Contents

Synopsis xiii
Acknowledgments xxiii

1. **Introduction** 1
   1.1. Definition of Framboids 1
      1.1.1. Microscopic Size 1
      1.1.2. Spheroidal to Sub-spheroidal Form 2
      1.1.3. Discrete Microcrystals 3
      1.1.4. Equant and Equidimensional Microcrystals 3
   1.2. History of Framboid Research 4
      1.2.1. Discovery of Microcrystals in Framboids 4
      1.2.2. Advances in Microscopy and Understanding Framboid Structure 7
      1.2.3. Discovering the Nature of Framboids 11
   1.3. Distribution of Framboids 11
      1.3.1. Framboid Numbers 11
      1.3.2. Distribution of Framboids in Sediments and Sedimentary Rocks 14
      1.3.3. Hydrothermal Framboids 17
      1.3.4. Cryptic Framboids 18

2. **Framboid Sizes** 21
   2.1. Framboid Size Distributions 22
      2.1.1. Log-normal Distribution 22
      2.1.2. Framboid Mean Diameters 24
   2.2. Measurement Errors 26
   2.3. Framboid Sizes 27
      2.3.1. Sedimentary Environments 28
      2.3.2. Other Environments 31
   2.4. Sedimentary Framboids 32
      2.4.1. Framboids in Sedimentary Rocks 32
      2.4.2. Framboids in Marine Sediments 34
      2.4.3. Framboids in Non-marine Sediments 34
   2.5. Framboids in Other Environments 36
      2.5.1. Framboids in Water Columns 36
      2.5.2. Framboid Size-Frequency Distributions and the Oxygenation State of Paleo-Water Columns 37

2.6. Hydrothermal Framboids 39
2.6.1. Mineralized Sediments 42
2.7. Polyframboid Sizes 44
2.8. The Maximum and Minimum Sizes of Framboids 44

3. Framboid Shapes 47
3.1. Spheroidal Framboids 48
3.1.1 Sphericity 49
3.1.2. Deviations from Perfect Sphericity 49
3.2. Ellipsoidal Framboids 51
3.2.1. Ellipsoidal Framboids Produced by Deformation 51
3.2.2. Primary Ellipsoidal Framboids 51
3.2.3. Effect of Gravity on Framboid Sphericity 53
3.3. Faceted Framboids 55
3.3.1. Polyhedral Framboids 55
3.3.2. Framboids with Partial Facets 57
3.4. Polyframboids 60

4. Microcrystal Morphology 63
4.1. Microcrystal Sizes 63
4.2. Numbers of Microcrystals in Framboids 64
4.2.1. Packing Densities 67
4.2.2. Ostwald Ripening 69
4.3. Microcrystal Size and Geologic Age 71
4.4. Pyrite Crystal Habits 71
4.5. Framboid Microcrystal Habits 73
4.5.1. Cubic Microcrystals 75
4.5.2. Pyritohedral Microcrystals 76
4.5.3. Octahedral Microcrystals 78
4.5.4. Higher Order Forms 80
4.5.5. Spheroidal Crystals 81
4.5.6. Hollow Microcrystals 83
4.5.7. Incomplete Microcrystals 86

5. Framboid Microarchitecture 90
5.1. Framboid Sections 91
5.2. Single Domain Microarchitectures 92
5.2.1. Cubic Close Packing 92
5.2.2. Close Packed Spheres 95
5.3. Multiple Domain Microarchitectures 98
5.3.1. Pseudo-icosahedral Domain Structure 99
5.3.2. Other Multiple Domain Microarchitectures 104
5.4. Disordered Framboids 105
5.5. The Microarchitecture of Microcrystalline and Nanocrystalline Pyrite 108

6. The Crystallography of Pyrite Framboids 110
6.1. Pyrite Structure 111
6.2. Framboid X-ray Diffraction 114
6.3. Electron Backscatter Diffraction 119
6.3.1. Accuracy of Pyrite EBSD 121
6.3.2. Framboid Microcrystals Are Single Crystals 122
6.3.3. Microcrystal Orientations 123
6.4. Framboid Crystallography and Self-Organization 125
6.4.1. Origins of Different Crystallographic Orientations of Microcrystals in Framboids 127

7. Organic Matter in Framboids 129
7.1. Framboids as Fossilized Microorganisms 130
7.1.1. Schneiderhöhn's Fossil Bacteria 130
7.1.2. Love's Microfossils 131
7.1.3. Pyrite Precipitation within Prokaryotic Cells 133
7.1.4. Framboids as Fossil Microbial Colonies 133
7.1.5. Framboids as Fossil Giant Sulfur Bacteria 134
7.1.6. Framboids as Fossil Eukaryotic Microorganisms 134
7.1.7. Polyframboids as Steinkerns 137
7.2. Framboidal Organic Matter 141
7.2.1. Framboids and Biofilms 142
7.2.2. Geopolymers and Framboid Organic Matter 145
7.2.3. The Form of Protokerogen 147
7.2.4. Extrusion of Framboidal Organic Matter 148
7.2.5. Epigenetic Organic Matter 149
7.2.6. Composition of Infilling Materials within Framboids 150
7.3. Organic Matter in Framboids 151

8. Framboid Mineralogy 153
8.1. Non-pyritic Framboids 153
8.2. Sulfide Minerals, Other Than Pyrite, in Framboids 155
8.2.1. Marcasite Framboids 155
8.2.2. Greigite, Fe_3S_4, Framboids 156
8.2.3. Copper Sulfide Framboids 159
8.2.4. Sphalerite Framboids 161
8.3. Oxide Framboids 163
8.3.1. Magnetite Framboids 163
8.3.2. Iron and Mn (Oxyhydr)oxide Framboids 165

9. Geochemistry of Framboids 169
9.1. Pyrite Stoichiometry in Framboids 170
9.2. Pyrite Composition 173
9.2.1. Trace and Minor Elements in Sedimentary Pyrite 173
9.2.2. Trace Elements in Pyrite in Coal 175
9.2.3. Trace and Minor Elements in Hydrothermal Pyrite 177

9.3. Framboid Composition 179
9.3.1. Trace and Minor Element Compositions of Framboids 179
9.3.2. Trace Element Compositions of Hydrothermal Framboids 187
9.3.3. Sulfur Isotope Compositions of Framboids 187
9.4. Controls on the Trace Element Concentrations in Framboids 189

10. Pyrite Framboid Formation Chemistry 191
10.1. Pyrite Chemistry 191
10.1.1. Pyrite Solubility 192
10.1.2. Pyrite Formation Chemistry 193
10.2. The Polysulfide Reaction 193
10.2.1. Polysulfide Reactants 193
10.2.2. The Polysulfide Reaction Mechanism 194
10.2.3. Aqueous FeS as a Reactant 195
10.2.4. Protonated Iron Sulfide Complexes as Reactants 198
10.2.5. Aqueous Fe(II) as a Reactant 200
10.2.6. Iron Sulfide Minerals as Reactants 203
10.2.7. Nanoparticulate FeS 206
10.3. The H_2S Reaction 207
10.3.1. The H_2S Reaction Mechanism 208
10.3.2. Microbial Mediation 209
10.3.3. Iron (III) (oxyhydr)oxide 210
10.4. Pyrite Framboid Syntheses 210
10.4.1. Microframboids and Nanoframboids 216
10.4.2. Microspheres 217
10.4.3. Nanoparticulate Pyrite and Pyrite Clusters 218
10.5. Comparison of the Polysulfide and H_2S Pathways for Framboid Formation 220

11. Nucleation of Framboids 222
11.1. Burst Nucleation: The LaMer Theory 222
11.2. Homogeneous and Heterogeneous Nucleation of Framboids 223
11.3. Classical Nucleation Theory 225
11.3.1. Critical Supersaturation 226
11.3.2. Surface Energy of Pyrite Nuclei 228
11.3.3. Pyrite Critical Nucleus Size 229
11.4. Framboid Size and Supersaturation 231
11.5. Nucleation of Framboids 232
11.5.1. Heterogeneous Nucleation of Pyrite 232
11.5.2. Nucleation of Pyrite Framboids 234

12. Framboid Microcrystal Growth 235
12.1. Origin of Pyrite Microcrystal Habits 235
12.1.1. Pyrite Surface Energies 235
12.1.2. Spectator Ions and Adsorption 240

12.2. Growth Mechanisms and Microcrystal Habit 241
12.2.1. Screw-Dislocation Growth 241
12.2.2. Surface Nucleation Growth 243
12.2.3. Crystallization by Particle Attachment (CPA) 244
12.2.4. Ostwald Ripening 245
12.2.5. Interrelationship between Monomer Attachment, CPA, and Ostwald Ripening 246
12.2.6. Supersaturation and Pyrite Framboid Microcrystal Growth Forms 249
12.3. Origin of Framboid Sizes and the Rate of Pyrite Framboid Formation 250
12.3.1. Crystal Size Distribution (CSD) Theory 251
12.3.2. Diffusion-Controlled Growth 252
12.3.3. The Rate of Pyrite Framboid Formation 253
12.3.4. The Rate of Polyframboid and Framboid Cluster Formation 256
12.4. Molecular Mechanism of Pyrite Crystal Growth 257
12.4.1. Effect of Temperature 258
12.4.2. Effect of pH 260

13. Framboid Self-Assembly and Self-Organization 262
13.1. Self-Assembly: The DVLO Theory 262
13.1.1. Hamaker Constant 265
13.1.2. Electrostatic Interactions 265
13.1.3. The Debye Length and Microcrystal Self-Assembly 266
13.1.4. Pyrite Surface Charge 268
13.1.5. Net DVLO Forces in Pyrite Framboid Self-Assembly 269
13.2. Self-Organization 271
13.2.1. Organic Templates 272
13.2.2. Spatial Constraints: Coacervates 272
13.2.3. Spatial Constraints: Sediment Pores 273
13.2.4. Topotactic Solid Phase Transformations 275
13.2.5. Compaction and Dewatering of Sediments 276
13.2.6. Microcrystal Alignment by Epitaxial Growth and Secondary Nucleation 276
13.3. The Self-Organization Process in Framboids 277
13.3.1. The Development of Framboid Shapes 278
13.3.2. The Development of the Framboid Microarchitecture 280

List of Symbols and Abbreviations 283
List of Units 287
Glossary 289
References 301
Index 327