Mineral Aspects of Dentistry

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Mineral Aspects of
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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-

crinerals’ 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 CO2 (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 presence of Na+, Mg2+ and CO2 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 CO3-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 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
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) CaHP04H20
DMFS decayed-missing-filled surfaces
DMFT decayed-missing-filled teeth
DOHA defective hydroxyapatite Ca9(HP04)(P04)5(0H)
DSP distrotrium phosphate SrHP04
ESR electron spin resonance
FA fluorapatite Ca10(PO4)6F2
HCDOHA heavily carbonated defective hydroxyapatite Ca9(P04)4 5(C03)1 5(0H)1. 5
HSP hexastrotrrium phosphate Sr6H3(P04)5 . 2H20
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)1 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(P04)6(OH,V,C03,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