

SUPPLEMENTARY MATERIALS

Study on nanophase iron oxyhydroxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan

Seungyeol Lee, Zhizhang Shen, and Huifang Xu*

NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison,
Madison, Wisconsin 53706

* Corresponding author:

Prof. Huifang Xu,

Email: hfxu@geology.wisc.edu

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1. cif file of proto-goethite structure (online electronic file)
2. Supplementary Figure. S1: Rietveld refinement result of Chemin XRD pattern of Rockness at Gale Grater, Mars.

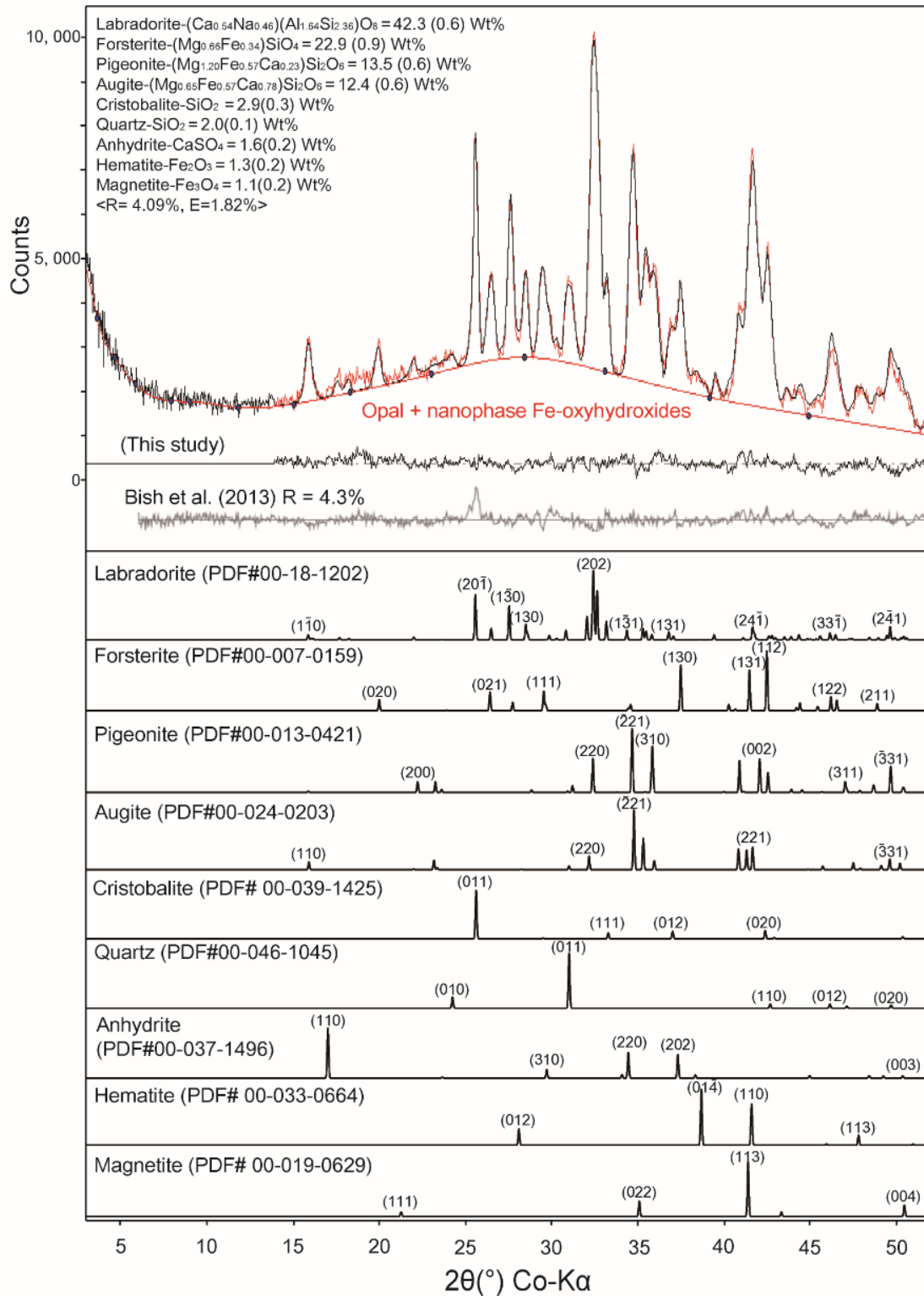


Figure 1S. Rietveld refinement results of XRD pattern of Rockness at Gale Grater. Observed (red) pattern versus calculated (black) pattern with residual curve at the bottom. The hump background

from 14° ($\sim 7.32 \text{ \AA}$) to 53° ($\sim 2.00 \text{ \AA}$) likely results from amorphous or poorly crystalline phases of silica (opal-like) and Fe-oxyhydroxides with adsorbed phosphate, silicate, and sulfate anions. Input structure models of labradorite, forsterite, pigeonite, augite, cristobalite, quartz, anhydrite, hematite, magnetite for Rietveld analysis are from Went et al. (1980), Artioli et al. (1995), Alvaro et al. (2010), Gualtieri (2000), Downs and Palmer (1994), Hazen et al. (1989), Bezou et al. (1995), Maslen et al. (1994), Haavik et al. (2000), respectively. Data is from a published article (Bish et al. 2013) and its residual curve (gray) from Rietveld refinement result is also inserted. The diffraction pattern may not be strongly influenced by aluminum light shield, which contain two strong peaks at $\sim 25.6^\circ$ and $\sim 32.0^\circ$ (Blake et al. 2012). The difference peak at $\sim 25.6^\circ$ may be mainly due to scattering from cristobalite.

3. Detail parameters for DFT calculations

VASP version:

vasp.5.2.2

POSCAR file of proto-goethite:

Proto-goethite

1.0

4.8730001450	0.0000000000	0.0000000000
0.0000000000	4.3319997787	0.0000000000
0.0000000000	0.0000000000	2.9630000591

Fe H O

2 2 4

Direct

0.0000000000	0.238399997	0.0000000000
0.5000000000	0.761600018	0.5000000000
0.509299994	0.204400003	0.0000000000
0.009299994	0.795599997	0.5000000000
0.320499986	0.481599987	0.0000000000
0.820500016	0.518400013	0.5000000000
0.620700002	0.992500007	0.0000000000
0.120700002	0.007499993	0.5000000000

POSCAR file of goethite:

Goethite

1.0

9.9133996964	0.0000000000	0.0000000000
0.0000000000	3.0127999783	0.0000000000
0.0000000000	0.0000000000	4.5799999237

Fe H O

4 4 8

Direct

0.145899996	0.250000000	0.951399982
0.645900011	0.250000000	0.548600018
0.854099989	0.750000000	0.048599999
0.354099989	0.750000000	0.451400012
0.898999989	0.250000000	0.601000011
0.101000004	0.750000000	0.398999989
0.601000011	0.750000000	0.101000011
0.398999989	0.250000000	0.898999989
0.800999999	0.250000000	0.284999996
0.199000001	0.750000000	0.715000033
0.699000001	0.750000000	0.784999967

0.300999999	0.250000000	0.215000004
0.948300004	0.250000000	0.804000020
0.051700000	0.750000000	0.195999995
0.551699996	0.750000000	0.304000020
0.448300004	0.250000000	0.695999980

POSCAR file of goethite:

Lepidocrocite

1.0

3.0720000267	0.0000000000	0.0000000000
0.0000000000	12.5159997940	0.0000000000
0.0000000000	0.0000000000	3.8729999065

Fe H O

4 4 8

Direct

0.500000000	0.177800000	0.250000000
0.500000000	0.822200000	0.750000000
0.000000000	0.677800000	0.250000000
0.000000000	0.322200000	0.750000000
0.000000000	0.000000000	0.820999980
0.000000000	0.000000000	0.320999980
0.500000000	0.500000000	0.820999980
0.500000000	0.500000000	0.320999980
0.000000000	0.288899988	0.250000000
0.000000000	0.711099982	0.750000000
0.500000000	0.788900018	0.250000000
0.500000000	0.211100012	0.750000000
0.000000000	0.073799998	0.250000000
0.000000000	0.926200032	0.750000000
0.500000000	0.573799968	0.250000000
0.500000000	0.426200002	0.750000000

POSCAR file of akaganeite:

akaganeite

1.0

10.5869998932	0.0000000000	0.0000000000
0.0000000000	3.0311000347	0.0000000000
-0.0055054170	0.0000000000	10.5149989021

Fe H O

8 8 16

direct

0.854399979	0.000000000	0.342400014
0.354399979	0.500000000	0.842400014
0.654799998	0.000000000	0.855000019

0.154799998	0.500000000	0.355000019
0.145600021	0.000000000	0.657599986
0.645600021	0.500000000	0.157599986
0.345200002	0.000000000	0.144999996
0.845200002	0.500000000	0.644999981
0.367000014	0.000000000	0.625999987
0.633000016	0.000000000	0.374000013
0.866999984	0.500000000	0.125999987
0.132999986	0.500000000	0.874000013
0.347999990	0.000000000	0.405000001
0.652000010	0.000000000	0.595000029
0.847999990	0.500000000	0.904999971
0.152000010	0.500000000	0.094999999
0.662999988	0.000000000	0.288300008
0.337000012	0.000000000	0.711699963
0.162999988	0.500000000	0.788300037
0.837000012	0.500000000	0.211699992
0.662000000	0.000000000	0.042900000
0.338000000	0.000000000	0.957099974
0.162000000	0.500000000	0.542900026
0.838000000	0.500000000	0.457100004
0.294600010	0.000000000	0.335099995
0.705399990	0.000000000	0.664900005
0.794600010	0.500000000	0.835099995
0.205399990	0.500000000	0.164900005
0.037400000	0.000000000	0.324999988
0.962599993	0.000000000	0.675000012
0.537400007	0.500000000	0.824999988
0.462599993	0.500000000	0.175000012

An Example of INCAR file:

System = proto-goethite

PREC = Accurate

ISPIND = 2

ISPIN = 2

MAGMOM = 1*5 1*-5 6*0

IBRION = 2

NSW = 281

ISIF = 3

ENCUT = 700

ISMEAR = -5

LDAU = .TRUE.

LDAUTYPE = 2

LDAUL = 2 -1 -1

LDAUU = 4.0 0.0 0.0
 LDAUJ = 1.0 0.0 0.0
 EDIFF = 1E-5

An example of KPOINTS file

Proto-goethite
 0
 M
 8 8 16
 0 0 0
 Akaganaite : 4*1* 4
 Goethite: 4*12*8
 Lepidocrocite: 16*4*16

An example of POSCAR for ZPE calculations:

Proto-goethite
 1.0000000000000000
 4.8981564515133318 0.0000000000000000 0.0000000000000000
 0.0000000000000000 4.3470467922933578 0.0000000000000000
 0.0000000000000000 0.0000000000000000 2.9595856315078568
 Fe H O
 2 2 4
 select dynamics
 Direct
 -0.0135007399329752 0.2697619514077492 0.0000000000000000 F F F
 0.4864992600670249 0.7302380635922555 0.5000000000000000 F F F
 0.5033712405100045 0.2054780483660750 0.0000000000000000 T T T
 0.0033712405100045 0.7945219516339248 0.5000000000000000 T T T
 0.3302761309678476 0.4867348170824118 0.0000000000000000 F F F
 0.8302761609678428 0.5132651829175882 0.5000000000000000 F F F
 0.6303533504551269 0.0160807021910512 0.0000000000000000 F F F
 0.1303533504551267 -0.0160807021910511 0.5000000000000000 F F F

An example of INCAR file for ZPE calculations

System = proto-goethite
 PREC = Accurate
 ISPIND = 2
 ISPIN = 2
 MAGMOM = 1*5 1*-5 6*0
 IBRION = 5
 NFREE = 2
 POTIM = 0.01
 NSW = 1

ISIF = 2
ENCUT = 700
ISMear = -5
LDAU = .TRUE.
LDAUTYPE = 2
LDAUL = 2 -1 -1
LDAUU = 4.0 0.0 0.0
LDAUJ = 1.0 0.0 0.0

4. REFERENCES CITED

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