Mineral Aspects of Dentistry

Monographs in Oral Science

Vol. 10

Editor
Howard M. Myers, Philadelphia, Pa.


Mineral Aspects of Dentistry

F. C. M. Driessens
Institute of Dental Materials Science, Subfaculty of Dentistry.
Catholic University, Nijmegen

29 figures and 33 tables, 1982


Monographs in Oral Science

National Library of Medicine, Cataloging in Publication
Driessens, Ferdinand C. M.
Mineral aspects of dentistry
(Monographs in oral science; v. 10)
I. Title II. Series
W1 M0568E v.1O/WU 270 D779m
ISBN 3-8055-3469-8

Drug Dosage
The author and publisher have exerted every effort to ensure that drug selection and dosage set forth in this text are in accord with current recommendations and practice at the time of publication. However, in view of ongoing research, changes in government regulations, and the constant flow of information relating to drug therapy and drug reactions, the reader is urged to check the package insert for each drug for any change in indications and dosage and for added warnings and precautions. This is particularly
important when the recommended agent is a new and/or infrequently employed drug.

All rights reserved
No part of this publication may be translated into other languages, reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording, microcopying, or by any information storage and retrieval system, without permission in writing from the publisher.

© Copyright 1982 by S. Karger AG, P.O. Box, CH-4009 Basel (Switzerland)
Printed in Switzerland by Friedrich Reinhardt AG, Basel
ISBN 3-8055-3469-8

Contents

Acknowledgements IX
Preface XI
List of Symbols XIV
1. Introduction 1
1.1. Scope 1
1.2. Body Fluids 2
1.3. Importance of Solubility for the Interaction of Minerals with Body Fluids 3
1.4. Physico-Chemical Factors Relevant to the Aqueous Phase 4
1.5. Mineral Compounds and Mineral Solid Solutions 5
1.6. Solubility Product Principle for Mineral Compounds 7
1.7. Solubility Behaviour of Mineral Solid Solutions 8
1.8. Conclusion 11
2. Calcium Phosphates 12
2.1. Scope 12
2.2. Pertinent Calcium Phosphates 12
2.3. Solubility and Solubility Product of Calcium Phosphates; Potential Diagram 13
2.4. Intermediate Phases in the Precipitation of Calcium Phosphates 18
2.5. Calcium-Rich Calcium Phosphates Prepared at High Temperatures 23
2.6. Equilibration of Calcium-Rich Calcium Phosphates in Aqueous Solutions 25
2.7. Crystal Growth Studies 28
2.8. Dissolution Studies of Calcium Phosphates 29
2.9. Conclusion 30
3. Effect of Carbonate on Calcium Phosphates 32
3.1. Scope 32
Solutions 82
7.7. Electrochemical Potential Measurements on Tooth Enamel Membranes 83
7.8. Adsorption Model for Tooth Enamel Mineral 85
7.9. Hydrodynamic Models for the Comparison of Pore Volume Distribution and Diffusion Coefficients 88
7.10. Conclusion 90
8. Early Caries, a Reversible Phenomenon in Man 91
8.1. Scope 91
8.2. Caries, a Multifactorial Disease 91
8.3. Early in vivo Carious Lesions 94
8.4. Artificial Carious Lesions 96
8.5. Possible Mechanisms of Enamel Demineralization 99
8.6. Mathematical Simulation of Enamel Demineralization 101
8.7. Reactions of Tooth Enamel Mineral during Initial Demineralization 105
8.8. Remineralization Cycles in the in vivo Caries Process 107
8.9. Caries Prevalence and Composition of Saliva 108

Contents VII

8.11. Anticariogenic Effect of Phosphate Supplementation in Animal Experiments 110
8.12. Conclusion 111
9. Effect of Fluoride on Calcium Phosphates 113
9.1. Scope 113
9.2. Fluoride-Containing Calcium Phosphates; High-Temperature Studies 113
9.3. Fluoride-Containing Calcium Phosphates from Aqueous Solutions 116
9.4. Solubility of Fluoride-Containing Compounds 116
9.5. Thermodynamic Analysis of the Solubility Data of OHA-FA Solid Solutions 119
9.6. Equilibration of Fluoroxyhydroxyapatites 123
9.7. Precipitation, Crystal Growth and Dissolution Studies 126
9.8. Hydrolysis of Calcium Phosphates in the Presence of Fluoride Ions 127
9.9. Conclusion 128
10. Fluoride and Caries 129
10.1. Scope 129
10.2. Caries Prevalence and Fluoride in the Drinking Water 129
10.3. Mechanisms Proposed for the Anticariogenic Effect of Fluoride 130
10.4. Fluoride and Plaque 131
10.5. Pre-Eruptive Fluoride in Tooth Enamel 133
10.6. Posteruptive Fluoride and Tooth Enamel 135
10.7. Topical Applications of Fluoride
10.8. More Complex Fluorides for Topical Application
10.9. Water-Borne Fluoride and Animal Caries Reduction
10.10. Conclusion

11. Effect of Strontium on Calcium Phosphates
11.1. Scope
11.2. Strontium-Containing Calcium Phosphates; High-Temperature Studies
11.3. Strontium Phosphates and Ca-Sr-Phosphates from Aqueous Solutions
11.4. Solubility Studies in the System SrO-P2O5-H2O
11.5. Solubility Relations in the System CaO-SrO-P2O5-H2O
11.6. Other Ions Participating in Strontium Phosphates
11.7. Conclusion

12. Strontium and Caries
12.1. Scope
12.2. Caries-Reducing Effect of Water-Borne Strontium
12.3. Partition of Strontium in Tooth Enamel Mineral
12.4. Mechanism of the Anticariogenic Action of Strontium
12.5. Anticariogenic Effect of Strontium in Animals
12.6. Conclusion

13. Calculus
13.1. Scope
13.2. Dental Calculus in Man; Structure and Composition of the Mineral
13.3. Dental Calculus in Animals
13.4. Salivary Gland and Duct Stones
13.5. Physico-Chemical Factors Contributing to the Formation of Calculus
13.6. Conclusion

14. The Mineral in Dentin and Bone
14.1. Scope
14.2. The Mineral in Dentin
14.3. Composition of Bone Mineral vs Composition of Bone
14.4. X-Ray Diffraction and Electron Microscopy of Bone Mineral
14.5. Infrared Studies of Bone Mineral
14.6. Solubility of Bone Mineral and Osteoporosis
14.7. Fluoride and Bone Mineral
14.8. Strontium and Bone Mineral
14.9. Conclusion

References

Subject Index
Acknowledgements

I would like to express my gratitude to the ‘staf medische tekenkamer’ for preparing the figures and to Mr. van der Kamp and Mr. Bongaarts for drawing the figures. My task in writing this monograph was made easier by excellent secretarial assistance from Mrs. M. Strijbos.

Many concepts applied to biological calcium phosphates in this book have been developed in fields outside of dentistry, especially in the disciplines of solid-state chemistry and thermodynamics. My personal experience in these disciplines in the sixties was guided by Prof. Dr. G. D. Rieck of the University of Technology in Eindhoven, by Prof. Dr. H. Schmal-zied of the Max Planck Institute für Physikalische Chemie in Göttingen and by Prof. Ir. A. L. Stuyts of the Philips Research Laboratories in Eindhoven.

After my introduction in 1968 and 1969 in the field of dentistry by Dr. G. Brauer of the National Bureau of Standards, Washington, DC, and by Dr. W. E. Brown, Director of the ADA Health Foundation, stationed at the NBS, Washington, DC, I have applied the principles of solid-state chemistry and thermodynamics to the mineral aspects of dentistry. I enjoyed in the past years the inspiring and fruitful co-operation of Dr. Borggreven, Dr. van Dijk and Ing. Schaeken and later also of Dr. Scholberg in our Working Group on Enamel and Caries, which runs well not in the least by the much appreciated assistance of Ing. Hoppenbrouwers and Mr. Gorissen. Much of our work on calcium phosphates was so successful due to the essential and highly appreciated co-operation with Dr. Verbeeck and Dr. Thun from the State University Gent, Belgium, and with Ir. Heyligers from the University of Technology, Eindhoven. The editor has improved the text considerably.

The contribution of my wife Trudy and my children Manon, Pascale and Corine to this scientific work cannot be described by the word patience, but is more adequately indicated by the words stimulation, interest and persistence.

Preface

‘In the beginning there was apatite’
[Neuman and Neuman, 1973]

The theory of evolution is a fruitful working hypothesis although it may never be ‘proven’ in the same way as a single physical law by a straightforward path of physical experiments showing highly reproducible results. According to that theory the biosphere has evolved from the interactions between the lithosphere, the hydrosphere and the atmosphere. Today calcified tissues in living animals and man witness the dependence of even the latest products of evolution, on the lithosphere. Their mineralization is mediated through the internal medium, which reflects the original hydrosphere. Therefore, any theory about the mineral in
calcified tissues which neglects the rules that govern the lithosphere and the hydrosphere is bound to die. This book is intended to be a contribution to the demystification of our knowledge about the mineral in bone, dentine and especially tooth enamel. In the past too many investigators in this field of science have proposed too many hypotheses about nature and physiological behaviour of these minerals which neglect the rules of solid-state chemistry and thermodynamics, and which up to now serve too much as ad hoc proposals to explain some of the scientific observations qualitatively. An acceptable theory, however, is characterized by the fact that it gives a satisfactory explanation of all combined observations both qualitatively and quantitatively. The most important result of the reflections about the nature of the mineral in bone, dentine and tooth enamel based on the application of solid-state chemistry and thermodynamics is the multiphase concept of these minerals. This may be hard to accept especially for tooth enamel mineral, as by most of today’s physical observations only or mainly apatitic particles seem to be present. Yet, especially the solubility behaviour of these biological minerals in combination with the fact that different ma-

crominerals’ have a strong preference to be incorporated in different calcium phosphates necessitate the concept of a multiphase model. The multiphase models proposed by myself [1980] and with Verbeeck [1981a, b] may not be final. However, I feel that they can only be refined. This refinement will depend largely on the rate with which our physical and chemical methods of observation will develop to detect more and more detail about the physico-chemical behaviour of calcium phosphates. Epitaxy of two different apatite phases in each tiny mineral particle of bones and teeth may offer the main problems to ‘prove’ their existence therein physically. However, the chemical evidence summarized in this book is also evidence, although it may not seem to be so direct. Certainly it is not less conclusive.

Much research on the fundamental level about the physico-chemical behaviour of calcium phosphates is still necessary to give the three-phase model a better basis. In the present work much of the theory is derived from inductive instead of deductive thinking along the lines of solid state chemistry and thermodynamics. Unfortunately, many of the experiments carried out in the basic field of calcium phosphates stem from the thirties. Their results are tentative for the interpretations presented in the book, but these studies need reinvestigation and re-evaluation with today’s advanced experimental techniques. The fact that such studies have not been carried
out yet may be due to the circumstance that this ‘unbiological and unclinical’
type of research is so basic that despite of its fundamental contribution
it might seem to be irrelevant for dentistry. For some reasons it is unpopular
and has, in general, a low appreciation among most fellow
researchers in the dental field who must judge grant applications. This
makes progress much slower than it could be.

A conclusion derived from the multiphase model for the mineral in
calcified tissues is that the body fluids are constantly in or close to equilibrium
with that mineral. The frequently used expression as if body fluids
are highly supersaturated, does not apply in these general terms. Body
fluids are highly supersaturated with hydroxyapatite, but this mineral does
not form from the internal medium. This appears to be due to the constant
presence of Na+ and Mg2+ (remnants of the hydrosphere) and especially of
C02 (remnant of the atmosphere) in the internal medium. The view gained
by these reflections is that not some mystical action of the body through
complex biochemical reactions and several types of nucleation and crystal
growth inhibitors keep the body fluids supersaturated with hydroxyapatite;
no, it is the behaviour of calcium phosphates per se which in the

Preface XIII

presence of Na+, Mg2+ and C02 keeps the body fluids in metastable equilibrium
with bone mineral, and thus at a constantly high level of supersaturation
with hydroxyapatite.

One can only guess what the creatures who succeeded in precipitation
of calcium phosphates in some of their enchondral tissues have gained by
doing so. It is evident that this capacity created a constantly high level of
availability of phosphate ions to their living cells. This seems to fulfill a
basic need of living cells as living creatures act as scavengers of phosphate.
The best example to show this is the fact that phosphate ions have a certain
concentration in the deeper layers of the ocean which is in agreement with
the solubility product of a Na- and C03-containing apatite. However, the
phosphate concentration gradually decreases to very low values at the
ocean’s surface where there is biological activity.

As far as dentistry is concerned, there was and there still is a need to
find explanations for the mechanism of the anticariogenic actions of fluoride
and strontium. These explanations must be investigated on their
scientific acceptability both qualitatively and quantitatively, which ultimately
may serve the social acceptance of measures to diminish caries
experience. Similarly, the physiological factors which lead to the development
development of dental calculus should be identified in order to develop methods
to decrease the risk or the severity of parodontopathies. For these reasons
this book pays not only attention to fundamental aspects of minerals in
dentistry, but also to applied aspects. More conclusions with practical
implications about people’s dental health may be drawn from the contents
of this book than has been done here. Therefore, the book is an invitation
to the many investigators in the applied dental sciences to derive and apply
these conclusions.

Nijmegen, February 1981
F. C. M. Driessens

List of Symbols

Symbol Description Formula
ACP amorphous calcium phosphate Ca10(PO4)6(OH)2
APF acidulated phosphate-fluoride solution
Ca/P calcium/phosphorus molar ratio
CaOHA calcium hydroxyapatite Ca10(PO4)6(OH)2
DCP dicalcium phosphate (monetite) CaHPO4
DCPD dicalcium phosphate dihydrate (brushite) CaHP042H2O
DMFS decayed-missing-filled surfaces
DMFT decayed-missing-filled teeth
DOHA defective hydroxyapatite Ca9(HP04)((P04)5(0H)
DSP distronium phosphate SrHP04
ESR electron spin resonance
FA fluorapatite Ca10(PO4)6F2
HCDOHA heavily carbonated defective hydroxyapatite Ca9(P04)4 5(C03)1 5(OH)1. 5
HSP hexastrontium phosphate Sr6H3(P04)5 . 2H2O
Iax ion activity product for compound AX
IR infrared
K-ax solubility product for compound AX
MFP monofluorophosphate P03F2_
MWH magnesium whitlockite Ca9Mg(HP04)((P04)6
NCCA Na- and C03-containing apatite Ca8 5Na1. 5(P04)4 5(C03)i 5
NMR nuclear magnetic resonance
OA oxyapatite Ca10(PO4)6O
OCP octocalcium phosphate Ca8(P04)4(HP04)2 . 5H20
OHA hydroxyapatite Ca10(PO4)6(OH)2
p negative logarithm of -log
SCOHA slightly carbonated hydroxyapatite Ca10(PO4)6(OH,V,CO3,Cl,F)2
SrFA strontium fluorapatite Sr10(PO4)6F2
SrOHA strontium hydroxyapatite Sr10(PO4)6(OH)2
TCP tricalcium phosphate Ca3(P04)2
TSP tristrontium phosphate Sr3(P04)2
WH whitlockite Ca10(HPO4)(PO4)6