Journal of Solid State Chemistry **151,** 163–169 (2000)
doi:10.1006/jssc.1999.8615, available online at http://www.idealibrary.com on IDEAL®

Effects of Nickel on Calcium Phosphate Formation

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Received June 8, 1998; in revised form August 16, 1999; accepted December 15, 1999

We have investigated the effect of nickel on calcium phosphate formation from aqueous solutions. The calcium phosphates prepared under different reaction conditions (pH, temperature, and nickel concentration) were characterized by X-ray diffraction, FTIR spectroscopy, and chemical analysis. The apatite compounds were also studied thermogravimetrically. From the combined results of the techniques employed we have determined that nickel favors the formation of brushite and amorphous calcium phosphate. We have found, as well, that the presence of nickel in the solution inhibits calcium hydroxyapatite (CaHAP) and octacalcium phosphate formation. However in the synthesis performed at basic pH and 95°C the apatitic phase (HAP) could be obtained. The present results suggest that the presence of nickel may modify the precipitation of oral calcium phosphate. © 2000 **Academic Press**

INTRODUCTION

The calcium phosphates have been studied extensively because of their occurrence in normal and pathological calcifications and also because of their use in bone implant materials or as coating for such implants. These systems include brushite (DCPD), octacalcium phosphate (OCP), monetite, calcium hydroxyapatite (CaHAP), and whitlockite [1].

In particular, the conversion of amorphous calcium phosphate (ACP), monetite, and DCPD into crystalline hydroxyapatite has been studied by different methods [2–4]. The results of investigations performed by various authors reveal that the reaction conditions, such as pH, temperature, and the presence in the mother solution of stabilizing or inhibiting agents, influence the reaction products obtained. The inhibitory effect of Mg^{2+} is well known, and Zn^{2+} and Mn^{2+} have been found to have a similar effect [5–7]. Despite the unquestionable progress in this field of work, uncertainties remain about the effect of ions such as Ni^{2+}, Co^{2+}, and Cr^{2+} on calcium precipitation [8].

It has been shown that nickel, tin, and chromium can elute from dental casting alloys *in vitro* and *in vivo* [9–11]. This metal elution may occur in the mouth from dental castings as a result of corrosion of the metal induced by the environmental tissue. The presence of those metals in the mouth might influence oral calcium phosphate formation. For this reason, it is important to investigate the effect of these metals on calcium phosphate precipitation.

The aim of this work is to understand the effect of nickel on calcium phosphate formation. To that end, calcium phosphates were prepared under different reaction conditions (pH, temperature, and nickel concentration). All products were investigated using X-ray diffraction, FTIR spectroscopy, and chemical analysis. Thermal analysis of the apatite and the amorphous compounds was also performed.

MATERIALS AND METHODS

Analytical reagent grade chemicals and freshly distilled water were used throughout the preparation of the solutions.

Pure samples of calcium phosphate were prepared for comparative use according to different methods reported in the literature [12–14].

Pure brushite was prepared by the method of Toubborg-Jensen and Rathlev [12]. A solution containing $Na_2HPO_4 \cdot 8H_2O$ and KH_2PO_4 and a solution containing $CaCl_2 \cdot 6H_2O$, both 0.1 M, were prepared. These solutions were added simultaneously, at the same rate, to a constantly stirred solution containing 0.1 M KH_2PO_4 at 25°C; the addition rates were maintained in order to keep the pH at 4.8. The precipitate was filtered, washed with 0.05% H_3PO_4, and dried at 60°C.

Amorphous tricalcium phosphate was prepared by adding a solution containing $Ca(NO_3)_2$ to a vigorously stirred $(NH_4)_2HPO_4$ solution at pH 10, followed by immediate

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0022-4596/00 $35.00

filtration of the precipitate, which was then washed with NH_4OH and acetone.

Finally, the preparation of pure samples of CaHAP was performed, after Hayek and Newseley [14], by the addition of an aqueous $(NH_4)_2HPO_4$ solution in NH_4OH (pH 12) to an aqueous solution of $Ca(NO_3)_2$ in NH_4OH (pH 12).

To study the effect of nickel on calcium phosphate formation from aqueous solutions, different reaction conditions were used. The phosphates were prepared by dropwise addition of two 0.2 M solutions (one of calcium and nickel acetate and the other of ammonium phosphate) to a stirred solution of ammonium acetate.

The synthesis process can be represented by

$$\begin{gathered} HPO^{2-}_{4\,aq} + Ni^{2+}_{aq} + Ca^{2+}_{aq} + H_2O \\ \rightarrow (Ca, Ni)_{10}(PO_4)_6(OH)_2 + H^+. \end{gathered}$$

During the synthesis an increase in H^+ is produced. Then, to keep the pH of the solutions constant, 0.1 M NH_3 or acetic acid was added.

The experimental reaction conditions were temperature 25 and 95°C, pH 7 and 9. The conditions chosen were designed to observe the influence of pH and temperature on the formation of calcium phosphates. Hydrolysis of ACP and DCPD (95°C) in solutions containing Ca^{2+} and Ni^{2+} ions at pH 7 was also performed.

The composition of the solution was varied in steps, from pure calcium acetate to 25% Ni and 75% calcium acetate. The precipitate was stored for 30 h in contact with its solution and then filtered off, washed with distilled water, and dried at 100°C. In the case of the apatite compounds, they were dried at 200°C for 6 h to improve their crystallinity.

The pH measurements were made with an MV 870 Digital pH-Messegerät using a combined glass electrode. The latter was calibrated at 25°C with a buffer prepared according to the National Bureau of Standards [13]. The composition of the products was checked by the determination of Ca, Ni, and P contents. Calcium was determined by complexometry with EDTA [13]. Nickel was determined by atomic absorption spectrophotometry (Perkin–Elmer Model 3110), and phosphorous was determined spectrophotometrically by a method developed by Portal [15].

For IR absorption analysis, 1 mg of the powdered sample was carefully mixed with 300 mg of KBr (infrared grade) and pelletized under vacuum. The FTIR spectra were recorded with a Bruker 66 spectrometer in the range 4000–400 cm^{-1}.

The X-ray diffraction (XRD) patterns were obtained using a standard Philips PW-1710 diffractometer with a scintilation counter and an exit beam graphite monochromator. Cu$K\alpha$ ($\lambda = 1.5406$ Å) radiation was used to obtain data in the $5 \leq 2\theta \leq 70°$ range at a scanning speed of 1°/min.

The thermogravimetric and differential thermal analyses were done with a Mettler TA2 system. One hundred milligrams of material was heated in pure, dry N_2 up to 500 and 1000°C and the weight loss was recorded (heating rate 5°C/min).

RESULTS

The calcium phosphate phases, obtained using different reaction conditions, were characterized by XRD and FTIR. The results are shown in Table 1.

From the Products of the Reaction at 25°C and pH 7

The solid phases, obtained from [Ni/Ca] molar ratio solutions ranging from 0.03 to 0.25 and dried at 100°C, were characterized by X-ray diffraction, FTIR, and chemical analyses. In all cases the only phase found corresponds to (Ca, Ni)$HPO_4 \cdot 2H_2O$ (DCNPD). The FTIR spectrum of the sample obtained from the [Ni/Ca] 0.03 solution has not shown any significant difference from the corresponding spectrum of brushite. The same result was obtained with the increase in the [Ni/Ca] ratio to 0.2. A poorer resolution of the PO absorption bands was observed in the DCNPD obtained from the solution with [Ni/Ca] 0.25. The spectra of DCPD and DCNPD are shown in Fig. 1. This figure illustrates the lack of resolution and/or shift of the frequencies in all the DCNPD samples. In particular the resolution of the components at 1200–1000 cm^{-1} decreases with the increment of nickel content in the precipitate. Shoulders in the bands at 563 and 506 cm^{-1}, respectively, were observed in the spectra of the materials prepared from the solutions with the higher nickel concentrations.

The comparison of the DCNPD XRD pattern with that of DCPD showed a shift in the principal reflections. Then the changes in the unit cell parameters produced when the nickel content in solution was incremented were computed and are presented in Table 2. An increase in the line width was observed in the X-ray pattern of the DCNPD obtained from the [Ni/Ca] 0.25 solution, thus indicating reduction in the crystallite size and/or increase in the strain.

TABLE 1
Effect of Nickel on Calcium Phosphate Formation

[Ni/Ca]	pH 7 (25°C)	pH 7 (95°C)	pH 9 (25°C)	pH 9 (95°C)
0	HAP	HAP	HAP	HAP
0.03	DCNPD	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.05	DCNPD	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.1	DCNPD	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.2	DCNPD + ACNP	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.25	DCNPD + ACNP	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP

Note. DCNPD = Ni-substituted DCPD. ACNP = Ni-contained ACP.

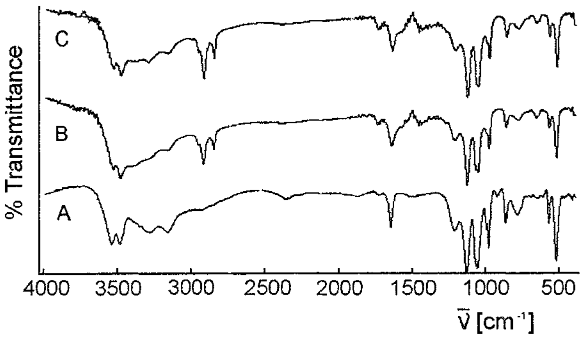

FIG. 1. IR spectra of (Ca, Ni)$HPO_4 \cdot 2H_2O$ obtained from solutions with different [Ni/Ca] ratios: (A) 0, (B) 0.03, and (C) 0.05.

From the Products of the Reaction at 95°C and pH 7

Under this reaction condition no precipitates were observed after 24 h. Another 24 h in contact with the solution was needed to obtain a solid phase. The concentration of Ni in solution determines the formation of ACP or the formation of ACP and its posterior transformation to a calcium-deficient apatite. At the lowest [Ni/Ca] ratio 0.03, the formation of Ni-containing amorphous calcium phosphate, which transformed to CaHAP after 48 h in solution, was obtained. At the highest [Ni/Ca] concentration, 0.25, the amorphous phase was stabilized. It remained amorphous even after 100 h in contact with the mother liquor. This behavior is similar to that observed after hydrolysis, at 100°C, in a solution free of Ni. Table 3 summarizes the formation and transformation of amorphous phosphates in the presence of different concentrations of Ni in solution. As was observed in previous works [16, 17], increasing the Ni content in solution stabilizes the amorphous calcium nickel phosphate (ACNP) obtained (Fig. 2). The transformation of ACNP to other crystalline phases is possible only at a low [Ni/Ca] ratio. Brushite, whitlockite, or other Ni phosphates have not been observed as products of the transformation of ACNP. However, at very high nickel concentrations, [Ni/Ca] ratio larger than 0.6, it has been determined that $NiNH_4PO_4 \cdot nH_2O$ is formed [16].

The thermal analysis showed that the ACNP crystallizes to HAP in aqueous solution, whereas in a dry atmosphere it crystallizes to TCP on heating (Fig. 3). A peak around 130°C corresponds to dehydration of ACP. No other mass loss is observed in the thermogram; this is due to the high [Ca]/[P] ratio, which favored the formation of β-TCP.

TABLE 2
Crystallographic Data Obtained from the Least-Square Refinement of the Cell Parameters

Sample	*a* axis (Å)	*b* axis (Å)	*c* axis (Å)	β angle (°)	Volume (Å)	Symmetry
DCPD	6.363	15.19	5.815	118.5	493.93	Monoclinic
Ni_5	6.363 (1)	15.178 (2)	5.811 (1)	118.53 (2)	493.2 (1)	Monoclinic
Ni_{10}	6.359 (1)	15.171 (2)	5.808 (1)	118.49 (2)	492.5 (1)	Monoclinic
Ni_{15}	6.356 (2)	15.166 (3)	5.802 (1)	118.45 (2)	491.7 (2)	Monoclinic
Ni_{20}	6.361 (4)	15.16 (1)	5.807 (4)	118.52 (5)	492.2 (4)	Mixture

From Reaction at pH 9 and Two Different Temperatures (25 and 95°C)

The results of the XRD and FTIR analysis of the products of the reactions at pH 9 showed the formation of an apatitic phase. The increase in Ni content in the solution causes a decrease in its crystallinity (see Figs. 4A–B/C). A higher degree of crystallinity was observed in the products obtained at 95°C (see Figs. 4C and 4D). The determination of nickel content in the solid phase (see Table 4) showed that the incorporation of nickel into the reaction product structure is very limited. Moreover, the increase in Ni concentration in solution does not produce higher incorporation of Ni into the crystal structure. Table 4 also shows that the products of the reaction at 95°C, present an incorporation of Ni in the solid phase lower than that of the products obtained when the reaction was performed at 25°C. In the 95°C reaction most of the Ni in the solution forms the complex $[(Ni(NH_3)_6)].Cl_2$.

All the products of the reaction performed at pH 9 were thermally treated at 200°C. The treated samples showed a decrease in Ni content (Table 5). The IR spectra also showed differences. The absorption bands characteristic of the internal PO_4^{3-} and OH^- modes appeared sharper and more intense after heat treatment (Fig. 5). The phosphate signals at 963 and 566 cm^{-1} are shifted from the HAP bands positions. This finding reinforced the assumption that Ni is incorporated in the apatite structure. The absence of other bands at 970, 940, 580, and 550 cm^{-1} confirms, in agreement with the XRD results, that another phase like whitlokite is not present. However, the presence of bands at 1278, 877, and 575 cm^{-1} suggests the existence of HPO_4^{2-} in the sample. It is known that at pH in the alkaline region the systems $Ca{-}PO_4^{2-}{-}OH^-$ do not favor the incorporation of HPO_4^{2-}. However, the absence of the band corresponding to CO_3^{2-} in the region of 1500–1400 cm^{-1} in the IR spectra allows us to interpret the signal at 870 cm^{-1} as due to the presence of HPO_4^{2-} ions. These could be forming a new phase. They could also be incorporated in the HAP crystal structure or adsorbed on its surface. The XRD patterns of Ni, Ca phosphates only show the HAP pattern. The absence of $CaHPO_4 \cdot 2H_2O$ and $CaHPO_4$ reflections (0, 2, 0), (0, 2, 1), and (1, 1, 1) demonstrated that the ion HPO_4^{2-} does not form another phase. These results also indicate that HPO_4^{2-} is part of a structure that can be described as $(Ca, Ni)_{10}(PO_4)_{6-x}(HPO_4)_x(OH)_2$.

The thermogravimetric analyses carried out to gain further insight into the structural changes produced by the incorporation of Ni in the apatite phase (Fig. 6), showed, for

TABLE 3
Stability of Synthetic Amorphous Calcium Phosphates

Contributing ions [Ni/Ca]	In mother liquor (24 h)	In mother liquor (48 h)	In mother liquor (96 h)	In H_2O (100°C)
0.03	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.05	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.1	ACNP	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.2	ACNP	ACNP	(Ca, Ni)HAP	(Ca, Ni)HAP
0.25	ACNP	ACNP	ACNP	ACNP

Note. h, hours.

the (Ca, Ni)HAP prepared at 95°C and basic pH, different weight losses. According to Arends *et al.* [18] the losses produced up to 200°C (on the samples treated at 200°C) are due to H_2O liberation while the apatite structure is retained and the ones in the ranges 200–500°C (with possible additional H_2O loss) and 700–890°C can be related to the HPO_4^{2-} ions through

$$2\ HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$$

$$P_2O_7^{4-} + 2HO(-) \rightarrow 2PO_4^{3-} + H_2O.$$

The 200–500°C zone has been characterized by other authors. However, their results cannot be compared with the present ones because they have studied samples previously treated at 300 to 500°C to improve crystallinity [6]. The observed weight lost between 750 and 890°C can be attributed to the conversion of (Ca, Ni)HAP into two phosphate phases (apatite and TCP). This transformation is a characteristic of nonstoichiometric CaHAP [19].

DISCUSSION

$Ca_{10}(PO_4)_6(OH)_2$ (CaHAP) is the most stable of the calcium phosphates. Therefore, we expected that small quantities of Ni in the solution would induce (Ca, Ni)HAP formation. However, this was not observed when the reaction proceeded at neutral pH. The presence of nickel in the solution favored the formation of the ACP and DCPD phases and inhibited the formation of HAP. In the absence of nickel, under all the reaction conditions, it is possible to synthesize CaHAP. A small concentration of nickel in the solution changes the reaction products, inducing the formation of a compound less stable than the stoichiometric CaHAP. This is due to the replacement of calcium (ionic radius 0.99 Å) by nickel (ionic radius 0.66 Å), which provokes strain in the PO_4^{3-} net due to the shortening of the M–PO_4 and M–M bond length distances. It also induces voids in the structure that can be occupied by small ions or molecules such as water. It also needs to be taken into account that the amount of nickel entering into the structure is smaller than expected. A limited proportion of nickel in the structure provokes calcium deficiency and vacancies. Thus, the number of vacancies (or voids) will be larger than the amount foreseen from a one-to-one substitution of nickel for calcium. This will induce a [(Ca, Ni)/P] ratio smaller than the expected 1.67, helping to further destabilize the HAP structure. As a consequence, compounds that are

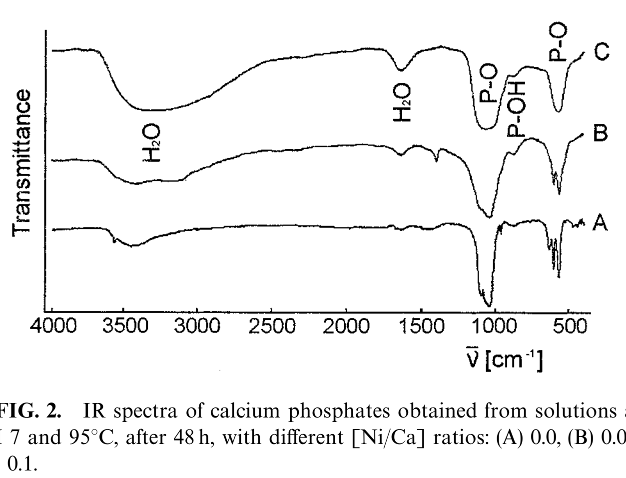

FIG. 2. IR spectra of calcium phosphates obtained from solutions at pH 7 and 95°C, after 48 h, with different [Ni/Ca] ratios: (A) 0.0, (B) 0.05, (C) 0.1.

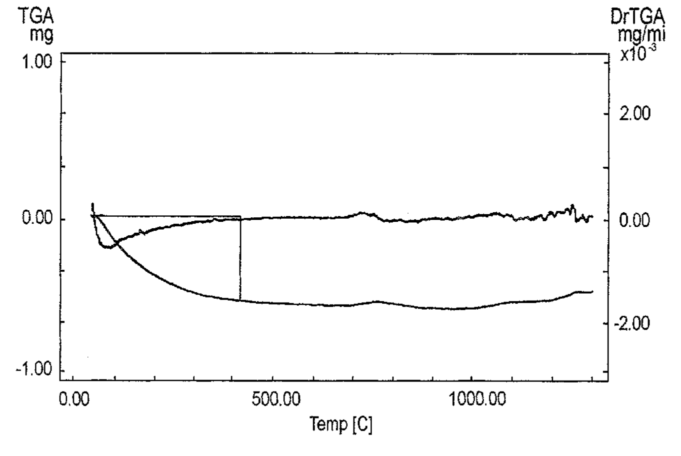

FIG. 3. TGA curves of the ACNP synthesized from a pH 7 and 95°C solution with a [Ni, Ca] ratio of 0.05. Total mass loss; – 0.54 mg.

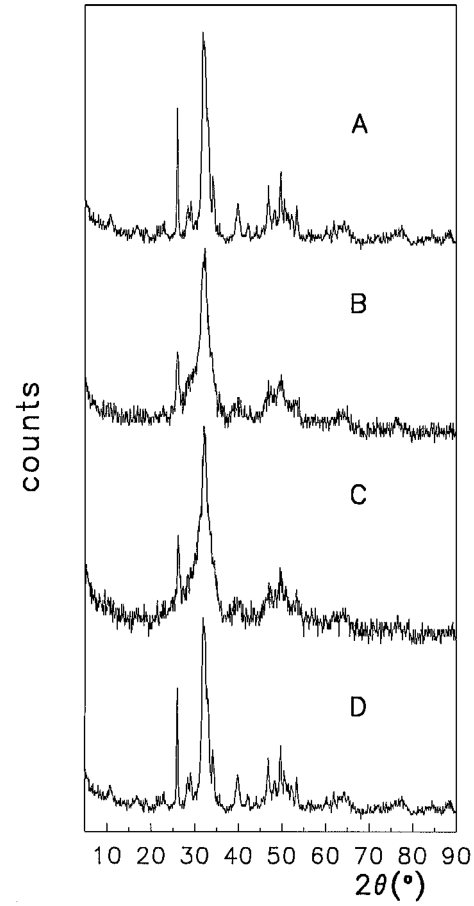

FIG. 4. XRD patterns of the samples obtained at pH 9 and 25°C from solutions with different [Ni/Ca] ratios: (A) 0.03, (B) 0.05, (C) 0.20, and (D) 0.20, but obtained at pH 9 and 95°C.

both structurally and energetically less stable than HAP, such as DCNPD or ACP, are formed. In the latter two compounds the relation Ca/P is similar and the Ca positions are less constrained than those in CaHAP.

An explanation similar to the above applies to the higher stability of ACP when compared with DCPD. The (Ca, Ni)/P ratio is optimum for this compound. Besides, the Ni ion has a great capacity to form hydrates. Its presence favors water incorporation into the structure and, therefore, favors the amorphous phase $(\mathrm{Ca, Ni})_3(\mathrm{PO_4})_{2-y}(\mathrm{HPO_4})_y \cdot n\mathrm{H_2O}$.

TABLE 4
Nickel Concentration in the Solid Phases Obtained at pH 9

Sample	25°C	95°C
Ni3	0.99	0.86
Ni5	1.14	0.98
Ni10	1.9	1.11
Ni15	4.25	2.4
Ni20	5.22	2.8

TABLE 5
Nickel Concentration of Precipitates Obtained by Precipitation at 25°C (% in wt)

Sample	Heat treatment (100°C)	Heat treatment (200°C)
Ni3	1.90	0.99
Ni5	2.81	1.14
Ni10	6.82	1.90
Ni15	13.6	4.25
Ni20	19.3	5.22

The present results have shown that the formation of DCPD, at the expense of apatite, was favored in the presence of Ni at neutral pH and 25°C. The presence of a small Ni concentration in solution inhibits the formation of the apatite structure and favors the formation of a brushite structure. The latter shows a contraction in the *c* cell parameter that can be related to the smaller nickel's radius size. The lack of resolution of the P–O modes, observed in the FTIR spectra, can be associated with the decreasing crystallite size and increasing strain in the samples as a function of the nickel content. This, along with the appearance of shoulders in the 563 and 506 $\mathrm{cm^{-1}}$ bands, in the spectra of materials prepared from higher nickel concentration, can be associated with the shortening of the mean interatomic distance between the cation and the oxygen atoms when going from calcium to nickel. The changes detected in the $(\mathrm{Ni, Ca})\mathrm{HPO_4} \cdot 2\mathrm{H_2O}$ compounds are in agreement with the decrease in ionic radius from Ca^{2+} to Ni^{2+}. An increase in the temperature favors the formation of the ACP. This phase is the most stable when formed *in vitro* from solutions containing Ni at neutral pH and above room temperature. Besides, our results showed, in agreement with the Abbona and Baronnet observations [20], that the crystallization process of ACNP to HAP does not include successive transformations of the type ACP–OCP–HAP or ACP–DCPD–OCP–HAP.

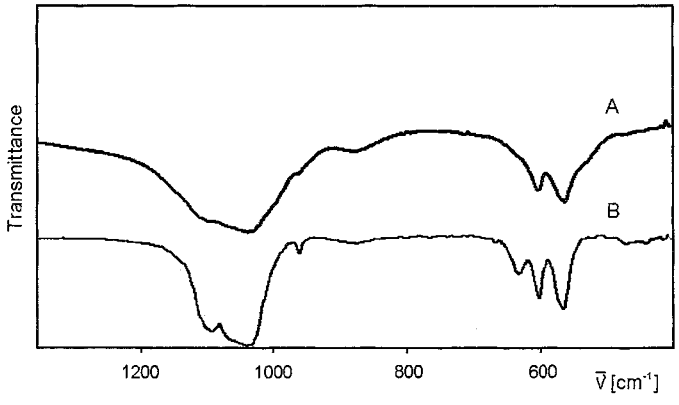

FIG. 5. IR spectra of (Ca, Ni)HAP obtained at pH 9 and 95°C from a solution with a [Ni/Ca] ratio of 0.1. (A) As obtained; (B) thermally treated at 200°C.

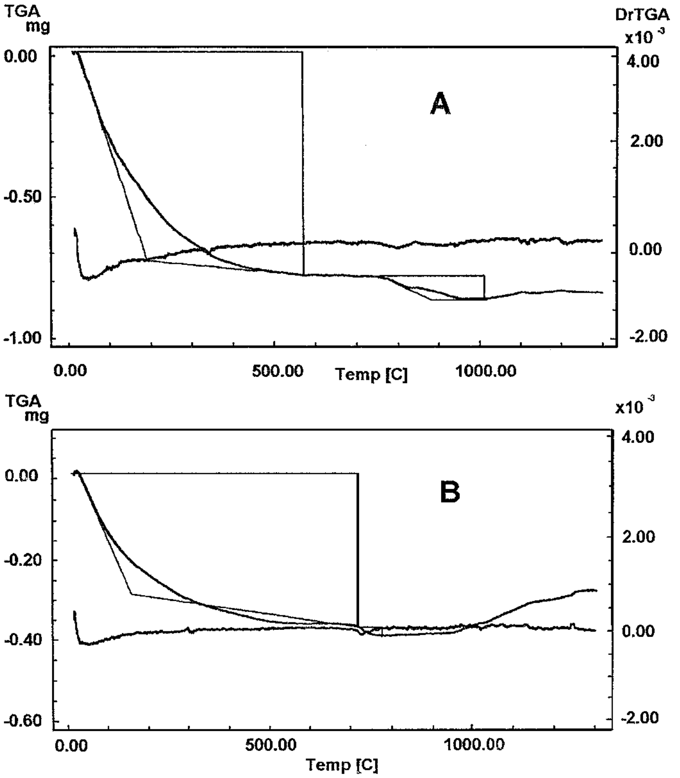

FIG. 6. TGA curves of the (Ni, Ca)HAP synthesized at pH 9 and 95°C from solutions with different [Ni/Ca] ratios: (A) 0.2 and (B) 0.05.

The present results demonstrate the importance of the [Ni/Ca] molar ratio in solution and of the pH and temperature of the solution in promoting, or inhibiting, the *in vitro* formation of different types of calcium phosphate: DCPD, ACP, and HAP. Although solution mixtures were followed only for 96 h, the results within this period seemed to indicate that longer aging processes would not alter the phosphate formation significantly. In the case of the synthesis at pH 7 at 25 and 95°C, longer periods of incubation were tried (up to 4 months) and no change in the results has been observed [16].

The relatively small incorporation of Ni into the reaction products seems to indicate that the presence of NH_4^+ in the solution has impaired nickel access to the apatite phase due to the formation of an ammoniacal complex. However, this thesis can be disregarded due to the results of the reaction performed at pH 9 and $T = 25°C$. Under these reaction conditions no complex formation was observed. This is because complex formation requires temperatures higher than 80°C. Despite the fact that no ammoniacal complexes were found, the nickel content in the reaction products was similar to the one found with the other reaction conditions. Therefore, it can be safely assumed that the degree of Ni incorporation in the reaction's products is independent of the method of reaction. Besides, recent investigations performed on samples of (Ca, Ni)HAP aged up to 4 months in a solution rich in Ni and at neutral or slightly acid pH have shown that the samples do not present changes in the proportion of Ni in the solid phase [16].

From the present results it can be established that the stability of the amorphous phase increases with the increment of [Ni/Ca] in solution and that when the [Ni/Ca] in solution is higher than 0.2 the transformation to CaHAP does not occur. These results would also suggest that ACNP is unlikely to be a precursor of HAP in bone formation.

Another significant result of the present study is the absence of the whitlockite phase in all the products of the reactions. According to some authors the incorporation of Ni in the solid phase inhibits the formation of the apatite phase and induces the formation of the whitlockite phase [8, 21]. The departure of our reaction products from that behavior might have been induced by the high concentration of ammonium in the solutions and by the reactions conditions that make possible the formation of the complex $[Ni(NH_3)_6]Cl_2$. It should be mention that the temperatures used in the process of synthesis in the present work were not the same as those reported in the literature. Further investigation of the nature of $(Ca, Ni)_3(PO_4)_2$ formation would require more in-depth study of the formation mechanisms.

The observed increase in the induction period when nickel is present in ACP can be explained as due to the high hydration capability of nickel. It is certainly higher than that of calcium. Only mono- and dihydrates of calcium are found in the literature while hexa- and heptahydrates of nickel compounds are known to exist. Studies performed on the influence of magnesium ions in the transformation process of ACP to HAP have also shown larger induction times [22, 23].

The results that we have presented here have confirmed the inhibitory effect of Ni on calcium hydroxyapatite formation. The apatite, which can be obtained as a unique crystalline phase, exhibits broadening of the X-ray diffraction lines and of the IR bands. The changes in their XRD patterns can be attributed to the reduction of the crystallites' size with the increase of [Ni/Ca]. The apatites obtained at 25°C are more affected by the presence of Ni. However, the apatites obtained at both reaction temperatures show thermal conversion into TCP above 700°C. This is further evidence of the inhibitory effect of Ni.

The observed effects of Ni on the formation and tansformation of synthetic CaHAP may explain, in part, the formation and stability of biological CaHAP in the presence of this ion. The common calcium phosphates found in renal and dental calculi include HAP, DCPD, and β-TCP [14, 21]. Struvite and newberyite have been also observed. Depending on [Ni/Ca] and pH these crystal phases can form; however, the acid solutions favor the formation of brushite while the alkaline ones benefit HAP obtainment.

The present study indicates that to avoid mouth health problems the elution of nickel from dental casting should be controlled or eliminated.

CONCLUSIONS

The [Ni/Ca], pH, and temperature of a solution influence calcium phosphate formation in the presence of Ni. Increasing [Ni/Ca] in solution induces the formation of DCPD and ACP. These phases are clearly stabilized at neutral pH. The presence of Ni in solution inhibits HAP and OCP formation. However, HAP can be synthesized in the presence of Ni at basic pH and at a temperature of 95°C.

The effect of nickel is very close to that exhibited by magnesium. This suggests that, as happens with magnesium, the interaction of the nickel with the apatitic phase might be limited to the crystal surface.

ACKNOWLEDGMENTS

The authors thank R. Viña for helpful discussions, the Fundación Antorchas, DAAD (Deutscher Akademischer Austauschdienst, Germany), DAAD–Fundación Antorchas, Alexander von Humboldt–Fundación Antorchas, and British Council–Fundación Antorchas Awards to the German–Argentinean and to the British–Argentinean cooperation agreement, respectively, as well as the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) PIP4695/96, the Agencia Nacional de Promoción Científica y Tecnológica (PICT 122), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), República Argentina, for financial support. The authors are also indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina, for financial support and to the Fundación Antorchas for the National Award to the Argentinean cooperation. G.P. and C.O.D.V. are members of CONICET.

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