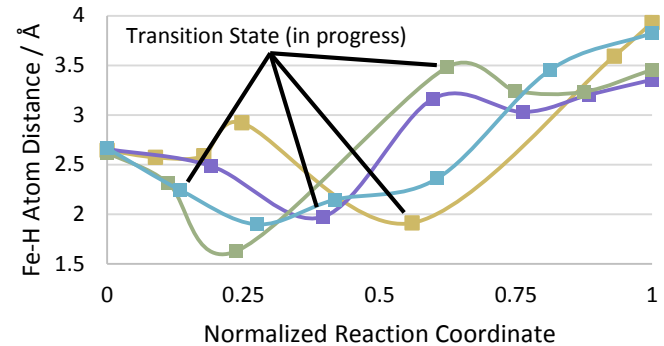
Collaborators

Prof. Alan Weimer (Univ. of Colorado Boulder)

Prof. Ryan O'Hayre (Colorado School of Mines)

Dr. Ann Deml (NREL)

Dr. Aaron Holder (NREL)

Dr. Vladan Stevanovic (NREL)

Technology Transfer Activities

None to date

Future Work

1. Determine whether our approach for predicting the H_2 production capacities extends to a broader set of metal oxides.

2. Applied our STWS approach for predicting water splitting abilities to additional binary perovskites and then to ternary perovskites and other metal oxides.

3. Extend our descriptor model of oxygen vacancy formation energy to systems with various spin and oxygen vacancy configurations, including "smart" scripts for automated searches.

4. Continue to develop a model to predict H_2 formation kinetics (which are rate-limiting) based on fundamental materials descriptors and validate it with direct transition state calculations and kinetics experiments.

5. Develop automated processes for analyzing the materials data calculated to determine correlations between STWS redox abilities and fundamental materials properties.

Summary

1. Identified a simple criteria and approach for assessing the redox capabilities of metal oxides.

2. Developed and experimentally validated an approach to predict the H_2 production capacities and redox mechanisms in metal oxides. Extending approach to other systems.

3. Applied our previously developed model to predict the water splitting abilities of over 1000 binary perovskites (as of 4/10/2015) and identified ~200 materials with redox thermodynamics capable of splitting water.

4. Extended descriptor model of oxygen vacancy formation energy. Model applies well to systems with limited numbers of low energy spin configurations.

5. Calculated Developing automated approaches to examine the effects of local atomic and spin arrangements on oxygen vacancy formation energy and redox thermodynamics.

6. Developing a model to predict H_2 formation kinetics (which are rate-limiting) based on fundamental materials descriptors.

Acknowledgements

Back-up slides

Spinel structure

Normal

Inverse

FeAl$_2$O$_4$

CoFe$_2$O$_4$

Tetrahedral

Octahedral

Tetrahedral

Tetrahedral

Octahedral

Octahedral

Tetrahedral

Tetrahedral

Octahedral

Tetrahedral

Tetrahedral

Octahedral
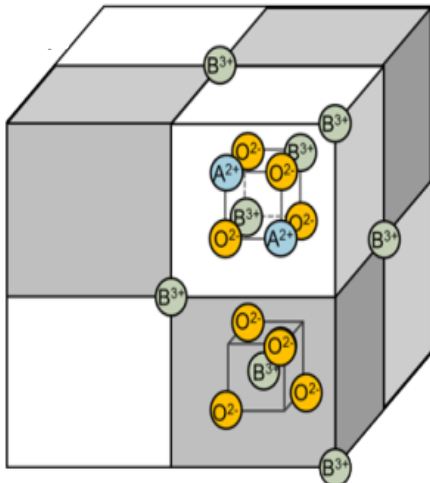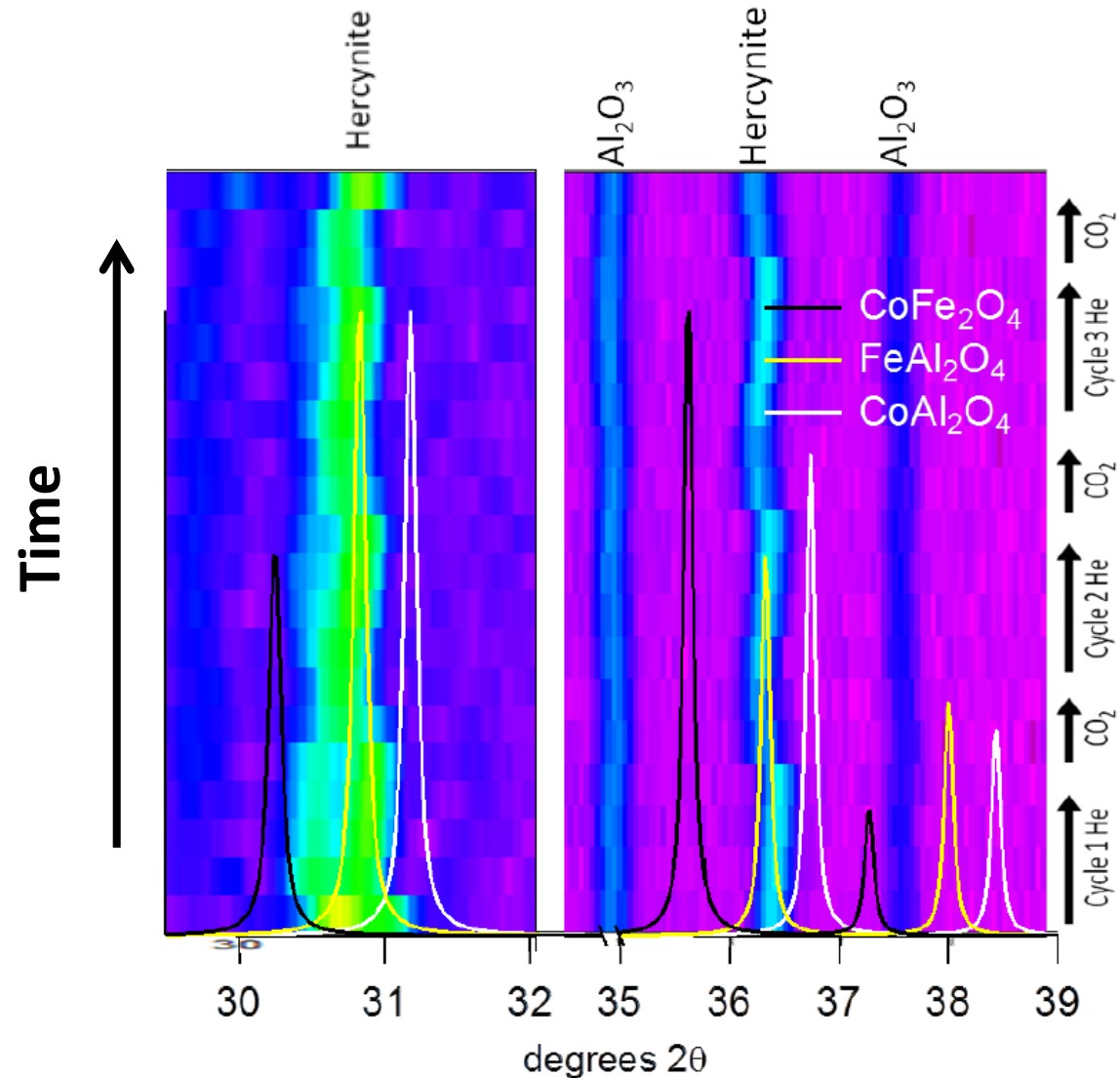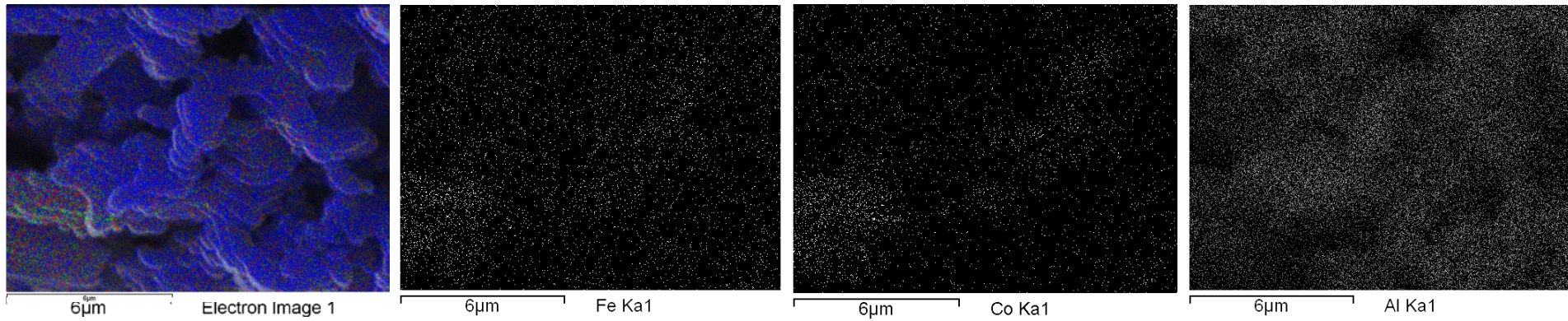
Octahedral
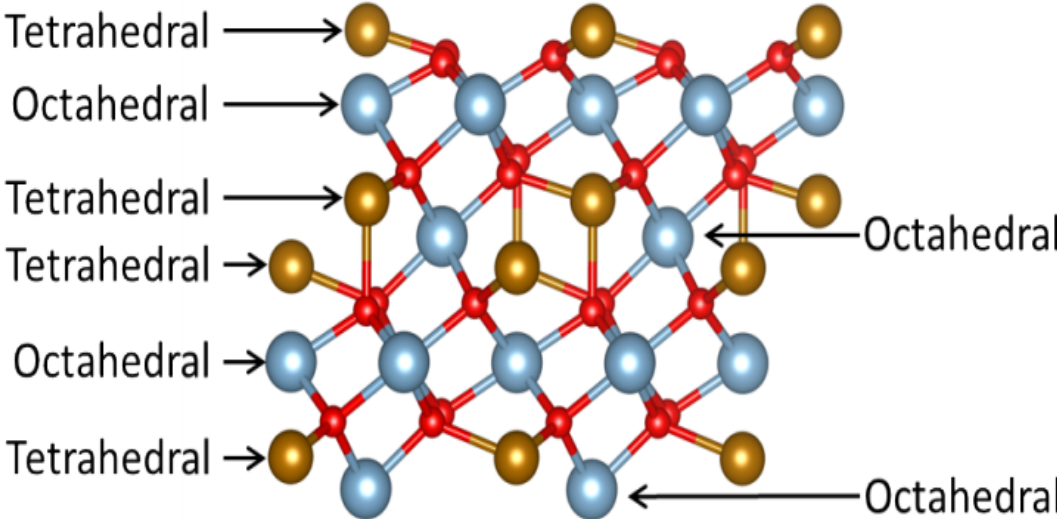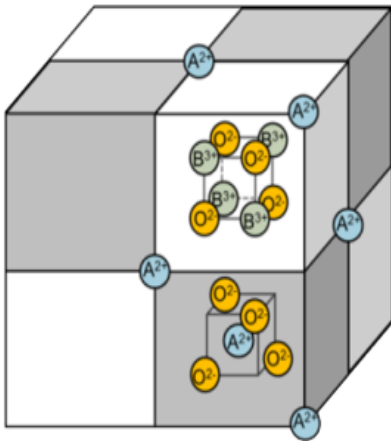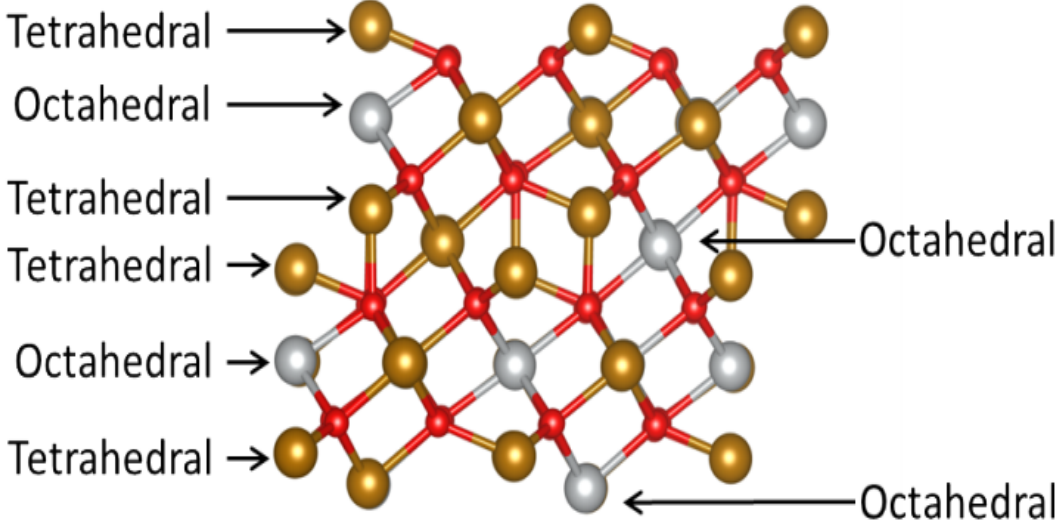
High temperature XRD also suggests an O-vacancy mechanism for the hercynite cycle

EDS analysis of phase segregation in the hercynite material
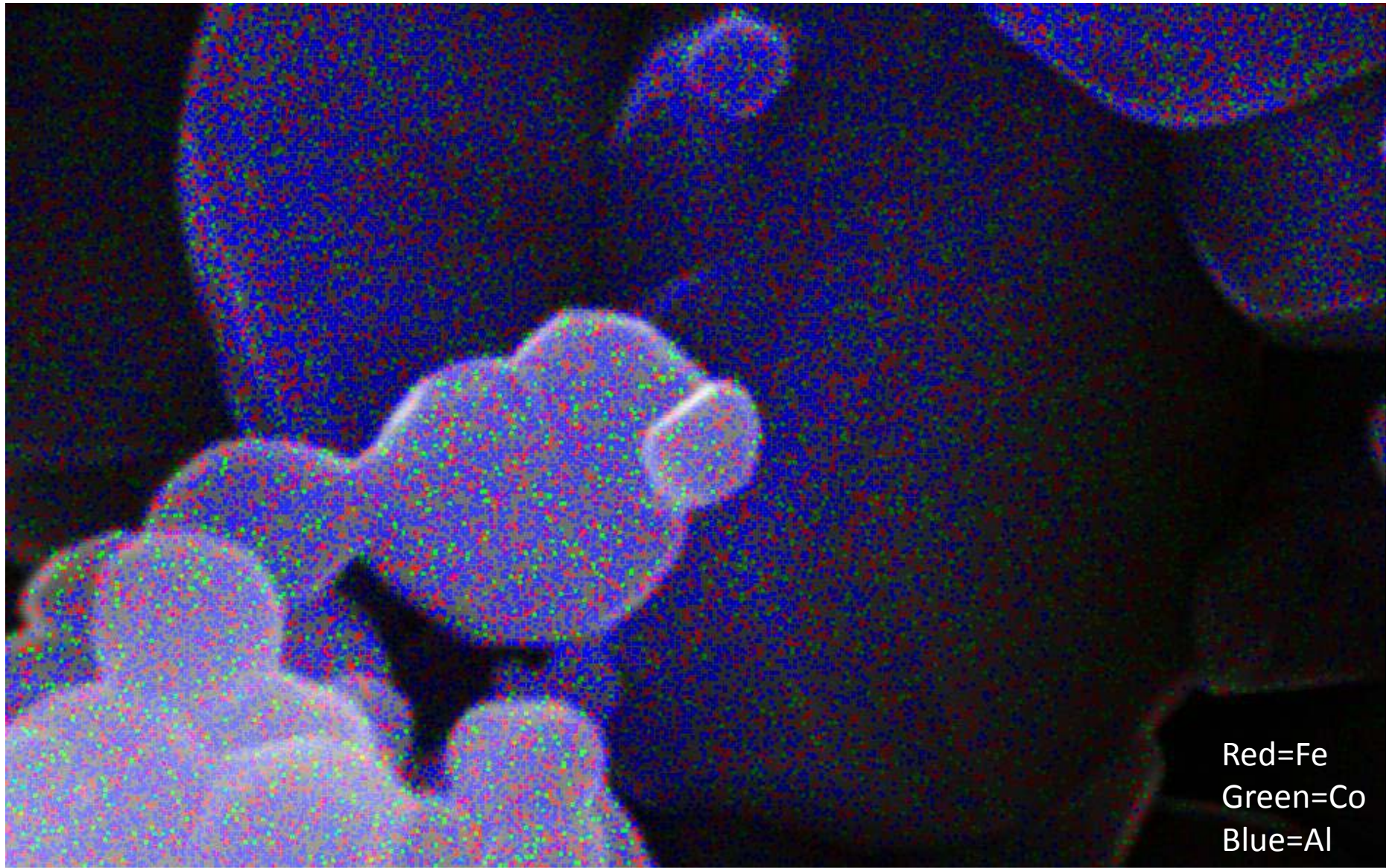
Reduced

Oxidized in CO$_2$
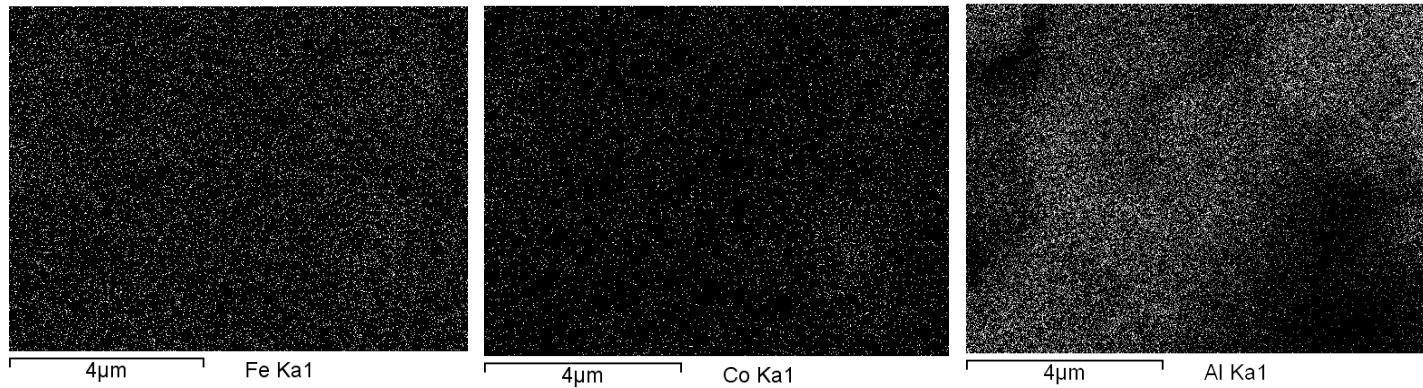
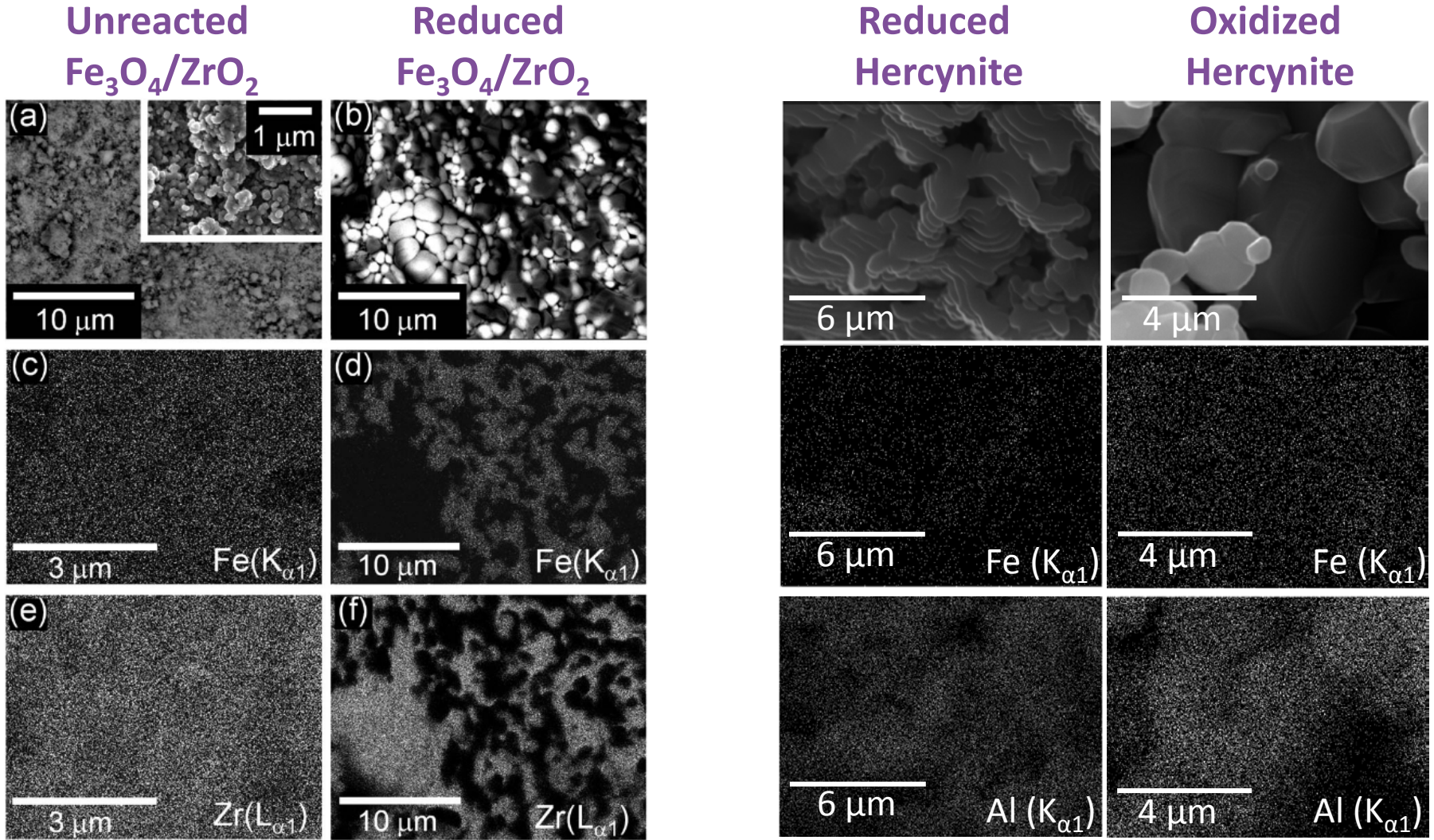# EDS analysis of phase segregation in the hercynite material
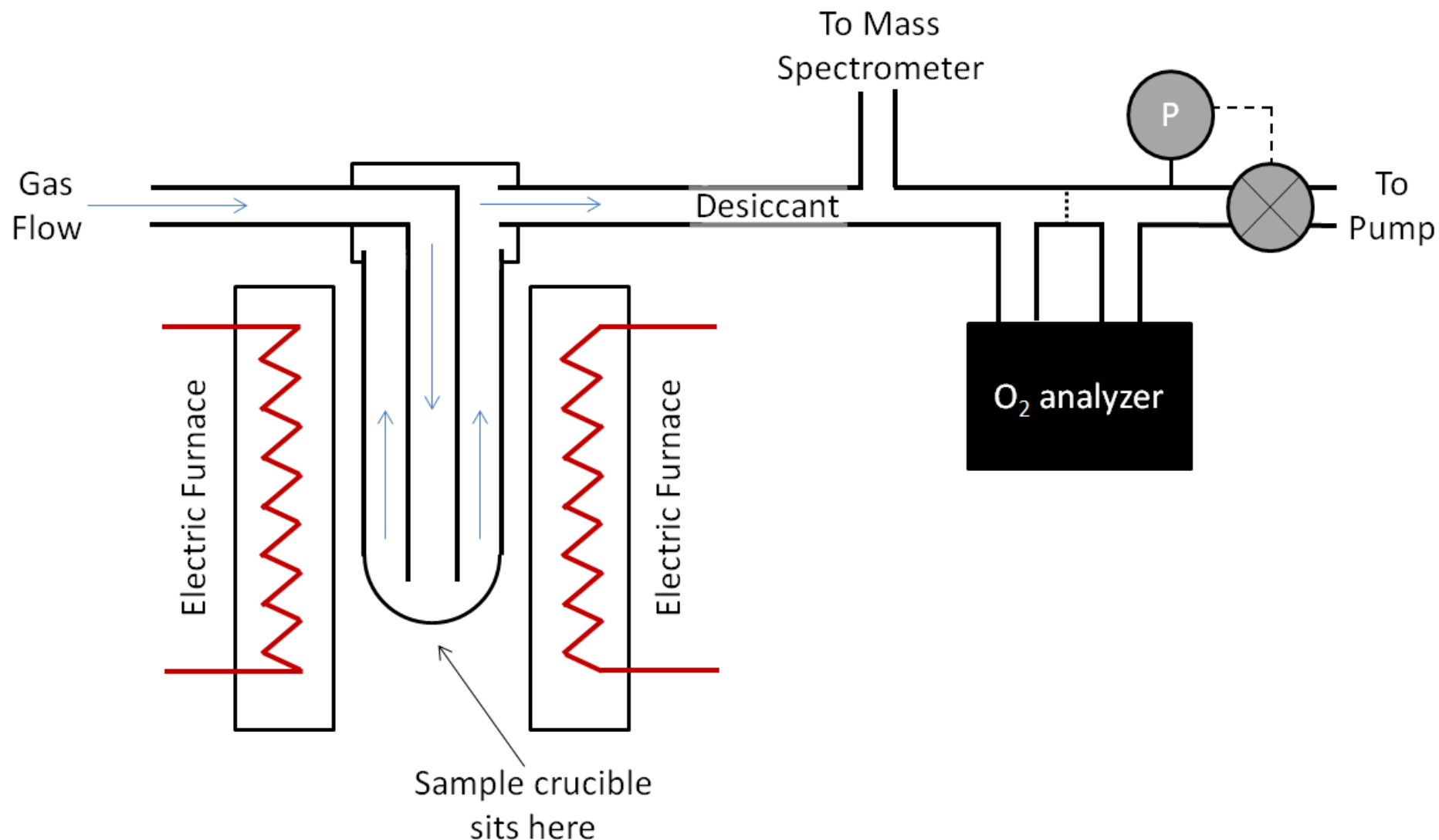

Red=Fe
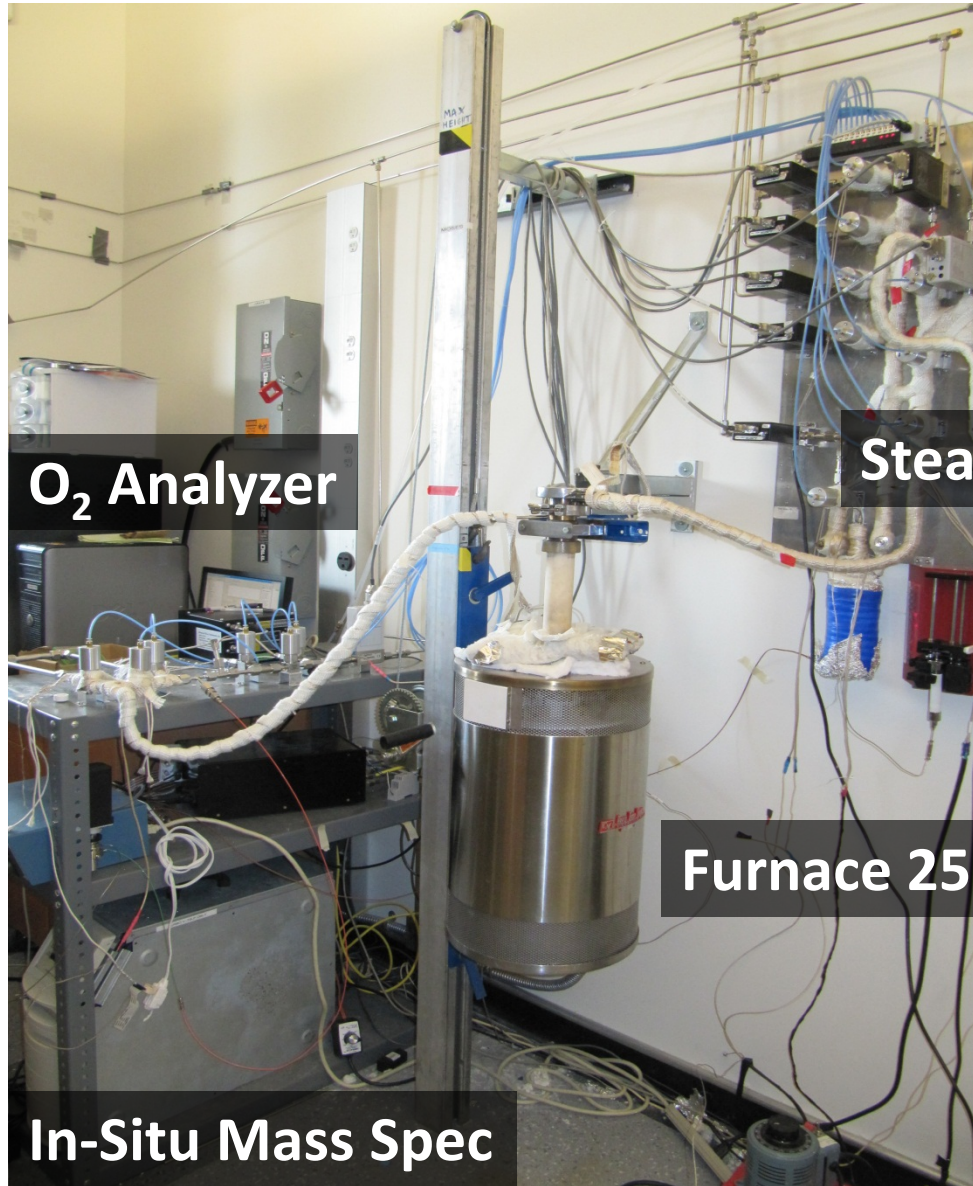Green=Co
Blue=Al

4μm

STWS phase separation or no separation

Unreacted Fe₃O₄/ZrO₂ — Unreacted Fe_3O_4/ZrO_2

Reduced Fe₃O₄/ZrO₂ — Reduced Fe_3O_4/ZrO_2

Reduced Hercynite

Oxidized Hercynite

Scheffe et al. E&ES, 2013, **6**, 963

Stagnation Flow Reactor

Gas Flow

To Mass Spectrometer

P

To Pump

Desiccant

Electric Furnace

Electric Furnace

O_2 analyzer

Sample crucible sits here

Water Splitting Reactor Set-up

O₂ Analyzer
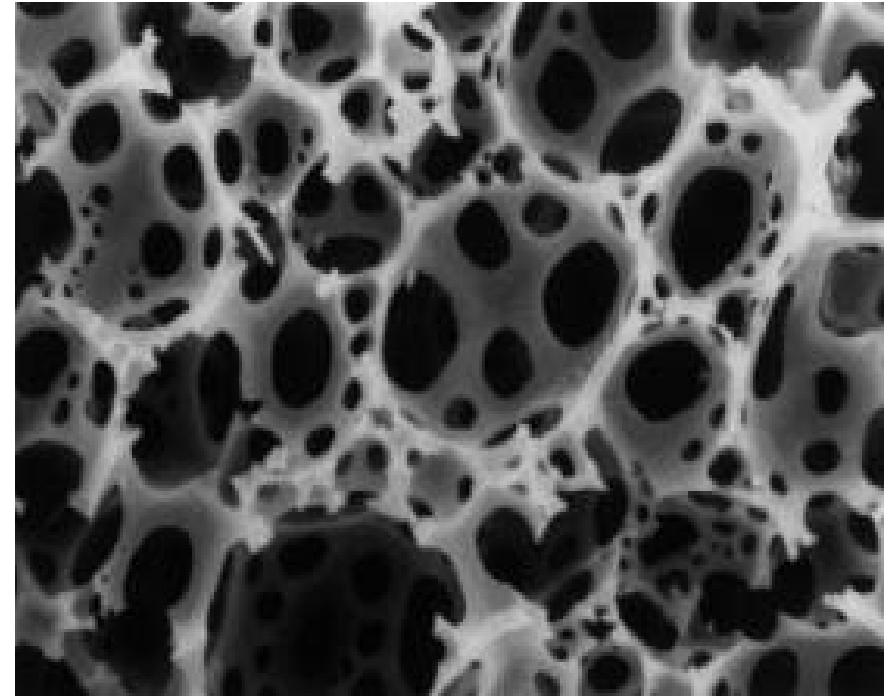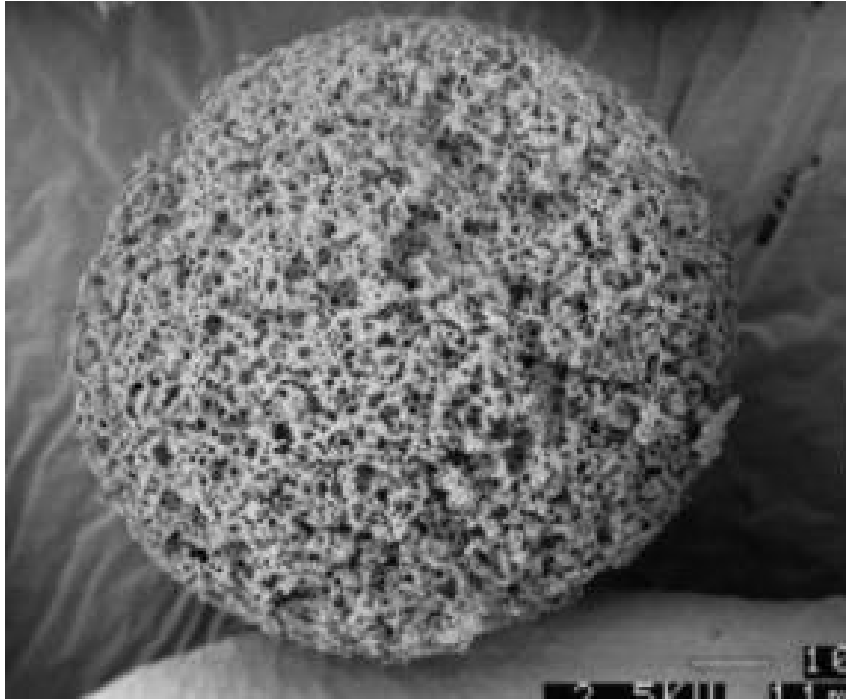
Steam Generator
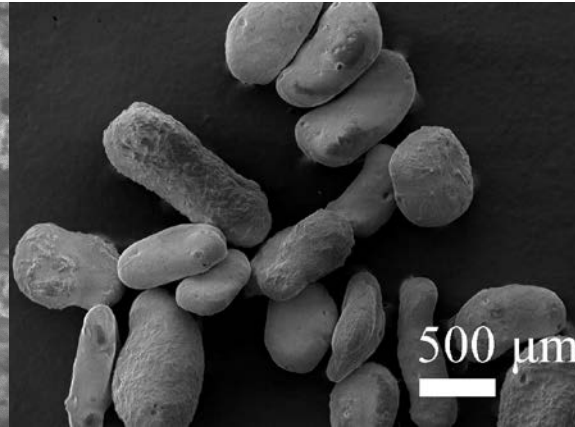
Furnace 25 – 1700 °C

In-Situ Mass Spec

Highly Porous Scaffolding

- Cavilink^{TM} Porous Polymer
- Maximum internal volume > 90%
- Density (typical) < 0.1 g/cc
- Cavity diameter up to 30 μm
- Composition – many polymer formulations possible

Particle Coating

(a)

500 μm

1 μm

(b)

Alumina film

50 nm

- SEM and TEM of Al_2O_3 coatings on polymer Scaffolding