

Studies in Inorganic Chemistry 18

Structure and Chemistry of the Apatites and Other Calcium Orthophosphates

J.C. Elliott

*Department of Child Dental Health
The London Hospital Medical College
Turner Street, London E1 2AD, U.K.*



ELSEVIER

Amsterdam — London — New York — Tokyo 1994

CONTENTS

| | |
|--|------|
| Preface | v |
| Acknowledgements | viii |
| Chapter 1 | |
| General chemistry of the calcium orthophosphates | 1 |
| 1.1 Introduction | 1 |
| 1.2 Monocalcium phosphates (monohydrate and anhydrous) | 9 |
| 1.3 Octacalcium phosphate | 12 |
| 1.3.1 Introduction | 12 |
| 1.3.2 Structure | 12 |
| 1.3.3 Preparation | 13 |
| 1.3.4 Optical properties, density and habit | 13 |
| 1.3.5 Kinetics of nucleation and crystal growth | 15 |
| 1.3.6 Solubility and reactions in solution | 16 |
| 1.3.7 Thermal decomposition | 18 |
| 1.3.8 Infrared, Raman and NMR spectroscopy | 20 |
| 1.3.9 Double salts of octacalcium phosphate and dicarboxylic acids | 22 |
| 1.4 Dicalcium phosphate dihydrate, brushite | 23 |
| 1.4.1 Introduction | 23 |
| 1.4.2 Structure | 24 |
| 1.4.3 Preparation | 24 |
| 1.4.4 Optical properties, density and habit | 26 |
| 1.4.5 Kinetics of crystal growth and dissolution | 26 |
| 1.4.6 Solubility and reactions in solution | 27 |
| 1.4.7 Thermal decomposition and properties | 29 |
| 1.4.8 Infrared, Raman and NMR spectroscopy | 30 |
| 1.5 Dicalcium phosphate anhydrous, monetite | 30 |
| 1.5.1 Introduction | 30 |
| 1.5.2 Structure | 31 |
| 1.5.3 Preparation | 32 |
| 1.5.4 Optical properties, density and habit | 32 |
| 1.5.5 Solubility and reactions in solution | 33 |
| 1.5.6 Thermal decomposition and properties | 33 |

| | |
|---|----|
| 1.5.7 Infrared, Raman and NMR spectroscopy | 34 |
| 1.6 Anhydrous tricalcium phosphates and whitlockite | 34 |
| 1.6.1 Occurrence and importance | 34 |
| 1.6.2 Structures | 35 |
| 1.6.3 Optical properties, density and habit | 42 |
| 1.6.4 Preparation | 43 |
| 1.6.5 Solubility and reactions in solution | 46 |
| 1.6.6 Thermal decomposition | 47 |
| 1.6.7 Infrared and NMR spectroscopy | 50 |
| 1.7 Tetracalcium phosphate | 50 |
| 1.8 Amorphous calcium phosphates | 53 |
| 1.8.1 Introduction | 53 |
| 1.8.2 Preparation | 53 |
| 1.8.3 Chemical composition | 54 |
| 1.8.4 Transformation reactions | 55 |
| 1.8.5 Infrared and NMR spectroscopy | 58 |
| 1.8.6 Structure | 60 |
| 1.8.7 Thermal decomposition | 61 |
| 1.8.8 ESR of X-irradiated ACP | 61 |
| Chapter 2 | |
| Fluorapatite and chlorapatite | 63 |
| 2.1 Introduction | 63 |
| 2.2 Structures | 64 |
| 2.2.1 Fluorapatite and the apatite structure | 64 |
| 2.2.2 Structural relationships of apatite | 70 |
| 2.2.3 Chlorapatite structure | 75 |
| 2.3 Substitutions in apatites | 80 |
| 2.3.1 Hexad axis substitutions | 80 |
| 2.3.2 Substitutions for calcium ions | 82 |
| 2.3.3 Substitutions for phosphate ions | 94 |
| 2.4 Preparation of powders | 95 |
| 2.4.1 High temperature methods | 95 |
| 2.4.2 Solution methods | 97 |
| 2.5 Growth of single crystals | 97 |
| 2.5.1 Fluorapatite | 97 |
| 2.5.2 Chlorapatite | 98 |
| 2.6 Infrared and Raman spectra | 99 |
| 2.6.1 Fluorapatite | 99 |

| | |
|---|-----|
| 2.6.2 Chlorapatite | 102 |
| 2.7 Other physical and chemical studies | 104 |

Chapter 3

| | |
|---|-----|
| Hydroxyapatite and nonstoichiometric apatites | 111 |
| 3.1 Introduction | 111 |
| 3.2 Structure of hydroxyapatite | 112 |
| 3.3 Preparation of stoichiometric hydroxyapatite powders | 118 |
| 3.3.1 Introduction | 118 |
| 3.3.2 Syntheses based on theoretical compositions | 119 |
| 3.3.3 Equilibrium syntheses in solution | 121 |
| 3.3.4 Miscellaneous methods | 124 |
| 3.4 Preparation of other apatites with hydroxyl ions | 125 |
| 3.4.1 Calcium-deficient and nonstoichiometric apatites | 125 |
| 3.4.2 Calcium-rich apatites | 127 |
| 3.4.3 Apatites with oxygen in different oxidation states | 127 |
| 3.4.4 Miscellaneous preparations, including solid solutions | 133 |
| 3.5 Growth of hydroxyapatite single crystals | 137 |
| 3.6 Special analytical methods | 139 |
| 3.6.1 Hydroxyl ion content | 139 |
| 3.6.2 Acid phosphate content | 141 |
| 3.6.3 Miscellaneous analyses | 145 |
| 3.7 Structure of calcium-deficient hydroxyapatites | 148 |
| 3.7.1 Introduction | 148 |
| 3.7.2 Surface adsorption | 148 |
| 3.7.3 Lattice substitutions | 149 |
| 3.7.4 Intercrystalline mixtures of OCP and OHAp | 153 |
| 3.7.5 Summary | 154 |
| 3.8 Kinetics of nucleation and crystal growth | 154 |
| 3.9 Solubility and interfacial phenomena | 157 |
| 3.10 Reactions in solution | 159 |
| 3.10.1 Adsorption and surface reactions | 159 |
| 3.10.2 Reactions with fluoride ions | 160 |
| 3.10.3 Rate of dissolution | 164 |
| 3.11 Infrared and Raman spectroscopy | 169 |
| 3.11.1 Introduction | 169 |
| 3.11.2 Hydroxyapatite spectrum | 170 |
| 3.11.3 High temperature OH stretching bands | 173 |
| 3.11.4 Bands from surface hydroxyl ions | 175 |

| | |
|--|-----|
| 3.11.5 Perturbations of OH bands by <i>c</i> -axis substitutions | 175 |
| 3.11.6 Other "hydroxyapatites" | 179 |
| 3.12 NMR spectroscopy | 182 |
| 3.13 Other physical and chemical studies | 186 |

Chapter 4

| | |
|---|-----|
| Mineral, synthetic and biological carbonate apatites | 191 |
| 4.1 Introduction | 191 |
| 4.1.1 Occurrence, nomenclature and early structural work | 191 |
| 4.1.2 Growth of single crystals | 196 |
| 4.2 Francolite and dahllite | 199 |
| 4.2.1 X-ray diffraction, chemical and optical studies | 199 |
| 4.2.2 Infrared and Raman spectroscopy | 207 |
| 4.2.3 Other physical and chemical studies | 212 |
| 4.3 A-type carbonate apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3$ | 213 |
| 4.3.1 Preparation | 213 |
| 4.3.2 Infrared and Raman spectroscopy | 215 |
| 4.3.3 Structure | 218 |
| 4.3.4 Other physical and chemical studies | 222 |
| 4.4 Synthetic high temperature B-type carbonate apatites | 223 |
| 4.4.1 Apatites containing fluoride ions | 223 |
| 4.4.2 Fluoride-free compounds | 225 |
| 4.4.3 Sodium-containing compounds | 227 |
| 4.5 Carbonate apatites from aqueous systems | 229 |
| 4.5.1 Introduction | 229 |
| 4.5.2 Assignment of IR and Raman carbonate bands | 230 |
| 4.5.3 Precipitated apatites (fluoride- and alkali-free) | 234 |
| 4.5.4 Precipitated apatites containing monovalent cations | 239 |
| 4.5.5 Precipitated apatites containing fluoride | 243 |
| 4.5.6 Reaction between alkaline phosphate solutions and calcium carbonate | 246 |
| 4.5.7 Thermal decomposition | 248 |
| 4.5.8 Other physical and chemical studies | 254 |
| 4.6 Biological apatites | 259 |
| 4.6.1 Introduction | 259 |
| 4.6.2 X-ray diffraction studies | 263 |
| 4.6.3 Infrared and Raman spectroscopy | 267 |
| 4.6.4 Thermal decomposition | 275 |
| 4.6.5 Reactions in solution | 281 |

| | |
|--|-----|
| 4.6.6 NMR spectroscopy and other physical and chemical studies . | 287 |
| 4.6.7 Calcium phosphates in biomaterials | 295 |
| 4.7 Electron spin resonance of X-irradiated carbonate apatites | 298 |
| 4.8 Summary | 301 |
| Appendix | |
| Calculated X-ray diffraction patterns of the calcium orthophosphates . . . | 305 |
| References | 311 |
| Index | 371 |