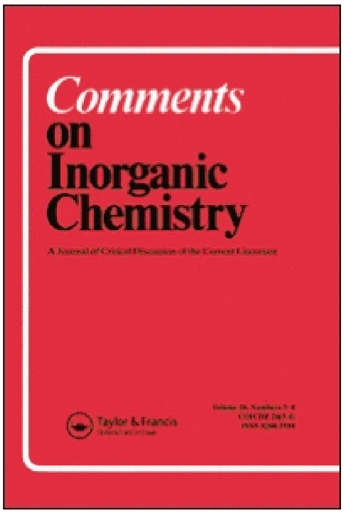

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Inorganic Chemistry of the Dissolution Phenomenon: the Dissolution Mechanism of Calcium Apatites at the Atomic (Ionic) Level

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Based on an example of the dissolution process of calcium apatites, a new chemical approach to elaboration of basic dissolution mechanisms of inorganic solids in liquids at the atomic (ionic) level has been proposed and discussed The approach is based on experimental results on the surface state analysis, passed through the logic of chemical equations, and describes the dissolution process as a sequence of the successive chemical reactions occurring on the solid–liquid interface. According to the approach elaborated, the chemical mechanism of apatite dissolution appears to be incongruent (non-stoichiometric) at the atomic (ionic) level.

Keywords: *inorganic chemistry of dissolution, chemical equations, dissolution mechanism, apatites, calcium phosphates, surface phenomena, solid-liquid interaction, atomic (ionic) level*

INTRODUCTION

The dissolution chemistry of solids in liquids turns out to be of great importance for a wide range of processes, like corrosion, electronic chip production, chemical separation and purification, not to mention utiliza-

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tion of industrial wastes.[1] That is why scientific investigation in this field continue to increase.[2] Currently, the general approach to the dissolution process looks like this: "At the fundamental level reactions between solids and liquids involve a coupled sequence of mass transport, adsorption/desorption phenomena, heterogeneous reaction, chemical transformations of intermediates, etc., whose identification, separation and kinetic quantification are all necessary if the "mechanism" of the process is to be fully understood and described" (Ref. 3, p. 10416). Ignoring the problems of mass transport and adsorption/desorption phenomena, a new approach to the chemical mechanisms of heterogeneous reactions among inorganic compounds is considered and discussed below. The dissolution mechanism of apatites in aqueous media is chosen here only as an example.

CHOICE OF THE APPROACH

The best way to investigate fundamentals of the dissolution/crystallization phenomena would be to the directly follow the dissolution/precipitation of *single* atoms, ions and molecules into/from a solution, but currently this is impossible. Despite the lack of such experimental techniques, first attempts to describe the dissolution process at the atomic (ionic) level have begun to appear[2–4] and the dissolution mechanism of apatite has turned out to be one among many others.[5–11]

Calcium apatites (fluorapatite $Ca_{10}(PO_4)_6F_2$ and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$) happen to be the main source of inorganic phosphorus in nature.[6] Natural fluorapatite is widely used as a phosphate rock for the production[7] of phosphorus containing fertilizers, and hydroxyapatite is the main inorganic part of animal and human bones and teeth.[8–11]As a result, the chemistry of apatite dissolution and crystallization is being widely investigated both for the fertilizer production industry[7] and for medicine,[8] including the problem of artificial bone creation (biomineralization[9] and bioceramics[10]), as well as that of dental caries protection.[11]

From the chemical point of view, such different processes, like phosphorus containing fertilizers production,[7] dental caries[11] and demineralization of bones as a result of some diseases,[9] appear to be rather similar, because all of them are well simulated with dissolution of calcium apatites.[6,7] The structure and chemical composition of the biogenic inorganic crystals,[12] including those of natural teeth and bones,[13] appear to be much more complicated, if compared with chemically pure apatite[6]; but synthetic apatites, mainly as non-stoichiometric hydroxycarbonateapatite (often with additives of some organic and biological substances), are widely used for the experimental investigations.[6,8–11]

Many attempts to elucidate dissolution mechanisms of solids in liquids are found in the literature.[1–4] Unfortunately, different researches often have different points of view of what is meant by the dissolution mechanism. For example, diffusion and kineticly controlled,[14,15] self-inhibition,[16,17] mono- and polynuclear,[18,19] two-site,[20] stoichiometric/non-stoichiometric (or congruent/incongruent),[5,21] etched pit formation,[22-24] ion exchange[25] and hydrogen catalytic[14,15,18,19] models have been proposed and elaborated for the acidic dissolution of apatite. These models are based on the results on dissolution kinetics and solution equilibrium in the system $Ca(OH)_2$–H_3PO_4–H_2O. This system appears to be very complicated, because phosphoric acid is known to be able to lose some water and form polymers ($H_4P_2O_7$ and $(HPO_3)_n$ are the simplest)[6], not to mention that calcium apatites are often found in a non-stoichiometric form, like $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ and $Ca_{10}(PO_4)_6(OH)_{2-2x}O_xV(OH)_x$ where $0 < x < 1$ and V(OH) means vacancy in the OH sublattice of the crystal structure.[6,8–11] The latter explains differences in the solubility constants of apatites measured by different researches (e.g., $pK_s \approx 114 - 119$ for hydroxyapatite and $pK_s \approx 121–127$ for fluorapatite).[6]

The difficulties above result in a situation where a great number of dissolution models have already been proposed.[14–25] Each model appears to be able to describe the dissolution process rather well but only within the experimental conditions investigated. On the other hand, the products of chemical interaction between apatites and acid solution are always the same: acidic calcium phosphates does not dependent on the dissolution model chosen for simulations The latter unambiguously points out that the basic chemical mechanism of apatite dissolution is always the same. Currently, the following chemical reactions are always used for the description of apatite dissolution[5–11,14–25]:

$$Ca_5(PO_4)_3(F.OH) + 7H^+ = 5Ca^{2+} + 3H_2PO_4^- + HF.H_2O \quad (1)$$

$$Ca_5(PO_4)_3(F.OH) \longrightarrow 5Ca^{2+} + 3PO_4^{3-} + F^-.OH^- \quad (2)$$

Both reactions "do not necessary give the mechanism but only express the net reactions" (Ref. 26, p. 333) and appear to contradict there being only one dissolution model as discussed above.[14–25] The latter points out that reactions (1) and (2) turn out to be more fundamental, if compared with other dissolution models.

Which reaction (1) or (2) describes the dissolution mechanism better was discussed by Pearce and Chow.[27] For the acidic dissolution of apatites, reaction (1) represents the direct chemical interaction between solid apatite and liquid acid (H^+), while Pearce suggests[27] the dissolution process might also happen according to reaction (2) followed by chemical interaction among the dissolved ions of apatite and those of acid in solution *near* the crystal surface:

$$5Ca^{2+} + 3PO_4^{3-} + F^-, OH^- + 7H^+ = 5Ca^{2+} + 3H_2PO_4^- + HF, H_2O \quad (3)$$

Currently, the unambiguous choice between two basic chemical models of dissolution (1) or (2) + (3) can not be made. To do so, one should succeed in following direct the detachment of *single* ions from the crystal surface into the bulk solution, but this is still impossible.

To conclude, the goal of this Comment should be formulated clearly. As mentioned above, previous investigations on the dissolution kinetics and solubility equilibrium resulted in a great number of dissolution models for apatites.[14–25] Each of them should be called "a mechanism" because each one appears to be valid within the limited experimental conditions (pH, hydrodynamics, undersaturation, temperature, etc.) only. However, all the above models deal with only one and the same chemical process: transformation of apatites into acidic calcium phosphates, as is described by the net reactions (1) and (2) + (3). If so then the basis "mechanism" of dissolution should describe transformation processes at the atomic (ionic) level. This "mechanism" should be sensitive neither to the dissolution kinetics nor to any external parameters (pH, hydrodynamics, undersaturation, temperature, crystal size, etc.) because it only deals with atoms, ions and molecules. The latter are objective and are only able to take part in the chemical transformations. Thus, the goal of this Comment is to demonstrate an application of the chemical approach in creation of basic dissolution mechanisms of inorganic solids in liquids using only apatites as an example.

EXPERIMENTAL BACKGROUND

Various sources of the experimental data on apatite dissolution were used in this presentation. For example, crystal surface of fluorapatite treated in acid was studied with three different methods of surface state analysis: Auger-electron spectroscopy (AES), scanning electron microscopy (SEM) and IR-spectroscopy.[5,28] During the investigations fluorine was found to leave the crystal surface completely, and a surface Ca:P ratio changed from that of apatite (1.65 ± 0.05) to that of acidic calcium phosphate (1.30 ± 0.05) (the results of AES); chemical changes of phosphate anions and the appearance of the libration band of hydroxyl were detected on the surface with IR-spectroscopy; acidic calcium phosphates $CaHPO_4{\cdot}2H_2O$ and $Ca(H_2PO_4)_2{\cdot}H_2O$ were found to have conductivity similar to that of apatites treated in acid (the results of SEM).[5,28] All these events were found to occur within the very thin surface layer, equal to penetration of the IR radiation, Auger- and secondary electrons, respectively (several nm, approximately). So, it is hardly possible to speculate about a new phase precipitated on the surface of apatites during dissolution.

Analysis of the references available was also used to extend the above information about surface phenomena of apatite dissolution. For example, the surface of apatites was found to be charged positively in acidic media and negatively in basic ones (i.e., an electrical double-layer at the interface between apatites and solution was detected).[29,30] According to the references, in acidic media the positive charge on apatites appears as a result of chemosorption either of protons[29] or calcium cations and protons[30] from the solution. Certainly, both of them are only hypotheses, because an experimental set-up able to verify unambiguously if the chemosorbed protons and/or calcium cations really cause the surface positive charge is not yet available.

Other results used are devoted to the sequence of ionic dissolution of apatites in acidic media. Fluorapatite was found to dissolve non-stoichiometrically (incongruently)[21,31,32]; moreover, the following sequence of atomic (ionic) dissolution was established: fluorine, next calcium and then phosphate.[31] This conclusion was made after determination of the specific dissolution rates of F^-, Ca^{2+} and PO_4^{3-} ions. A non-stoichiometrically high amount of fluorine dissolved compare to that of calcium and phosphate was also measured by other investigators.[21,32] Other investigators proposed the possibility that a surface coating formation on apatites being dissolved; the coating was supposed to consist of acidic calcium phosphates. [19,33,34]

Results obtained by Mika *et. al.*, should especially be described.[35] The authors investigated the role of the surface reactions in dissolution of stoichiometric hydroxyapatite at ranges of pH values within 4.90–9.94. They found that "the dissolution of hydroxyapatite in aqueous medium is always non-stoichiometric", but "when the solid was successively equilibrated at any given pH, the solution Ca:P ratio approached a limiting value of 1.67. Once this limiting value was reached, the solid only maintained this solution ratio by dissolving stoichiometrically" (Ref. 35, p 700). Moreover, "successive re-equilibration of hydroxyapatite at any given pH results in the formation of a surface whose composition is unique for that particular pH" (Ref. 35, p. 700). In other words, based on the results on Ca:P ratio in solution (chemical analysis), the authors found that a local non-stoichiometry always presented on the surface of hydroxyapatite dissolved, while in the bulk of solution the non-stoichiometry appeared at the very beginning of dissolution only and was transformed into the stoichiometry when dissolution progressed.

The experimental results on the surface modifications of hydroxyapatite ceramics in aqueous media by X-ray photoelectron spectroscopy (XPS) and Fourier-transformed IR-spectroscopy (FTIR) were also found.[36] An intermediate formation of $HPO_4{}^{2-}$ anions on the surface of apatite dissolved was established with FTIR. Moreover, a decrease of the Ca:P atomic ratio from the initial value of 1.50 (a non-stoichiomentic apatite was investigated) to 1.30 and even to 1.0 (the latter was interpreted as $CaHPO_4 \cdot 2H_2O$ formation on the surface) was measured with XPS on the surface of apatite dissolved. These changes were found to happen on the very surface of hydroxyapatite (the estimated depth 3–4 nm only). Moreover, using different angles of the XPS measurements (15, 45 and 90°), the authors found that the Ca:P ratio on the very surface of apatite was as low as 0.95–0.97 (investigations at an angle of 15°), while it increased to 1.13–1.18 (the same at an angle of 45°) and even to 1.26–1.30 (angle of 90°) with the increasing depth.[36] The latter points out that the surface layer is not homogeneous (it should be remembered that the overall thickness is only 3–4 nm, the latter corresponds to 3–5 unit cells of apatite[37]); it consists of different acidic calcium phosphates. The uppermost layer appeared to be more acidic, if compared with the internal ones, while the latter appeared to be more acidic, if compared with the bulk of apatite.[36]

Grechkin *et al.*[38] gave a thorough physicochemical analysis on the surface state both of natural and synthetic crystals of fluorapatite, as well as that of synthetic fluorapatite in which a fraction of Ca^{2+} ions were replaced with that of Ba^{2+}. The authors found that ions of Ba^{2+}

were distributed in the crystal lattice of $Ca_4Ba_6(PO_4)_6F_2$ non-uniformly: a relatively large portion of Ba^{2+} was in the Ca II sites and a smaller amount was in the Ca I sites.[39] The following dissolution experiments showed that despite the initial non-uniformity of Ca^{2+} and Ba^{2+}distribution in the crystal lattice of $Ca_4Ba_6(PO_4)_6F_2$, both ions always enter into the acidic solution in amounts proportional to their molar content. Hence, as the authors notice, "dissolution involves preferential cation removal neither from position I, nor from position II of the apatite structure" (Ref. 38, p. 1099). The latter points out that the dissolution of apatites occurs from the surface only: no dissolution from inside the crystals was found.

CHEMICAL INTERPRETATION

After the experimental results on apatite dissolution currently available have been described, one should ask whether it is possible to describe the chemical transformations of apatites into acidic calcium phosphates based on the above results. An application of the logic of chemical equations is demonstrated below.

At the very beginning it should be remembered that one molecule of apatite consists either of 42 (fluorapatite $Ca_{10}(PO_4)_6F_2$) or 44 (hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$) atoms. Is it possible to imagine that 42 or 44 atoms equal to a "single molecule" of apatite are simultaneously detached from the crystal surface to the bulk of solution according to net reaction (2) and dissolved according to net reaction (3)? Certainly this is hardly possible, and the experimental results above point to the non-stoichiomentic dissolution process of apatites[5,21,28,31–36]: first fluoride is dissolved[5,21,31,32], followed by calcium and then by phosphate.[5,31] What kind of dissolution model can be created from these results? Let's try thinking in a chemical way.

As soon as the apatites were found to dissolve, mainly in acids,[14,25] the role of protons became noteworthy. According to the results of AES[5] and references above,[21,31,32] fluoride ions of in fluorapatite should be dissolved first. But the results of IR-spectroscopy[5] pointed to hydroxyl incorporation into the crystal lattice of fluorapatite. Hydroxyl is known to be easily replaced with fluoride and back in the lattice channels parallel to the *c* axis.[6,11] So, it would be quite logical if an initial chemical equation describes the exchange of fluoride with hydroxyl or water:

$$Ca_5\,(PO_4)_3\,F + H_2O{+}H^+ = Ca_5\,(PO_4)_3\,(H_2O)^+ + HF \qquad (4)$$

Here incorporation of water instead of hydroxyl is chosen, because in strongly acidic solutions investigated (2–7 M H_3PO_4) incorporation of basic hydroxyl seems to be very unusual. The proton in Equ. (4) is supposed to be previously chemosorbed on the surface of fluorapatite crystals (positive charge formation[29,30]) and is used as a catalyst [14,15,18,19] for removing fluorine and water incorporation instead. The possibility of such a substitution was discussed in literature.[40] Moreover, Eq. (4) gives another possible explanation of the surface positive charge formation on apatites. Here the positive charge is a result of replacing negatively charged fluoride anions with neutral molecules of water. It does not mean that this article contradicts the previous explanation given in the references (sorption of protons)[29,30]; this article gives only another reasonable hypothesis.

When fluoride has been dissolved completely, the surface differences between fluorapatite and hydroxyapatite disappear and formation of acidic calcium phosphates is described in a similar way. As soon as chemical Equ. (4) results in simultaneous surface positive charge formation, a possibility for further interaction of other protons with the surface decreases. To solve the problem, a dissolution of one calcium cation might easily be supposed:

$$2Ca_5\,(PO_4)_3\,(H_2O)^+ = 3Ca_3\,(PO_4)_2 + Ca^{2+} + 2H_2O \qquad (5)$$

Chemical reaction (5) corresponds completely with the references (calcium dissolves ahead of phosphate[31] and a surface non-stoichiometry of dissolution appears[35]) and partly with the results of AES,[5,28] because for intermediate $Ca_3(PO_4)_2$ obtained, the Ca:P ratio is 1.50 (i.e., the ratio is already below 1.65 ± 0.05, but it still exceeds 1.30 ± 0.05). The suggestion about the possibility of intermediate $Ca_3(PO_4)_2$ formation according to reaction (5) becomes more reasonable after taking into consideration that this substance was found to be a precursor of apatite formation during chemical crystallization.[6,41] If $Ca_3(PO_4)_2$ appears to be a precursor of apatite crystallization, it is quite logical to suppose that it also might happen to be a virtual intermediate product of apatite dissolution.

After removing of the local positive charge in reaction (5), further interaction between protons and intermediate $Ca_3(PO_4)_2$ obtained might be described as follows:

$$Ca_3\,(PO_4)_2 + 2H^+ = Ca^{2+} + 2CaHPO_4 \qquad (6)$$

Here another calcium cation was replaced with two protons. Equation (6) corresponds completely to the references (calcium dissolves ahead of phosphate,[31] a surface non-stoichiometry of dissolution appears,[35] and intermediate $CaHPO_4{\cdot}2H_2O$ is formed on the very surface[19,33,34,36]), with the results of SEM and IR-spectroscopy[5,28] and partly with those of AES,[5] because for $CaHPO_4{\cdot}2H_2O$ the Ca:P ratio is already 1:1 (i.e.), below 1.30 ± 0.05). A possible explanation of this difference is very easy: an intermediate mixture of $CaHPO_4{\cdot}2H_2O$ and $Ca_3(PO_4)_2$ is formed on the surface of the apatite dissolved, as directly follows from the results of XPS measurements.[36] It should be noted that $CaHPO_4{\cdot}2H_2O$ was also found to be a precursor of apatite formation.[41] Thus, reaction (6) contradicts nothing.

At last, phosphate ions also dissolve:

$$CaHPO_4 + 2H^+ = Ca^{2+} + H_3PO_4 \qquad (7)$$

Reaction (7) describes the final stage of apatite dissolution. The products obtained are rather obvious: a calcium containing salt CaX_n(X is an acidic anion) and phosphoric acid, if an acid HX used for dissolution is stronger than H_3PO_4. If apatites are dissolved in acids less strong than H_3PO_4, reaction (8) should be written instead of (7):

$$CaHPO_4 + H^+ = Ca^{2+} + H_2PO_4^- \qquad (8)$$

As soon as the above dissolution of apatites occurs in aqueous media, all ions and molecules mentioned above should be hydrated, but the hydration effect, as well as an influence of acidic anions X^{n-} to the dissolution mechanism, are omitted everywhere for simplicity.

To conclude the chemical part, one should mention the investigations on the hydroxyapatite growth mechanism studied with atomic force microscopy. A cluster growth model was created as a result.[42]According to the model proposed, "hydroxyapatite contains two crystallographically distinct, but same size (8.15 Å × 8.7 Å) $Ca_9(PO_4)_6$ cluster units".[42] The above chemical mechanism (4)–(8) appears to be in good agreement with this model too, because three intermediate molecules of $Ca_3(PO_4)_2$ are supposed to appear in chemical reaction (5). One need not have a great imagination to suppose the formation of one intermediate cluster of $Ca_9(PO_4)_6$ instead

THEORETICAL PREDICTIONS

The above described logic of chemical equations provides an opportunity to extend an application of the dissolution mechanism (4)–(8) to the dissolution process of apatites in neutral and basic solutions. Numerical values of the solubility constants of apatites in water have already been mentioned above ($pK_s \approx 114–119$ for hydroxyapatite and $pK_s \approx 121–127$ for fluorapatite).[6] Both values correspond to concentration of the saturated solution of 10^{-6} M or 1 mg/L. So, dissolution of apatites in water also happens a little. What kind of dissolution models can be proposed in terms of the above logic of chemical equations?

Unfortunately, no information about the surface state of apatites in neutral and basic media was found in literature, except that of surface charge.[29,30] Apatites were found to have zero surface charge in neutral solutions ($pH \approx 6–8$) and be charged negatively in more basic solutions ($pH > 8$). The latter was explained by sorption of hydroxyl anions onto calcium cations of apatitic surface.[29,30] Taking into consideration the only experimental fact available, and supposing (as a first approximation) that the sequence of ionic dissolution of apatites remains the same, the system of successive chemical equations (4)–(8) might be modified as follows:

$$Ca_5(PO_4)_3F = Ca_5(PO_4)_3^+ + F^- \qquad (9)$$

$$2Ca_5(PO_4)_3^+ = 3Ca_3(PO_4)_2 + Ca^{2+} \qquad (10)$$

$$Ca_3(PO_4)_2 = 2CaPO_4^- + Ca^{2+} \qquad (11)$$

$$CaPO_4^- = Ca^{2+} + PO_4^{3-} \qquad (12)$$

A similar system of chemical equations (9)–(12) for dissolution of apatites in neutral solutions and water has been created as a result A surface positive charge, obtained in Eq. (9), is compensated by a negative one in Eq. (11). Thus, the experimental condition of zero surface charge [29,30] is fulfilled. One should notice that the system of chemical equations (9)–(12) represents possible intermediate stages for Eq. (2).

A dissolution model in strongly basic solutions can be proposed in a similar way:

$$Ca_5(PO_4)_3F + OH^- = Ca_5(PO_4)_3(OH) + F^- \qquad (13)$$

$$2Ca_5(PO_4)_3(OH) = 3Ca_3(PO_4)_2 + Ca(OH)_2 \qquad (14)$$

$$Ca_3(PO_4)_2 + 2OH^- = 2CaPO_4^- + Ca(OH)_2 \qquad (15)$$

$$CaPO_4^- + 2OH^- = Ca(OH)_2 + PO_4^{3-} \qquad (16)$$

Here the experimental condition of negative surface charge formation[29,30] is fulfilled in chemical equation (15). From a first point of view, the dissolution model (13)–(16) proposed seems to contradict the experimental results on hydroxyapatite solubility in alkali solutions of ammonia (pH = 11).[43] The hydroxyapatite was found to dissolve incongruently: the Ca:P ratio in the solution was as low as 0.01–0.02, while that in hydroxyapatite was 1.66–1.68.[43] The latter seems to point to the preference of phosphate dissolution compared to that of calcium, but it is not the only case. Here one should not mix two different phenomena: a solubility and a dissolution mechanism. The former describes an equilibrium between the crystal surface and the bulk of a solution, while the latter describes a process of chemical transformation of initial reagents into the final products. So, the experimental results on the Ca: P ratio of 0.01–0.02 found in the solution at pH = 11 can be explained by precipitation of $Ca(OH)_2$ on the surface of hydroxyapatite equilibrated in aqueous ammonium solution. Calcium hydroxide is known to have a low solubility, while ammonium phosphates are known to be highly soluble in basic solutions.[6,7] If so, the solution quickly becomes saturated and even supersaturated with calcium hydroxide and remains undersaturated with ammonium phosphates. The latter results in precipitation of $Ca(OH)_2$ and drastically decreases the Ca:P ratio in the solution as a result. It is interesting to note that the well-known[6,41]precursor of apatites crystallization–$Ca_3(PO_4)_2$ – happens to be predicted as an intermediate during dissolution of apatites both in neutral (10) and basic (14) media. So, this compound turns out to be of a special importance in the chemistry of apatite dissolution/precipitation.

At the end ofthis part, one should mention that the influence of water and other ions is also omitted in chemical reactions (9)–(16), as has been done in Eq. (4)–(8). The appropriate chemical changes in dissolution models (9)–(12) and (13)–(16) can be made when new experimental information about the surface properties of apatites in neutral and basic media become available.

CONCLUSIONS

Based on the example of acidic dissolution of apatites, a new chemical approach to investigation of the dissolution mechanisms of solids in liquids has been developed. The approach is based on the results of surface state analysis, passed through the logic of chemical equations. The mechanisms obtained appear to operate with molecules and ions only. The latter are objective and independent of the experimental conditions chosen. This provides a unique possibility for using and discussing any experimental results, taken from the references, independent of the specific dissolution conditions investigated. That is why the chemical mechanism of apatite dissolution in acids (4)–(8) appears to be insensitive to variations in crystal size, hydrodynamics, undersaturation, temperature, pH, etc.[5] These parameters were found to change the dissolution kinetics (i.e., the rates of chemical reactions (4)–(8)) only, but not the dissolution mechanism). The mechanism (4)–(8) turns out to be sensitive only to the presence or absence of ions, atoms and molecules, those able to make chemical competition in interaction with calcium, phosphate, hydroxyl and fluorine ions being dissolved. One can also expect that the similar dissolution models in neutral (9)–(12) and basic (13)–(16) media would also be insensitive to variations of the above parameters.

For the first time the new chemical models precisely describe a chemical irregularity (incongruence) of dissolution of different ions at the atomic (ionic) level, and they appear to be more basic if compared with other dissolution models suggested previously. Nevertheless, further precise investigations are necessary to verify the suggestions made in this Comment.

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