

 WILEY-VCH

R. M. Cornell, U. Schwertmann

The Iron Oxides

Structure, Properties, Reactions, Occurrences and Uses

Second, Completely Revised and Extended Edition



Contents

1	Introduction to the iron oxides	1
2	Crystal structure	9
2.1	General	9
2.2	Iron oxide structures	9
2.2.1	Close packing of anion layers	10
2.2.2	Linkages of octahedra or tetrahedra	13
2.3	Structures of the individual iron oxides	14
2.3.1	The oxide hydroxides	14
2.3.1.1	Goethite α -FeOOH	14
2.3.1.2	Lepidocrocite γ -FeOOH	18
2.3.1.3	Akaganéite β -FeOOH and schwertmannite $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n\text{H}_2\text{O}$	20
2.3.1.4	δ -FeOOH and δ' -FeOOH (feroxyhyte)	22
2.3.1.5	High pressure FeOOH	23
2.3.1.6	Ferrihydrite	23
2.3.2	The Hydroxides	27
2.3.2.1	Bernalite $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$	27
2.3.2.2	$\text{Fe}(\text{OH})_2$	27
2.3.2.3	Green rusts	28
2.3.3	The Oxides	29
2.3.3.1	Hematite α - Fe_2O_3	29
2.3.3.2	ϵ - Fe_2O_3	31
2.3.3.3	Magnetite Fe_3O_4	32
2.3.3.4	Maghemite γ - Fe_2O_3	32
2.3.3.5	Wüstite Fe_{1-x}O	34
2.4	The Fe-Ti oxide system	37
	Appendix	37
3	Cation substitution	39
3.1	General	39
3.2	Goethite and lepidocrocite	42
3.2.1	Al substitution	42

3.2.2	Other substituting cations	47
3.3	Hematite	51
3.3.1	Al substitution	51
3.3.2	Other cations	54
3.4	Magnetite and maghemite	55
3.5	Other iron oxides	57
4	Crystal morphology and size	59
4.1	General	59
4.1.1	Crystal growth	59
4.1.2	Crystal morphology	60
4.1.3	Crystal size	62
4.2	The iron oxides	63
4.2.1	Goethite	64
4.2.1.1	General	64
4.2.1.2	Domainic character	69
4.2.1.3	Twinning	71
4.2.1.4	Effect of additives	73
4.2.2	Lepidocrocite	74
4.2.3	Akaganéite and schwertmannite	75
4.2.4	Ferrihydrite	78
4.2.5	Hematite	81
4.2.6	Magnetite	87
4.2.7	Maghemite	92
4.2.8	Other Iron Oxides	94
5	Surface area and porosity	95
5.1	Surface area	95
5.2	Porosity	98
5.3	Surface roughness and fractal dimensions	100
5.4	The iron oxides	101
5.4.1	Goethite	102
5.4.2	Lepidocrocite	103
5.4.3	Akaganéite and schwertmannite	104
5.4.4	δ -FeOOH and feroxyhyte	105
5.4.5	Ferrihydrite	106
5.4.6	Hematite	108
5.4.7	Magnetite	109
5.4.8	Maghemite	109
6	Electronic, electrical and magnetic properties and colour	111
6.1	Electronic properties	111
6.1.1	Free Fe^{3+} and Fe^{2+} ions	111
6.1.2	Bound Fe ions	112
6.1.3	Molecular orbital description of bonding in iron oxides	113

6.2	Electrical properties	115
6.2.1	Semiconductor properties of iron oxides	116
6.3	Magnetic properties	118
6.3.1	Basic definitions	118
6.3.2	Types of magnetism	119
6.3.3	Magnetic behaviour of iron oxides	121
6.3.4	The different iron oxides	123
6.3.4.1	Goethite	123
6.3.4.2	Lepidocrocite	124
6.3.4.3	Akaganéite	124
6.3.4.4	δ -FeOOH, ferrihydrite and high pressure FeOOH	125
6.3.4.5	Ferrihydrite	125
6.3.4.6	Hematite	126
6.3.4.7	Magnetite and maghemite	128
6.3.4.8	Other Fe oxides	130
6.4	Colour	130
6.4.1	General	130
6.4.2	Colours	133
6.4.3	Pigment properties	136
7	Characterization	139
7.1	Introduction	139
7.2	Infrared spectroscopy	141
7.2.1	Goethite	141
7.2.2	Lepidocrocite	144
7.2.3	Ferrihydrite	144
7.2.4	Hematite	145
7.2.5	Other iron oxides	146
7.3	Raman spectroscopy	146
7.4	Ultraviolet-visible spectroscopy	147
7.4.1	General	147
7.4.2	Spectra of the different Fe oxides	148
7.5	Mössbauer spectroscopy	152
7.5.1	General	152
7.5.2	Spectra of the various Fe oxides	157
7.5.2.1	Goethite and lepidocrocite	157
7.5.2.2	Ferrihydrite	157
7.5.2.3	Hematite	158
7.5.2.4	Magnetite and maghemite	158
7.5.2.5	Other iron oxides	160
7.6	Magnetic properties (Magnetometry)	161
7.6.1	General	161
7.6.2	Magnetic susceptibility χ	162
7.6.3	Magnetic anisotropy, coercivity and saturation magnetization	163
7.6.4	Domain type	164

7.6.5	Curie temperature analysis	167
7.6.6	Applications	167
7.7	Other spectroscopic techniques	168
7.7.1	Photoelectron spectroscopy	169
7.7.2	X-ray absorption spectroscopy	171
7.8	Diffraction	172
7.8.1	X-ray diffraction	172
7.8.2	Other diffraction techniques	177
7.9	Microscopy	179
7.10	Thermoanalysis	181
7.11	Dissolution methods	183
8	Thermodynamics of the Fe-O₂-H₂O system	185
8.1	General	185
8.2	Standard free energy of reaction and the equilibrium constant	186
8.3	Redox reactions	189
8.4	Effect of complexing agents on redox potential	192
8.5	Stabilities of iron oxides	193
8.5.1	“Bulk” crystals	193
8.5.2	Effect of particle size and Al substitution	197
9	Solubility	201
9.1	General	201
9.2	The solubility product	201
9.3	The effect of hydrolysis reactions and pH on solubility	203
9.4	Other factors influencing solubility and the solubility product	208
9.4.1	Complexation	208
9.4.2	Redox reactions	209
9.4.3	Ionic strength	211
9.4.4	Properties of the solid	211
9.4.4.1	Particle size	211
9.4.4.2	Ageing and isomorphous substitution	214
9.5	Methods of determining or calculating the solubility product	214
9.6	Solubility products of the various oxides	217
10	Surface Chemistry and Colloidal Stability	221
10.1	Surface functional groups	221
10.2	Surface acidity and acidity constants	227
10.3	The electrical double layer and electrochemical properties	232
10.4	Point of zero charge	236
10.5	Stability of colloidal suspensions	241
10.5.1	General	241
10.5.2	Stability of iron oxide suspensions	243
10.6	Tactoids, gels and schiller layers	250
10.7	Rheological properties	250

11	Adsorption of Ions and Molecules	253
11.1	General	253
11.2	Treatment of adsorption data	254
11.2.1	The Langmuir, Freundlich and Temkin isotherm equations	254
11.2.2	Surface complexation models	255
11.3	Anion adsorption	258
11.3.1	Modes of coordination	265
11.3.2	Examples of inorganic ligands	267
11.3.2.1	Phosphate	267
11.3.2.2	Other anions	270
11.3.2.3	Organic anions and other organic compounds	273
11.4	Cation adsorption	279
11.4.1	General	279
11.4.2	Examples of cations	284
11.5	Adsorption from mixed systems	288
11.5.1	Competition between anions	289
11.5.2	Competition between cations	289
11.5.3	Interactions between cations and anions	290
11.5.4	Ternary adsorption	290
11.6	Adsorption of water	293
11.7	Adsorption of gases	293
11.8	Photochemical reactions	295
12	Dissolution	297
12.1	Introduction	297
12.2	Dissolution reactions and mechanisms	298
12.2.1	General	298
12.2.2	Protonation	299
12.2.3	Complexation	301
12.2.4	Reduction	306
12.2.4.1	General	306
12.2.4.2	Examples of reductants	312
12.2.4.3	Photochemical reduction	316
12.2.4.4	Biological and other reduction reactions	319
12.2.5	Comparison of the three different types of dissolution reactions	323
12.3	Dissolution equations	324
12.4	Individual iron oxides	326
12.4.1	Goethite	328
12.4.1.1	Unsubstituted goethite	328
12.4.1.2	Substituted goethite	330
12.4.1.3	Natural goethite and hematite	332
12.4.2	Lepidocrocite and akaganéite	334
12.4.3	Ferrihydrite	335
12.4.4	Hematite	337

12.4.5	Magnetite and maghemite	338
12.4.6	Comparison of different oxides	339
13	Formation	345
13.1	General	345
13.2	Formation in Fe^{III} systems	347
13.2.1	Hydrolysis reactions	347
13.2.2	Formation of the different Fe^{III} oxides	350
13.3	Formation in aqueous Fe^{II} systems	355
13.3.1	General	355
13.3.2	Effect of pH	356
13.3.3	Effect of oxidation rate	359
13.3.4	Effect of foreign compounds	360
13.4	Decomposition of Fe complexes	363
14	Transformations	365
14.1	Introduction	365
14.2	Thermal transformations	367
14.2.1	General	367
14.2.2	Goethite to hematite	369
14.2.3	Lepidocrocite to maghemite or hematite	373
14.2.4	Akaganéite and schwertmannite to hematite	375
14.2.5	δ - FeOOH and ferroxhyte to hematite	378
14.2.6	Ferrihydrite to hematite	378
14.2.7	Interconversions between maghemite and hematite	382
14.3	Via solution transformations	383
14.3.1	Lepidocrocite to goethite/hematite	383
14.3.2	Akaganéite to goethite/hematite	384
14.3.3	Schwertmannite to goethite	385
14.3.4	Maghemite and goethite to hematite	386
14.3.5	Ferrihydrite to other Fe oxides	388
14.3.5.1	Rate of transformation	388
14.3.5.2	Hematite versus goethite formation	390
14.3.5.3	Mechanism of transformation	391
14.3.5.4	Effect of foreign compounds	393
14.3.5.4.1	General	393
14.3.5.4.2	Anions and neutral molecules	395
14.3.5.4.3	Cations	398
14.4	Oxidative and reductive transformations	402
14.4.1	Oxidation of magnetite to maghemite or hematite	402
14.4.2	Reduction of Fe^{III} oxides to magnetite	405
14.4.3	Reduction of iron ores to iron	406
14.5	Interaction of iron oxides with other metal oxides and carbonates	407

15	Rocks and ores	409
15.1	Introduction	409
15.2	Magmatic and metamorphic rocks and ores	409
15.3	Sediments and sedimentary rocks	412
15.3.1	Red beds	413
15.3.2	Sedimentary iron ores	416
15.3.3	Other sediments	420
15.3.4	Ferricretes and bauxites	421
15.4	Recent geological environments	422
15.4.1	Terrestrial surfaces	423
15.4.2	Spring and ground water	423
15.4.3	Deep sea	424
15.4.4	Continental shelves	424
15.4.5	Lakes and streams	425
15.4.6	Hydrothermal marine environments	427
15.4.7	Martian surface	429
15.5	Iron fractionation in sediments	430
	Appendix	431
16	Soils	433
16.1	Soils – a unique environment for iron oxide formation in terrestrial ecosystems	433
16.2	Iron oxide formation in soils	435
16.3	Iron oxide content and soil development	437
16.4	Occurrence and formation	439
16.4.1	Historical aspects	439
16.4.2	Distribution pattern	440
16.4.3	The various oxides	441
16.4.3.1	Goethite	441
16.4.3.2	Hematite and its association with goethite	442
16.4.3.3	Lepidocrocite, ferrihydrite and green rust	447
16.4.3.4	Ferrihydrite and its association with goethite	448
16.4.3.5	Magnetite and maghemite	450
16.5	Properties	452
16.5.1	Surface area, crystal morphology and size	452
16.5.2	Aluminium substitution	456
16.6	Significance for soil properties	459
16.6.1	Colour	459
16.6.2	Charge and redox properties	461
16.6.3	Anion and cation binding	463
16.6.4	Aggregation and cementation	468
17	Organisms	475
17.1	General	475
17.2	Biotically-mediated formation	476

17.2.1	Goethite and lepidocrocite	476
17.2.2	Ferrihydrite	477
17.2.3	Magnetite	480
17.2.3.1	Magnetite in chitons' teeth	481
17.2.3.2	Magnetite in bacteria and other organisms	481
17.3	Biotically induced formation	486
18	Products of iron metal corrosion	491
18.1	General	491
18.2	Electrochemical corrosion	491
18.3	High temperature oxidation/corrosion in gases	494
18.4	Other forms of corrosion	496
18.5	The products of corrosion	497
18.5.1	Iron oxides formed by electrochemical corrosion	499
18.5.2	Iron oxides in passive films	503
18.5.3	Thermally grown oxide films	504
18.6	Prevention of corrosion; protective oxide layers	506
19	Applications	509
19.1	Historical background	509
19.2	Pigments	511
19.2.1	Natural pigments	512
19.2.2	Synthetic pigments	514
19.3	Magnetic pigments	516
19.4	Ferrites	517
19.5	Catalysts	518
19.6	Other uses of iron oxides	522
19.7	Undesirable iron oxides	524
20	Synthesis	527
20.1	Industrial synthesis	527
20.1.1	General	527
20.1.2	Solid state transformations	528
20.1.2.1	The copperas process	528
20.1.2.2	Other solid state processes	528
20.1.3	Reduction of organic compounds	529
20.1.4	Precipitation from Fe^{II} solutions	530
20.1.5	Other processes	531
20.1.6	Magnetic pigments	532
20.2	Laboratory synthesis methods	533
20.2.1	Goethite	533
	Other methods	533
20.2.2	Lepidocrocite	534
	Other methods	534
20.2.3	Akaganéite	534

	Other methods	534
20.2.4	Schwertmannite	535
20.2.5	Feroxyhyte	535
20.2.6	Ferrihydrite	535
	2-line ferrihydrite	535
	6-line ferrihydrite	535
	Other methods	536
20.2.7	Hematite	536
	Other methods	536
20.2.7.1	Coated hematite	537
20.2.8	ϵ -Fe ₂ O ₃	538
20.2.9	Magnetite	538
	Other methods	538
20.2.10	Maghemite	539
	Other methods	539
20.2.11	Fe(OH) ₂	540
	Other methods	540
20.2.12	Green rust	540
20.2.13	Other compounds	541
	FeO (nonstoichiometric)	541
	High pressure FeOOH	541
20.2.14	Production of iron oxides on substrates or in confined spaces	541
	Goethite, hematite and ferrihydrite	541
	Magnetite	541
	Precipitation of goethite, ferrihydrite or magnetite in vesicles	542
21	Environmental significance	543
21.1	Introduction	543
21.2	Retention of pollutants by Fe oxides in water purification and in natural systems	544
21.2.1	Water treatment systems	544
21.2.2	Natural systems	546
21.3	Acid mine tailings	547
21.4	Detoxification reactions	549
21.5	Bacterial turnover of environmental pollutants	551
21.6	Anthropogenic dust and industrial sites	551
21.7	Iron-oxide rich waste products	552

References 555

Subject Index 651

Sources of Figures and Tables 659