Incorporation of Lanthanides in Human Dental Enamel

Ugradnja Lantanida u caklinu ljudskih zuba

Jolán Bánóczy*
Z. Gintner*
J. Kiss**

* Department of Conservative Dentistry Semmelweis University of Medicine, Budapest, Hungary

**Institute of Mineralogy, Eötvös Lóránd University Budapest, Hungary

Summary

The incorporation of lanthanides in human dental enamel was investigated by means of X-ray microprobe analysis. Sound human premolar teeth - after extraction-were prepared and kept for 60 days in 10% solutions of neodymium-, samarium-, europium-, ytterbium resp. lanthanum-chloride at room temperature with constant shaking. Results of the X-ray microprobe analysis revealed 100-140 m depth penetration and incorporation of neodymium, with transformation of the apatite phases of enamel into neodymium-hydroxil-apatite-, resp. neodymium-hidrochlor-apatite. The changes were accompanied by a decrease in the values of calcium, magnesium and sodium. Samarium-, ytterbium-, europium and lanthanum-chloride treatments produced a phosphate-complex containing coherent layer on the enamel surface. However, no real incorporation into the apatite-lattice was observed. The incorporation of neodymium-apatites, and the formation of cerium-apatite into the dental enamel observed in previous studies might indicate the possibility of stabilizing the apatite structure, and discovering new ways of caries prevention.

Key words: *Incorporation of Lanthanides, Neodymium, Samarium, Ytterbium, Europium, Caries-Prevention.*

Acta Stomatol Croat
1996; 30: 37—48

ORIGINAL PAPER
Received: March, 15. 1996
Primljeno: 15. ožujka 1996.

The role of fluorides in the remineralization of incipient carious lesions of dental enamel is well known and can be performed succesfully by increasing the resistance of the tooth surface by means of ionic exchange. The resulting fluorapatite increases the microhardness and decreases the acid solubility of dental enamel (Koulourides 1980); moreover it promotes crystal growth (Featherstone 1984).

Furthermore, a wide variety of chemical agents have been tested, which could be applied in a similar way in order to strengthen dental enamel. Rare earth elements (REE), known (from crystalchemistry) for their rehardening effect on apatites have been tested. Their incorporation into naturally occurring apatites resulted in an increase in microhardness, and decrease in acid solubility (Deer et al. 1964.). Rare earth elements can be found in fo-

od and animal and human organisms, and have no accepted biological function (RDA 1989). They are not toxic for the living organism.

The toxicity of lanthanum is low (LD_{50} of lanthanum nitrate for mice: 150 mg pro kg), (Ozeki et al. 1979), and in internal organisms its accumulation is moderate (Shimano 1980, Sakurai 1982). Lanthanum salts have been used since about the early sixties in electronmicrospscopical investigations, because of their electron density and small particle size, mainly in epithelial permeability studies. The solutions used contained 1% lanthanum nitrate ($La(NO_3)_3 \cdot 3H_2O$) or lanthanum chloride ($LaCl_3 \cdot 7\ H_2O$), and caused only slight morphological damage to the tissues: some dilatation of capillaries and widening of intercellular spaces in the epithelium. However, these were not markedly greater than after using the protein tracer, horseradish peroxydase (Squier and Rooney 1975).

In dental literature Mühlemann (1975) reports on studies, performed in 1961. during which he found decrease in acid solubility of rat molar teeth when treated with cerium nitrate. Shrestha et al. (1972) and Collys et al. (1988) made similar observations in in vitro studies, using different trace-, and REE-s. Among the latter, three showed a considerable decrease of acid solubility in the samples prepared from bovine enamel; cerium 20%, dysprosium 24,7%, ant ytterbium 51,3%. Kobayashi et al. (1979b) treated non-carious extracted human teeth with a 8% lanthanum nitrate solution. An equilibrium was reached after three days, when 65% of the Ca^{2+} was displaced by La^{3+}. A surface coating, consisting of several different lanthanum phosphate compounds, analysed by X-ray diffraction analysis was developed (Kobayashi et al. 1980a), consisting of $LaPO_4$ $La(P_2O_7)_3$, LaP_5O_{14}, $LaHP_2O_7 \cdot 3H_2O$ and $LaP_3O_9 \cdot 3H_2O$.

Dissolution studies showed increased acid resistance of the observed surface coating. Enamel treated for five weeks included a considerable amount of La, Ca and P and were less dissolved (Kobayashi et al. 1980b).

Acid-solubility studies also point to the importance of the ion-radius similarity of rare earth cations with that of Ca^{2+} when investigating the efficacy of the incorporation of lanthanides into the apatites (Gintner 1992). In the course of these in vitro studies, Sm^{3+} and Nd^{3+} incorporation into dental enamel resulted in a significant decrease in acid-solubility.

The incorporation of cerium into natural, powdered carbonate apatites has been shown by Kiss et al. (1990), and that of lanthanum, samarium, europium, and ytterbium into synthetic chlorapatites by Baumer et al. (1991).

Fernandez-Gavarron et al. reported on the incorporation of radioactive 140 - lanthanum into human tooth dentine (1988), ant other studies - also performed in in vitro conditions on human teeth - showed the incorporation of cerium in dental enamel (Bnczy et al. 1990, Kiss et al. 1990). In these studies extracted human molar teeth were kept for 60 days in a 10% cerium nitrate solution, in order to investigate the incorporation of cerium into human sound and carious enamel by light-microscopic-, electron-, and microprobe methods. Cerium was incorporated in sound enamel, as well as into an incipient carious lesion, showing the histological characteristics of the remineralizing lesion. The mean values of the microanalysis data showed an increase in Ce^{3+} chaning place with the Ca^{2+}, Mg^{2+}, Na^{+}, the developing cerium-apatite being harder and resistant from a mineralo-phisical point of view (Kiss et al. 1990).

In a more recent study, the incorporation of lanthanum (La), europium (Eu), samarium (Sa), ytterbium (Yb) and neodymium (Nd) in human permanent enamel, dentine and deciduous enamel was investigated by neutron activation analysis. The lanthanides were incorporated - following the above sequence - in an increasing ratio into enamel and dentine, by forming new, more resistant REE-s containing apatite structures. These results corroborate those of previous experiments (Bnczy et al. 1990, Kiss et al. 1990). In order to avoid defects in the crystal-lattice of hydroxylapatite, due to the unequal presence of anions (OH-·Cl-·F-·$(CO_3)_2$-), it is possible to fill these, as well as one part of the Ca.Mg(Na)10-x positions with other cations: in this case with lanthanides (Bánóczy et al. 1992).

The aim of the present investigation was to study the effect of the chloride solutions of five REE-s (neodymium, samarium, europium, ytterbium and lanthanum) on the chrystalchemical characteristics of sound human dental enamel, by using X-ray microprobe analysis.

Material and Methods

For the investigation sound human premolar teeth were used and after extraction kept in 10% formalin solution then dried. The crowns of the teeth

were cut into halves following their longitudinal and horizontal axis, by means of a diamond discs, and the cut surfaces polished. One half of the tooth crown was treated, the other half remained untreated as a control covered with Canada balm, removed after treatment.

The test specimens were kept for 60 days in 10% solutions of neodymium-, samarium-, europium-, ytterbium-resp. lanthanum-chloride at room temperature with constant shaking. The samples were washed thoroughly in distilled water (to eliminate chloride), then in absolute alcohol, and dried at room temperature.

The X-ray microprobe measurements were performed, using Joel-Superprobe JCXA-733 equipment.

Results

Samples kept in neodymium-chloride showed unevenly distributed and noncoherent infilitrations both in enamel and dentine (fig. 1), which reached occasionally a depth of 140m-s. Immediately under the surface of the whole enamel, a layer developed of about 8-10 μm depth, poorer in neodymi

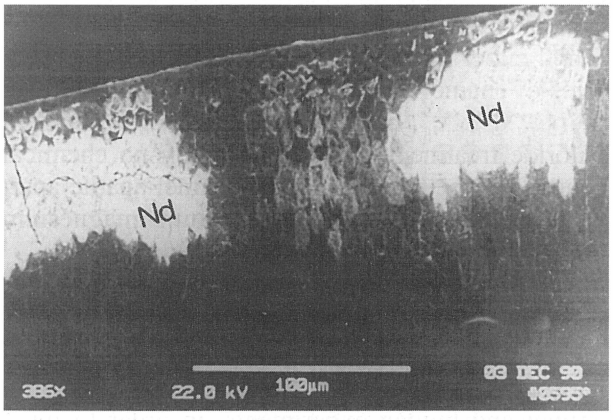

Figure 1. *Non coherent infiltrations of neodymium in human dental enamel. The surface layer (about 8-10 μm in depth) is poorer in neodymium.*

Slika 1. *Nekoherentna infiltracija neodija u caklinu zuba. Površni sloj je siromašniji s neodijem.*

um (Fig. 2, Table 1, point "e"), in the deeper layers showing different density of neodymium, depending upon the order, ratio, and volume of crystal phases of dental enamel. A significant part of carbonate-apatite (CAP), calcium-hydroxyl-apatite (CaHAP), hydroxyl-apatite (HAP) and chlor-apatite (ClAP) phases of enamel were transformed in the

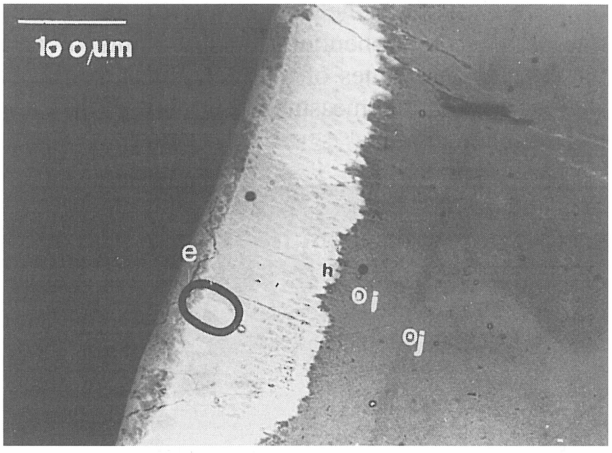

Figure 2. *Measurement points in neodymium-treated enamel. The infiltration is more coherent than in Fig. 1. However the neodymium-poor surface layer is clearly visible.*

Slika 2. *Mjerne točke u neodiju obrađenoj caklini. Infiltracija je koherentnija nego na slici 1. Međutim vidljiv je površni sloj siromašniji neodijem.*

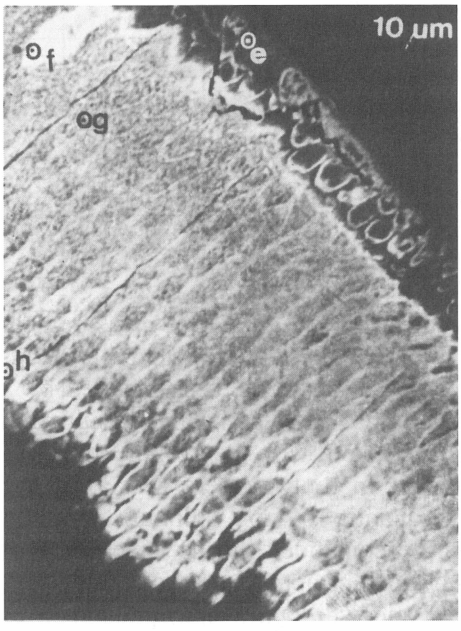

Figure 3. *Higher magnification of the marked part from Fig 2, with measurement points "f", "g", "h" (see also Table 1).*

Slika 3. *Veće povećanje označenoga dijela sa slike 2. s mjernim točkama "f", "g", "h" (vidi također Tablicu 1.)*

course of treatment into neodymium-hydroxil-apatite, resp. neodymium- hydrochlor-apatite (Fig. 3, "f", "g", "h", points of measurements). According to the above measurement points the incorporation

of neodymium from the enamel surface versus dentine decreased exponentially, and at points "i" and "j" reached the values of trace elements, resp. zero. Fig. 4 shows the measurement points of the control sample.

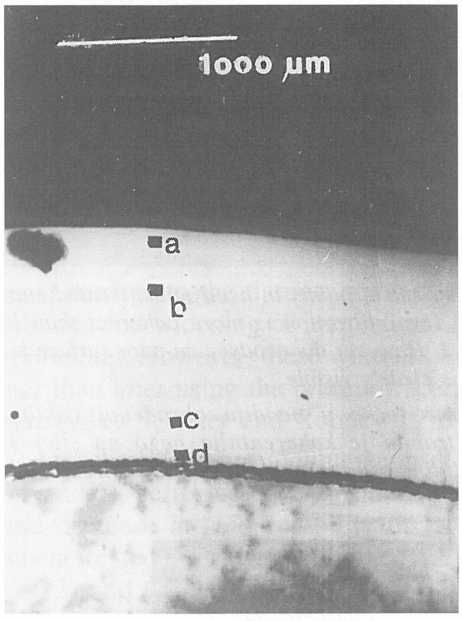

Figure 4. *Untreated sample of dental enamel, showing measurement points "a", "b", "c", "d" (see also Table 1).*

Slika 4. *Neobrađen uzorak zubne cakline, s mjernim točkama "a", "b", "c", "d" 8 (vidi također Tablicu 1.)*

Analysing the data in Table 1, at measurement points "e", "f", "g", and "h" a considerable increase of neodymium was found, accompanied by a decrease in the values of calcium, magnesium and sodium, when compared with the average values of untreated samples. In contrast there was a relative increase in the quantity of iron, sulphur and chlor. The latter can be concluded by the appearance of neodymium-hydrochlor-apatite, due to the disappearance of CAP and whitlockit (Wh) phases.

The effect of the samarium-chloride solution caused the appearance of the a coherent layer of phosphate-complex on the enamel surface and in the fissures of enamel (Table 2). The CAP, HAP, ClAP and Wh phases of the untreated samples formed, by disappearance of CAP and Wh, a HClAP-HAP structure, without incorporation of samarium. The samarium containing crystalline layer on the enamel surface originated from non-apatite complexes of the solution.

The samples treated with ytterbium-chloride also showed an ytterbium-phosphate containing a thin (1 m) surface layer, without apatite-lattice (Table 3). In measurement point "f" higher density of ytterbium could be found. However, in the surroundings the concentration corresponds to that of trace elements. This indicates that the diffusion of ytterbium changed the non-apatite-lattice, containing more soluble phase elements (as Wh) into phosphate complexes, in the course of which an increase in density of calcium, magnesium, potassium occurred (point "d"). In point "f" loss of calcium, phosphor, chlor and fluor-, resp. occurred and a relative increase in magnesium, sodium, potassium, silicium, aluminium and sulphur (Table3).

Data on treatment with europium solutions show similar crystalchemical behaviour to that of samarium. The increase in density of europium (point "d") is visible only in the 1-2 m deep layer. The effect of treatment caused a loss of CAP-Wh phases of enamel, and in their place europium phosphate complexes developed (Table 4).

Lanthanum-chloride (Table 5) showed the least affinity to enamel-apatite among the REE-s used. In small quantities it was present in both treated and untreated samples, however, no crystalchemical changes, experienced in other samples, could be found either on the surface, or in the deeper structures of enamel-apatite. According to measurement points "d", "e", and "f" the effect of lanthanum chloride treatment caused practically no chemical changes in the composition of enamel-apatite apart from slight mobilization in calcium, magnesium and phosphor.

Discussion

The favourable effects of lanthanides on dental hard tissues, has already provoked some in vitro, animal and human experiments, in order to investigate the possibility of using REE-s in caries prevention.

The effect of cerium, neodymium, samarium and ytterbium containing toothpastes has been studied on the acid-solubility of human dental enamel in vitro. The surface softened samples were enriched with different REE-s, concentration 1,5%. The grade of remineralization was characterised by the amount of dissolved phosphorus from the enamel samples. All the REE containing toothpastes decreased the acid solubility of samples. Significant reduction of enamel dissolution was obtained in the

Table 1. *Results of experiments with neodymium chloride*
Tablica 1. *Rezultati eksperimenta s neodij kloridom*

GROUP OF ELEMENTS	UNTREATED PREMOLAR TEETH ENAMEL					TREATED PREMOLAR; 10% Nd $CL_{3(aq)}$ - 60 days											
%	a	b	c	d	MEAN	e	Δ%*	f	Δ%	g	Δ%	h	Δ%	i	Δ%	j	Δ%
CaO	50.41	50.01	49.16	48.20	49.45	48.74	-0.71	39.03	-10.42	41.61	-7.84	37.09	-12.36	49.38	+0.38	51.28	+1.83
MgO	0.32	0.32	0.36	0.34	0.34	0.18	-0.16	0.11	-0.23	0.12	-0.22	0.23	-0.11	0.34	0.00	0.18	+0.16
FeO	0.00	0.00	0.01	0.03	0.01	0.03	+0.02	0.09	+0.08	0.07	+0.06	0.09	+0.08	0.00	-0.01	0.00	-0.01
Na_2O	0.91	0.91	1.01	0.92	0.94	0.40	-0.54	0.31	-0.63	0.36	-0.58	0.30	-0.64	0.64	-0.30	0.48	-0.46
K_2O	0.06	0.05	0.07	0.05	0.06	0.13	+0.07	0.23	+0.17	0.11	+0.05	0.11	+0.05	0.04	-0.02	0.05	-0.01
SiO_2	0.00	0.00	0.01	1.15	0.29	0.03	-0.26	0.09	-0.20	0.08	-0.21	0.05	-0.24	0.00	-0.29	0.00	-0.29
Al_2O_3	0.01	0.00	0.00	0.01	0.01	0.04	+0.03	0.12	+0.11	0.05	+0.04	0.05	+0.04	0.00	-0.01	0.00	0.01
P_2O_5	40.29	39.78	40.00	39.76	39.96	39.89	-0.07	36.77	-3.19	37.37	-2.59	38.15	-1.81	40.06	+0.10	41.07	+1.11
SO_3	0.02	0.01	0.02	0.02	0.02	0.05	+0.03	0.10	+0.08	0.08	+0.06	0.08	+0.06	0.02	0.00	0.02	0.00
Cl	0.35	0.33	0.25	0.17	0.28	0.60	+0.32	0.60	+0.32	0.58	+0.30	0.50	+0.22	0.42	+0.14	0.56	+0.28
F	0.00	0.00	0.00	0.00	0.00	0.01	+0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Nd_2O_3	0.02	0.01	0.04	0.00	0.02	2.75	+2.73	15.30	+18.28	12.02	+12.00	16.20	+16.18	0.01	-0.01	0.01	-0.01
Σ	92.39	91.42	90.93	90.65	91.38	92.85	-	92.75	-	92.45	-	92.86	-	91.36	-	93.65	-
%=	(7.61)	(8.58)	(9.07)	(9.35)	(8.62)	(7.15)	-	(7.25)	-	(7.55)	-	(7.14)	-	(8.64)	-	(6.35)	-
(H_2O+org)**																	

*Δ = changes in percentage compared to the untreated sample mean values

** = not measured, complementary quantity of H_2O and organic materials

Table 2. *Results of experiments with samarium-chloride*
Tablica 2. *Rezultati eksperimenta s samarij kloridom*

GROUP OF ELEMENTS	UNTREATED PREMOLAR TEETH ENAMEL				TREATED PREMOLAR; 10% $SmCl_{3(aq)}$ - 60 days							
%	a	b	c	MEAN	d	Δ%*	e	Δ%	f	Δ%	g	Δ%
CaO	48.90	50.17	49.15	49.41	43.36	-6.05	49.04	-0.37	49.76	+0.35	47.88	-1.53
MgO	0.35	0.76	0.43	0.51	0.75	+0.24	0.69	-0.18	0.41	-0.10	0.37	-0.14
FeO	0.01	0.01	0.00	0.01	0.00	-0.01	0.01	0.00	0.00	-0.01	0.00	-0.01
Na_2O	0.34	0.48	0.98	0.60	0.00	-0.60	0.40	-0.20	0.50	-0.10	0.91	+0.31
K_2O	0.03	0.03	0.04	0.03	0.06	+0.03	0.03	0.00	0.03	0.00	0.05	+0.02
SiO_2	0.02	0.01	0.01	0.01	0.02	+0.01	0.02	+0.01	0.01	0.00	0.00	-0.01
Al_2O_3	0.00	0.01	0.01	0.01	0.01	0.00	0.00	-0.01	0.01	0.00	0.00	-0.01
P_2O_5	40.77	40.44	39.08	40.09	39.99	-0.10	41.04	0.95	41.03	+0.94	38.97	-1.12
SO_3	0.00	0.00	0.00	0.00	0.01	+0.01	0.01	+0.01	0.00	0.00	0.01	+0.01
Cl	0.68	0.63	0.12	0.48	0.55	+0.07	0.65	0.17	0.67	+0.19	0.28	-0.20
F	0.02	0.00	0.00	0.01	0.03	+0.02	0.02	+0.01	0.01	0.00	0.01	0.00
Sm_2O_3	0.00	0.00	0.00	0.00	10.21	+10.21	0.03	+0.03	0.01	+0.01	0.00	0.00
Σ	91.12	92.54	89.82	91.16	94.99	-	91.84	-	92.44	-	88.48	-
%= (H_2O+org)**	(8.88)	(7.46)	(10.18)	(8.84)	(5.01)	-	(8.06)	-	(7.56)	-	(11.52)	-

*Δ = changes in percentage compared to the untreated sample mean values

** = not measured, complementary quantity of H_2O and organic materials

Table 3. *Results of experiments with ytterbium-chloride*
Tablica 3. *Rezultati eksperimenta s iterbij kloridom*

GROUP OF ELEMENTS	UNTREATED PREMOLAR TEETH ENAMEL				TREATED PREMOLAR; 10% $YbCl_{3(aq)}$ - 60 days									
%	a	b	c	MEAN	d	Δ%*	e	Δ%	f	Δ%	g	Δ%	h	Δ%
CaO	49.33	49.34	48.43	49.03	50.90	+1.87	50.52	+1.49	36.50	-12.53	48.16	-0.87	49.31	-0.28
MgO	0.24	0.19	0.44	0.29	0.49	+0.20	0.44	+0.15	0.31	+0.02	0.32	+0.03	0.30	+0.01
FeO	0.02	0.03	0.00	0.02	0.02	0.00	0.02	0.00	0.05	+0.03	0.00	-0.02	0.03	+0.01
Na_2O	0.50	0.53	0.46	0.05	0.35	-0.15	0.46	-0.04	0.78	+0.28	0.80	+0.30	0.72	+0.22
K_2O	0.01	0.04	0.03	0.03	0.04	+0.01	0.00	-0.03	0.11	+0.28	0.03	0.00	0.02	-0.01
SiO_2	0.01	0.01	0.00	0.01	0.08	+0.07	0.01	0.00	0.08	+0.07	0.01	0.00	0.00	-0.01
Al_2O_3	0.01	0.02	0.00	0.01	0.18	+0.17	0.00	-0.01	0.11	+0.10	0.00	-0.01	0.00	0.01
P_2O_5	40.37	39.79	38.20	39.45	41.32	+1.87	41.00	+0.55	29.53	-9.92	39.25	-0.20	39.89	+0.44
SO_3	0.00	0.00	0.01	0.003	0.04	+0.04	0.00	-0.003	0.02	+0.02	0.01	+0.01	0.01	+0.01
Cl	0.67	0.64	0.13	0.48	0.63	+0.15	0.67	+0.19	0.39	-0.09	0.32	-0.16	0.47	-0.01
F	(0.01)	(0.08)	0.00	0.03	0.01	0.02	0.00	-0.03	0.00	-0.03	0.00	-0.03	0.00	-0.03
Yb_2O_3	0.00	0.05	0.00	0.02	0.57	+0.55	0.05	+0.03	13.50	+13.48	0.00	-0.02	0.02	0.00
Σ	91.17	90.67	87.70	89.87	94.63	-	93.17	-	81.38	-	89.90	-	90.77	-
%= (H_2O+org)**	8.83	9.73	12.30	10.13	5.37	-	(6.83)	-	(18.62)	-	(11.10)	-	(9.23)	-

*Δ = changes in percentage compared to the untreated sample mean values

** = not measured, complementary quantity of H_2O and organic materials

Table 4. *Results of experiments with europium-chloride*
Tablica 4. *Rezultati eksperimenta s europij kloridom*

GROUP OF ELEMENTS		UNTREATED PREMOLAR TEETH ENAMEL			TREATED PREMOLAR; 10% $EuCl_{3(aq)}$ - 60 days							
%	a	b	c	MEAN	d	Δ%*	e	Δ%	f	Δ%	g	Δ%
CaO	50.66	50.22	48.54	49.78	50.98	-1.20	51.85	+2.07	49.46	-0.32	49.77	-0.01
MgO	0.18	0.34	0.50	0.34	0.17	-1.17	0.44	+0.10	0.44	+0.10	0.45	+0.11
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.51	0.56	1.14	0.74	0.27	-0.47	0.36	-0.38	1.01	+0.27	0.99	+0.25
K_2O	0.03	0.05	0.04	0.04	0.05	+0.01	0.03	-0.01	0.03	-0.01	0.05	+0.01
SiO_2	0.02	0.02	0.01	0.02	0.01	-0.01	0.02	0.00	0.01	-0.01	0.01	-0.01
Al_2O_3	0.00	0.00	0.00	0.00	0.02	+0.02	0.01	+0.01	0.00	0.00	0.00	0.00
P_2O_5	41.15	40.07	38.82	40.01	41.94	+1.93	41.43	+1.42	38.90	-1.11	38.98	-1.03
SO_3	0.01	0.01	0.00	0.01	0.01	0.00	0.00	-0.01	0.00	-0.01	0.01	0.00
Cl	0.66	0.54	0.12	0.44	0.70	+0.36	0.73	+0.29	0.22	0.22	0.20	-0.24
F	0.02	0.00	0.00	0.01	0.00	+0.01	0.00	-0.01	0.00	-0.01	0.00	-0.01
Eu_2O_3	0.00	0.04	0.00	0.01	2.43	+2.42	0.03	+0.02	0.00	-0.01	0.00	-0.01
Σ	93.24	91.85	89.08	91.40	96.58	-	94.90	-	90.07	-	90.46	-
%=	6.76	(8.15)	(10.92)	(8.60)	(3.42)	-	(5.10)	-	(9.93)	-	(9.54)	-
(H_2O+org)**												

*Δ = changes in percentage compared to the untreated sample mean values

** = not measured, complementary quantity of H_2O and organic materials

Table 5. *Results of experiments with lanthanium-chloride*
Tablica 5. *Rezultati eksperimenta s lantanij kloridom*

GROUP OF ELEMENTS		UNTREATED PREMOLAR TEETH ENAMEL			TREATED PREMOLAR; 10% $LaCl_{3(aq)}$ - 60 days					
%	a	b	c	MEAN	d	Δ%*	e	Δ%	f	Δ%
CaO	51,73	51.30	48.17	50.40	49.73	-0.67	49.73	-0.67	48.06	-2.34
MgO	0.26	0.29	0.53	0.36	0.30	-0.06	0.27	-0.09	0.36	0.00
FeO	0.01	0.00	0.00	0.003	0.01	+0.01	0.00	0.00	0.00	0.00
Na2O	0.59	0.65	0.97	0.74	0.81	+0.07	0.81	+0.07	1.07	+0.33
K2O	0.05	0.04	0.06	0.05	0.05	0.00	0.05	0.00	0.05	0.00
SiO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al2O3	0.00	0.00	0.00	0.00	0.00	0.00	0.01	+0.01	0.00	0.00
P2O5	41.55	41.49	39.80	40.95	40.64	-0.31	40.69	-0.26	39,83	-1.12
SO3	0.02	0.01	0.00	0.02	0.02	0.00	0.02	0.00	0.02	0.00
Cl	0.48	0.47	0.12	0.36	0.39	+0.03	0.36	0.00	0.18	-0.18
F	0.00	0.02	0.00	0.01	0.00	-0.01	0.00	-0.01	0.05	+0.04
La_2O_3	0.00	0.03	0.01	0.01	0.01	0.00	0.00	+0.01	0.01	0.00
Σ	94.69	94.30	89.68	92.90	91.96	-	91.94	-	89.63	-
%=	(5.31)	(5.70)	(10.32)	(7.10)	(8.04)	-	(8.06)	-	(10.37)	-
(H_2O+org)**										

*Δ = changes in percentage compared to the untreated sample mean values

** = not measured, complementary quantity of H_2O and organic materials

group of samarium ($p<0.01$). The result of this experiment indicates, that REE-s could be potential chemical agents in the prevention of dental caries (Gintner et al. 1993).

In animal studies effective caries reduction was obtained with 0.1- 0-01% lanthanum solution (Ozeki et al. 1979, Shimano 1980). However, it is not completely clear whether the observed caries reduction was related to the incorporation of lanthanum in the dental hard tissues, or to interference with plaque formation. Other experiments have shown that the adherence of Streptococcus mutans to lanthanum treated teeth was markedly inhibited (Ozeki 1982). The appearance time of S. mutans within the oral cavities of hamsters, fed a cariogenic diet and provided with drinking water containing 30 g pro ml lanthanum nitrate, was delayed, and the S. mutans were reduced in numbers (Kobayashi et al. 1979 a). Winter et al. (1980) also showed in biological and clinical experiments that lanthanum reduces the integrity and adherence of dental plaque by interfering with the formation of calcium bridges at the anamel-plaque interface.

Clinical rinsing experiments (Beazley et el. 1980), investigating the effect of SnF2, LaCl3, NaF and chlorhexidine on the amount of lipoteichoic acid formed in plaque, report clinical changes produced by four day rinsings with a 0.3% lanthanum chloride solution.

The plaques formed with the LaCl3 rinse program were loose, less adhesive and whiter.

Although all the aforementioned studies showed a promising effect of lanthanides for use in prevention of dental caries,. the mechanisms involved are rather contradictory. True incorporation into human dentine of 140-lanthanum, showing a depth of penetration between 5-15 m, was first shown by Fernandez Gavarron et al. (1988). In the present study treatment with neodymium-chloride caused a transformation in the apatite-lattice of enamel, by the formation of neodymium-hydroxil-apatite and neodymium-hydrochlor-apatite accompanied by the development of Ca3Nd(PO4)3 + NdPO4.

In the case of samarium-, europium-, and ytterbium treatments the REE-s were not incorporated into the apatite-lattice, but were present in small quantities in the form of phosphates. The formation of these non-apatite-lattice phosphates might be decreased by the lower concentration of treatment solutions.

Based on the formation of cerium-apatite, observed in our previous, similarly performed, experiments (Kiss et al. 1990), and the development of neodymium-apatites in the present study, cerium and neodymium seem to offer the possibility of stabilization of the apatite-structure of dental enamel.

Acknowledgements

This investigation was made possible by the support of the No. 1006 "OTKA" grant of the Hungarian Scientific Research Foundation.

UGRADNJA LANTANIDA U CAKLINU LJUDSKIH ZUBA

Address for correspondence:
Adresa za dopisivanje:

Sažetak

U radu je istraživana ugradnja lantanida u humanu caklinu zuba s pomoću rendgenske mikroanalize.

Zdravi ljudski premolari su poslije vađenja pripremljeni i držani kroz 60 dana u 10% otopinama neodij-, samarij-, iterbij i lantanij klorida na sobnoj temperaturi uz trajno miješanje. Rezultati rendgenske mikroanalize objelodanili su i potvrdili prodor i ugradnju neodija, s preobrazbom apatita cakline u neodij--hidroxil-apatit. Promjene su bile praćene smanjenjem vrijednosti kalcija, magnezija i kalija. Samarij, iterbij, europij i lantanij klorid u postupku su uzrokovali stvaranje kompleksa fosfata stvarajući

čvrst sloj na caklinskoj površini. Međutim, prava ugradnja u caklinsku strukturu nije primijećena. Inkorporacija neodij apatita i stvaranje cerij apatita, što je bilo primijećeno u prethodnim studijama, moglo bi ukazivati na mogućnost stabilizacija apatitne strukture i otkriće novih putova prevencije karijesa.

Ključne riječi: *ugradnja lantanida, neodij, samaij, iterij, europij, prevencija karijesa.*

Jolán Bánóczy
Department of Conservative Dentistry
Semmelweis University of Medicine
Miskszáth Kalmán Tér 5.
H-1099 Budapest, Hungary
Tel: 36-1-210-1223
Fax: 36-1-133-6508

References

1. BAUMER A, OHNENSTETTER D, PASQUI D, CARUBA R. Incorporation of trace elements in synthetic hydrothermal chlorapatites. Plinius 1991;5:17-18.
2. BÁNÓCZY J, KISS J, FEHÉRVÁRY E, GINTNER Z, ALBRECHT M. Kristallchemische Aspekte der Remineralisation des Zahnschmelzes. Stomatologie der DDR 1990; 40:200-202.
3. BÁNÓCZY J, KISS J BRÖDY A, GINTNER Z, ALBRECHT M. Studies on the incorporation of lanthanides in dental hard tissues. J Dent Ass South Africa. 1992; 47:197-199.
4. BEAZLEY V C C, THRANE P, RÖLLA G. Effect of mouthrinses with SnF_2, $LaCl_3$, Naf and chlorohexidine on the amount of lipoteichoic acid formed in plaque. Scand J Dent Res 1980; 88:193-200.
5. COLLYS K, SLOP D, COOMANS D. The influence of trace elements on de-, and remineralization properties of tooth enamel in vitro. Trace Elements in Medicine 1988; 5:161-169.
6. DEER W A, HOWIE R A, ZUSSMAN W A . Rock forming Minerals. Ch. 5. pp. 323-335. Longmans. London. 1964
7. FEATHERSTONE J O B. Diffusion phenomena and enamel caries development. In: Cariology, Gugenheim B (ed). p. 259. Karger. Basel. 1984.
8. FERNANDEZ-GAVARRON F, HUQUE T, RABINOWITZ J L, BRAND J G. Incorporation of 140-lanthanum into bones, teeth and hidroxyapatite. Bone and mineral 1988; 3:283-291.
9. GINTNER Z. cit in BÁNÓCZY J, KISS J, FEHÉRVÁRY E, GINTNER Z, ALBRECHT M. Studies on the incorporation of lanthanides in dental hard tissues. J Dent Ass South Africa; 47:197-199.
10. GINTNER Z, BÁNÓCZY J, KISS J. The effect of rare earth element containing toothpastes on the acid sloubility of human dental enemel in vitro. Caries Res 1993; 27:220.
11. KISS J, BÁNÓCZY J, FEHÉRVÁRY E, GINTNER Z, ALBRECHT M. Production of cerium-apatite in sound and carious dental enamel under in vitro conditions. Acta Morphologica Hungarica 1990; 38:61-70.
12. KOBAYASHI Y, OZEKI M, TAKEI M, SHIMANO R. Influence of lanthanum on oral microbs. J Dent Health (Tokyo) 1979a. 29:2-9.
13. KOBAYASHI Y, OZEKI M, TAKEI M, SHIMANO R. Absorption of lanthanum by the enamel surface of extracted human teeth. J Dent Health (Tokyo) 1979b; 29;276—290.
14. KOBAYASHI Y, OZEKI M, YAGI T, HOSOI T, TAKEI M. X-ray diffraction analysis of the reaction products of hydroxyapatite and lanthanum. J Dent Health (Tokyo). 1980a; 29:354-360.
15. KOBAYASHI Y, OZEKI M, YAGI T, HOSOI, T, TAKEI M. Aciduric resistance of lanthanum treated teeth. J Dent Health (Tokyo) 1980b; 30:388-402.
16. KOULOURIDES TH. Dynamics of biological mineralization applied to dental caries. In: The biological basis of dental caries. Menaker L, Morhart R E and Navia J M (eds Ch. 19, pp. 419-437. Harper and Row Hagerstown. 1980.
17. MÜHLEMANN H R. Pharmakologie und Parodontologie, Schweiz Mschr Zahnheilk 1975; 85:447-456.
18. OZEKI M. Relative changes of the oral microflora in the induction and the lanthanum inhibition of dental caries in rats. Aichi-Gakuin J Dent Sci 1982; 19-364-398.
19. OZEKI M, KOBAYASHI Y, TAKEI M, SHIMANO R. Inhibition of dental caries by lanthanum. J Dent Health (Tokyo) 1979; 28:448-454.
20. RDA. Recommended dietary allowances, Ch. 12. p. 262-263. 10th ed. National Academy of Science, Washington D.CD. 1989.
21. SAKURAI Y. Distribution and fate of lanthanum in the tissues of rats administered lanthanum salt solution- by means of swabbing the solutions on the teeth and through stomach tube. Aichi-Gakuin J Dent Sci 1982; 20:1-17.
22. SHIMANO R. A fundamental study on lanthanum as a preventive of dental caries. J Dent Health (Tokyo) 1980; 29:361-377.
23. SHRESTHA B M, MUNDORF S A, BIBBY B G. Enamel dissolution 1. Effects of various agents and titanium tetrafluorides. J Dent Res 1972; 5: 1561-1566.

24. SQUIER C A, ROONEY L. The permeability of keratinized and nonkeratinized oral epithelium to lanthanum in vitro. J Ultrastruct Res 1976; 54:286-295.

25. WINTER M R, RÖLLA G, WHITE A J. The effects of inorganic cations on dental plaque. In: Dental plaque and surface interactions in the Oral Cavity, S.A. Leach (ed), pp. 211.223. IRL Press. London. 1980.