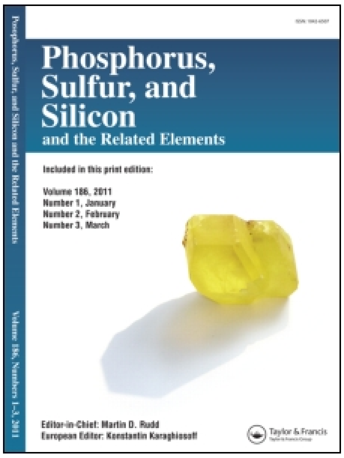
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Kinetics and Surface Energy Approaches to the Crystallization of Synthetic and Biological Calcium Phosphates

Wenju Wu; George H. Nancollas

To cite this Article Wu, Wenju and Nancollas, George H.(1999) 'Kinetics and Surface Energy Approaches to the Crystallization of Synthetic and Biological Calcium Phosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 125 — 128

To link to this Article: DOI: 10.1080/10426509908546198

URL: http://dx.doi.org/10.1080/10426509908546198

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 125-128
Reprints available directly from the publisher
Photocopying permitted by license only

Kinetics and Surface Energy Approaches to the Crystallization of Synthetic and Biological Calcium Phosphates

WENJU WU and GEORGE H. NANCOLLAS

Chemistry Department, State University of New York at Buffalo Buffalo, N. Y. 14260–3000 USA

Constant composition methods have been used to investigate the mechanisms of crystal growth and dissolution of synthetic and biological calcium phosphates. Interfacial tensions between water and each of these surfaces were calculated from measured contact angles using surface tension component theory. The data, 4.5×10^{-3}, $8.8 \times 10^{-3}$and 10.4×10^{-3} J m^{-2} for human dentin, human enamel and hydroxyapatite, respectively, compared well with the data calculated from dissolution kinetics experiments and provided information concerning the growth and dissolution mechanisms. The ability of a surface to nucleate other phases is closely related to the magnitude of the interfacial energies.

Keywords: Surface energy; mineralization; kinetics; dentin; tooth enamel; hydroxyapatite

INTRODUCTION

The mineralization of calcium phosphates, especially in biological systems, has often been suggested as proceeding through precursor phases such as amorphous calcium phosphate or octacalcium phosphate (OCP) before transformation to thermodynamically more stable phases such as hydroxyapatite (HAP) or fluorapatite (FAP). These processes may involve solid phase transformations or the dissolution of one phase and renucleation of the second phase on existing calcium phosphate surfaces. A factor which is usually ignored in discussions of such intergrowth processes is that of the surface free energy terms involved at the nucleating interface, despite the fact that surface free energy must play an important role. The kinetics of crystallization and dissolution of calcium phosphate phases both on synthetic minerals and dental hard tissues has been extensively investigated as a function of supersaturation, specific surface area, ionic strength and pH.. Recently, we have utilized either direct contact angle measurement with apolar and polar liquids or indirect measurement by thin layer wicking of test liquids through powder mineral samples, to estimate the surface and interfacial tensions using surface tension component theory. This paper discusses the role of interfacial tension in the mineralization and demineralization reactions of calcium phosphates.

METHODOLOGY

The constant composition (CC) method [1] was used to investigate the crystallization kinetics.

Contact angle measurements were made using a Gaertner (Chicago, IL) telemicroscope on smooth flat surfaces [2]. For finely divided powder particles, for which direct contact angle measurements cannot be performed, a thin layer wicking capillary rise procedure was used [2,3].

RESULTS AND DISCUSSION

Surface tension components of synthetic calcium phosphates and of dental enamel surfaces are summarized in TABLE I. It can be seen that the hydrophilicities and hydrophobicities vary widely; for example, dicalcium phosphate dihydrate (DCPD) is hydrophilic and relatively quite soluble while FAP is very hydrophobic and much less soluble. The hydrated layer of OCP is almost certainly hydrophilic in nature and it is more likely than the apatitic layer to result in a low interfacial free energy with an aqueous phase. In Table 1, it can be seen that a HAP surface has $\gamma^{-} = 16.0 \times 10^{-3}\ \mathrm{J\ m^{-2}}$ while for OCP, $\gamma^{-} = 19.7 \times 10^{-3}\ \mathrm{J\ m^{-2}}$. The surface properties of human dentin and human enamel are likely to be determined by the combined surface properties of apatite and proteins.

The mechanisms of crystal growth and dissolution are usually interpreted from the measured constant composition reaction rate as a function of thermodynamic driving forces. The effective order of reactions, n, for the calcium phosphate phases of interest in the present paper are summarized in TABLE I. It can be seen in TABLE I that interfacial tension values between the solutions and each of the mineral phases calculated from kinetics of crystallization and dissolution are of the same order of magnitude as those obtained from contact angle measurements. This provides strong justifications for the use of these methods to provide information about the mechanisms of crystallization and dissolution of these calcium phosphate phases.

TABLE I. Surface tension components (γ_S in 10^{-3} J m^{-2}) and interfacial tension (γ_{SL} in 10^{-3} J m^{-2}) between water and synthetic and biological calcium phosphates.

Solid	γ_S^{LW}	γ_S^+	γ_S^-	γ_{SL}^C	n	γ_{SL}^{KG}	γ_{SL}^{KD}	$\log S_\infty$
DCPD	26.4	1.6	31.7	-4.2	2.0	0.4	0.4	-2.22
OCP	21.6	2.2	19.7	4.3	3.3	7.1	2.9	-6.16
HAP	36.2	0.9	16.0	10.0	2.6	17.1	9.3	-6.44
FAP	32.4	0.6	9.0	18.5	2.1	30.0	17.1	-6.67
dentin	40.1	0.4	23.6	4.5	1.1	17.7	1.4	-5.78
Enamel	40.7	0.3	19.3	8.8	2.5	9.4	3.2	-6.11

γ^{KG} = interfacial tension from growth kinetics;

γ^{KD} = interfacial tension from dissolution kinetics.

S_∞ = solubility;

n = the reaction order based on growth (defined elsewhere[3,4]).

The crystal/solution interfacial tension may also related to the solubility, S_∞, of particles through equation (1)[4]

$$\gamma_{SL} = - A \log S_\infty + B \qquad (1)$$

where A and B are constants. It can be seen in Table 1 there is indeed a parallelism between interfacial tension and solubility, consistent with the model on which equation (1) is based, namely that during dissolution, some neighboring ions on the surface are replaced by water molecules to form units that escape into the bulk solution. Higher values of γ_{SL} indicate the greater difficulty in forming such an interface between the particles and the aqueous phase resulting in greater energy requirements for dissolution of the crystals.

In crystallization reactions, a smaller interfacial tension between the aqueous media and the solid phases suggests that the phase would have a greater tendency to be nucleated either on itself or on foreign surfaces. Despite the fact that the DCPD is the most soluble among the mineral phases in TABLE I, it forms under many physiological, geochemical and laboratory conditions. Hitherto, explanations for the preferential formation of DCPD in terms of reaction mechanisms have been only partially successful. In terms of surface tension data in TABLE I, however, this kinetic phenomenon may readily be explained in terms of the low interfacial tension values. At small thermodynamic driving forces for crystallization or dissolution, low vlaues of the interfacial tensions increase the tendency to precipitate or dissolve. The same arguments can be made for OCP. However, surfaces with low interfacial tensions also indicate thermodynamic instability, which would increase the tendency to transform to more stable apatite phases. This probably explains why DCPD and OCP have been so frequently implicated as possible precursors to the formation of apatites, especially in biological mineralization reactions involving tooth, bone, and calculus formation.

ACKNOWLEDGMENT

We thank the National Institute of Health (Grant DE 03223) for support of this work

References

[1] M. B. Tomson and G. H. Nancollas, *Science*, **200**, 1059 (1978).
[2] C. J. van Oss, *Interfacial Forces in Aqueous Media* (Marcel Dekker, New York, 1994), pp. 1–46.
[3] W. Wu and G. H. Nancollas, *Langmuir*, **13**, 861 (1997).
[4] W. Wu and G. H. Nancollas, *Adv. Dent. Res.* **11**, S66 (1997).